CHAPTER

18

The production of quicklime (CaO) from limestone ($CaCO_3$) in a rotary kiln at about 950°C.

Thermodynamics

CHAPTER OUTLINE

ESSENTIAL CONCEPTS

Laws of Thermodynamics The laws of thermodynamics have been successfully applied to the study of chemical and physical processes. The first law of thermodynamics is based on the law of conservation of energy. The second law of thermodynamics deals with natural or spontaneous processes. The function that predicts the spontaneity of a reaction is entropy. The second law states that for a spontaneous process, the change in the entropy of the universe must be positive. The third law enables us to determine absolute entropy values.

Gibbs Free Energy Gibbs free energy helps us to determine the spontaneity of a reaction by focusing only on the system. The change in Gibbs free energy for a process is made up of two terms: a change in enthalpy and a change in entropy times temperature. At constant temperature and pressure, a decrease in Gibbs free energy signals a spontaneous reaction. The change in the standard Gibbs free energy can be related to the equilibrium constant of a reaction.

Thermodynamics in Living Systems Many reactions of biological importance are nonspontaneous. By coupling such reactions to those that have a negative Gibbs free energy change with the aid of enzymes, the net reaction can be made to proceed to yield the desired products.

Interactive

Activity Summary

1. Interactivity: Entropies of Reactions (18.4)
2. Interactivity: Entropy vs. Temperature (18.4)
3. Interactivity: Free Energy—Equilibrium (18.6)

18.1 The Three Laws of Thermodynamics

In Chapter 6 we encountered the first of three laws of thermodynamics, which says that energy can be converted from one form to another, but it cannot be created or destroyed. One measure of these changes is the amount of heat given off or absorbed by a system during a constant-pressure process, which chemists define as a change in enthalpy (ΔH).

The second law of thermodynamics explains why chemical processes tend to favor one direction. The third law is an extension of the second law and will be examined briefly in Section 18.4.

18.2 Spontaneous Processes

One of the main objectives in studying thermodynamics, as far as chemists are concerned, is to be able to predict whether or not a reaction will occur when reactants are brought together under a specific set of conditions (for example, at a certain temperature, pressure, and concentration). This knowledge is important whether one is synthesizing compounds in a research laboratory, manufacturing chemicals on an industrial scale, or trying to understand the intricate biological processes in a cell. A reaction that *does* occur under the given set of conditions is called a *spontaneous reaction*. If a reaction does not occur under specified conditions, it is said to be nonspontaneous. We observe spontaneous physical and chemical processes every day, including many of the following examples:

- A waterfall runs downhill, but never up, spontaneously.

- A lump of sugar spontaneously dissolves in a cup of coffee, but dissolved sugar does not spontaneously reappear in its original form.

- Water freezes spontaneously below 0°C, and ice melts spontaneously above 0°C (at 1 atm).

- Heat flows from a hotter object to a colder one, but the reverse never happens spontaneously.

- The expansion of a gas into an evacuated bulb is a spontaneous process [Figure 18.1(a)]. The reverse process, that is, the gathering of all the molecules into one bulb, is not spontaneous [Figure 18.1(b)].

A spontaneous reaction does not necessarily mean an instantaneous reaction.

A spontaneous and a nonspontaneous process.
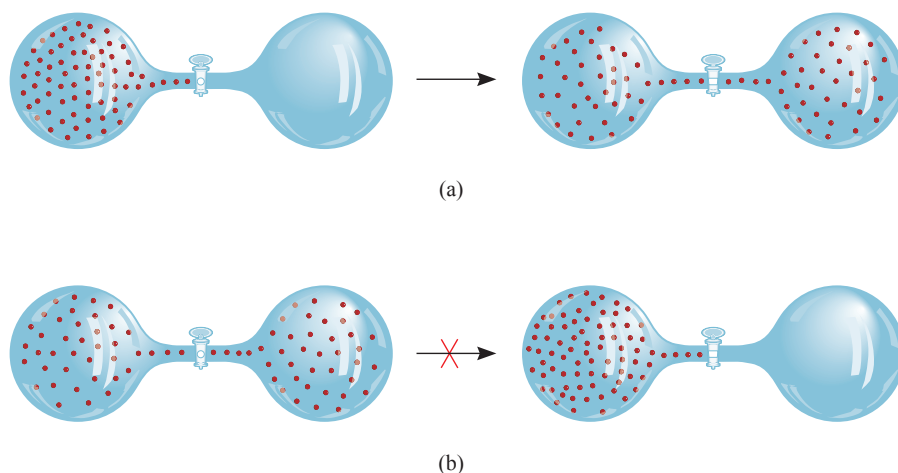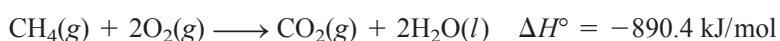© Harry Bliss, Originally published in *New Yorker Magazine.*

(a)

(b)

Figure 18.1
(a) A spontaneous process.
(b) A nonspontaneous process.

- A piece of sodium metal reacts violently with water to form sodium hydroxide and hydrogen gas. However, hydrogen gas does not react with sodium hydroxide to form water and sodium.

- Iron exposed to water and oxygen forms rust, but rust does not spontaneously change back to iron.

These examples show that processes that occur spontaneously in one direction cannot, under the same conditions, also take place spontaneously in the opposite direction.

If we assume that spontaneous processes occur so as to decrease the energy of a system, we can explain why a ball rolls downhill and why springs in a clock unwind. Similarly, a large number of exothermic reactions are spontaneous. An example is the combustion of methane:

<div style="float:left; width:30%; font-size:smaller; color:#8a1a1a;">Because of activation energy barrier, an input of energy is needed to get this reaction started.</div>

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \quad \Delta H° = -890.4 \text{ kJ/mol}$$

Another example is the acid-base neutralization reaction:

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

But consider a solid-to-liquid phase transition such as

$$H_2O(s) \longrightarrow H_2O(l) \quad \Delta H° = 6.01 \text{ kJ/mol}$$

In this case, the assumption that spontaneous processes always decrease a system's energy fails. Experience tells us that ice melts spontaneously above 0°C even though the process is endothermic. Another example that contradicts our assumption is the dissolution of ammonium nitrate in water:

$$NH_4NO_3(s) \xrightarrow{\text{H}_2\text{O}} NH_4^+(aq) + NO_3^-(aq) \quad \Delta H° = 25 \text{ kJ/mol}$$

This process is spontaneous, and yet it is also endothermic. The decomposition of mercury(II) oxide is an endothermic reaction that is nonspontaneous at room temperature, but it becomes spontaneous when the temperature is raised:

$$2HgO(s) \longrightarrow 2Hg(l) + O_2(g) \quad \Delta H° = 90.7 \text{ kJ/mol}$$
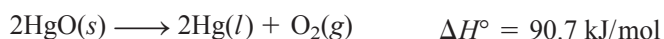
From a study of the examples mentioned and many more cases, we come to the following conclusion: Exothermicity favors the spontaneity of a reaction but does not guarantee it. Just as it is possible for an endothermic reaction to be spontaneous, it is possible for an exothermic reaction to be nonspontaneous. In other words, we cannot decide whether or not a chemical reaction will occur spontaneously solely on the basis of energy changes in the system. To make this kind of prediction we need another thermodynamic quantity, which turns out to be *entropy*.

When heated, HgO decomposes to give Hg and O_2.

18.3 Entropy

In order to predict the spontaneity of a process, we need to introduce a new thermodynamic quantity called entropy. **Entropy (S)** is often described as *a measure of how spread out or dispersed the energy of a system is among the different possible ways that system can contain energy.* The greater the dispersal, the greater is the entropy. Most processes are accompanied by a change in entropy. A cup of hot water has a certain amount of entropy due to the dispersal of energy among the various energy states of the water molecules (for example, energy states associated with the

translational, rotational, and vibrational motions of the water molecules). If left standing on a table, the water loses heat to the cooler surroundings. Consequently, there is an increase in entropy because of the dispersal of energy over a great many energy states of the air molecules.

As another example, consider the situation depicted in Figure 18.1. Before the valve is opened, the system possesses a certain amount of entropy. Upon opening the valve, the gas molecules now have access to the combined volume of both bulbs. A larger volume for movement results in a narrowing of the gap between translational energy levels of the molecules. Consequently, the entropy of the system increases because closely spaced energy levels leads to a greater dispersal among the energy levels.

Translational motion is motion through space of the whole molecule.

Microstates and Entropy

Before we introduce the second law of thermodynamics, which relates entropy change (increase) to spontaneous processes, it is useful to first provide a proper definition of entropy. To do so let us consider a simple system of four molecules distributed between two equal compartments, as shown in Figure 18.2. There is only one way to arrange all the molecules in the left compartment, four ways to have three molecules in the left compartment and one in the right compartment, and six ways to have two molecules in each of the two compartments. The eleven possible ways of distributing the molecules are called microscopic states or microstates and each set of similar microstates is called a distribution.[†] As you can see, distribution III is the most probable because there are six microstates or six ways to achieve it and distribution I is the least probable because it has one microstate and therefore there is only one way to achieve it. Based on this analysis, we conclude that the probability of occurrence
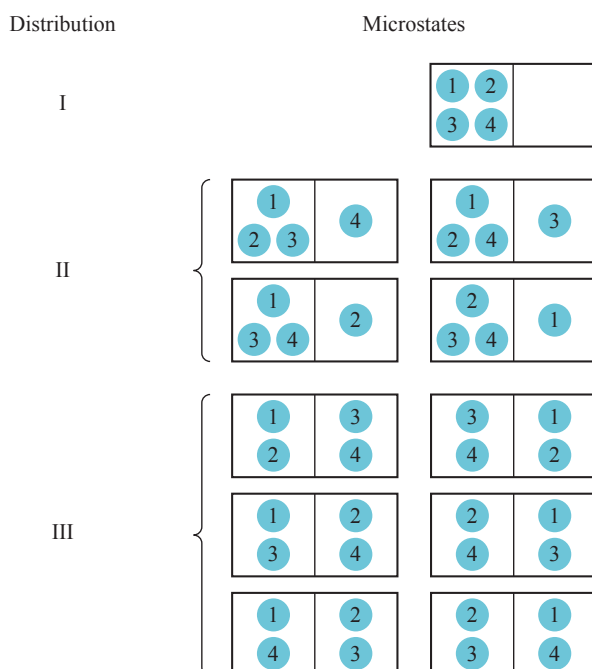

Figure 18.2
Some possible ways of distributing four molecules between two equal compartments. Distribution I can be achieved in only one way (all four molecules in the left compartment) and has one microstate. Distribution II can be achieved in four ways and has four microstates. Distribution III can be achieved in six ways and has six microstates.

[†]Actually there are still other possible ways to distribute the four molecules between the two compartments. We can have all four molecules in the right compartment (one way) and three molecules in the right compartment and one molecule in the left compartment (four ways). However, the distributions shown in Figure 18.2 are sufficient for our discussion.

of a particular distribution (state) depends on the number of ways (microstates) in which the distribution can be achieved. As the number of molecules approaches macroscopic scale, it is not difficult to see that they will be evenly distributed between the two compartments because this distribution has many, many more microstates than all other distributions.

In 1868 Boltzmann showed that the entropy of a system is related to the natural log of the number of microstates (W):

$$S = k \ln W \tag{18.1}$$

where k is called the Boltzmann constant (1.38×10^{-23} J/K). Thus, the larger the W, the greater is the entropy of the system. Like enthalpy, entropy is a state function (see Section 6.3). Consider a certain process in a system. The entropy change for the process, ΔS, is

$$\Delta S = S_f - S_i \tag{18.2}$$

where S_i and S_f are the entropies of the system in the initial and final states, respectively. From Equation (18.1) we can write

$$\begin{aligned} \Delta S &= k \ln W_f - k \ln W_i \\ &= k \ln \frac{W_f}{W_i} \end{aligned} \tag{18.3}$$

where W_i and W_f are the corresponding numbers of microstates in the initial and final state. Thus, if $W_f > W_i$, $\Delta S > 0$ and the entropy of the system increases.
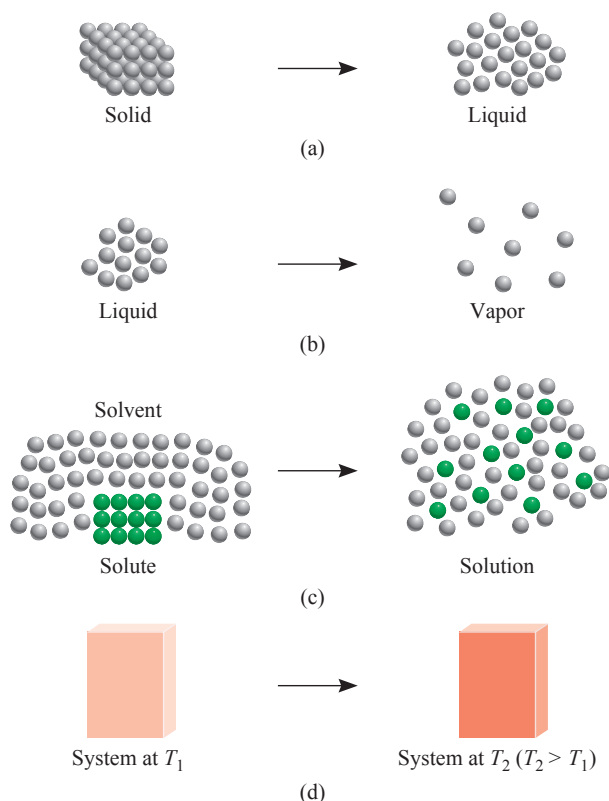
Changes in Entropy

Earlier we described the increase in entropy of a system as a result of the increase in the dispersal of energy. There is a connection between the qualitative description of entropy in terms of dispersal of energy and the quantitative definition of entropy in terms of microstates given by Equation (18.1). We conclude that

- A system with fewer microstates (smaller W) among which to spread its energy (small dispersal) has a lower entropy.
- A system with more microstates (larger W) among which to spread its energy (large dispersal) has a higher entropy.

Next, we will study several processes that lead to a change in entropy of a system in terms of the change in the number of microstates of the system.

Consider the situations shown in Figure 18.3. In a solid the atoms or molecules are confined to fixed positions and the number of microstates is small. Upon melting, these atoms or molecules can occupy many more positions as they move away from the lattice points. Consequently, the number of microstates increases because there are now many more ways to arrange the particles. Therefore, we predict this "order $\longrightarrow$ disorder" phase transition to result in an increase in entropy because the number of microstates has increased. Similarly, we predict the vaporization process will also lead to an increase in the entropy of the system. The increase will be considerably greater than that for melting, however, because molecules in the gas phase occupy much more space, and therefore there are far more microstates than in the liquid phase. The solution process usually leads to an increase in entropy. When a sugar crystal dissolves in water, the highly ordered structure of the solid and part of

Engraved on Ludwig Boltzmann's tombstone in Vienna is his famous equation. The "log" stands for "$\log_e$," which is the natural logarithm or ln.

Figure 18.3
Processes that lead to an increase in entropy of the system: (a) melting: $S_{liquid} > S_{solid}$; (b) vaporization: $S_{vapor} > S_{liquid}$; (c) dissolving; (d) heating: $S_{T_2} > S_{T_1}$.

the ordered structure of water break down. Thus, the solution has a greater number of microstates than the pure solute and pure solvent combined. When an ionic solid such as NaCl dissolves in water, there are two contributions to entropy increase: the solution process (mixing of solute with solvent) and the dissociation of the compound into ions:

$$\text{NaCl}(s) \xrightarrow{\text{H}_2\text{O}} \text{Na}^+(aq) + \text{Cl}^-(aq)$$
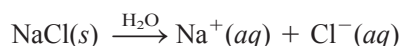
More particles lead to a greater number of microstates. However, we must also consider hydration, which causes water molecules to become more ordered around the ions. This process decreases entropy because it reduces the number of microstates of the solvent molecules. For small, highly charged ions such as Al^{3+} and Fe^{3+}, the decrease in entropy due to hydration can outweigh the increase in entropy due to mixing and dissociation so that the entropy change for the overall process can actually be negative. Heating also increases the entropy of a system. In addition to translational motion, molecules can also execute rotational motions and vibrational motions (Figure 18.4). As the temperature is increased, the energies associated with all types of molecular motion increase. This increase in energy is distributed or dispersed among the quantized energy levels. Consequently, more microstates become available at a higher temperature; therefore, the entropy of a system always increases with increasing temperature.

Standard Entropy

Equation (18.1) provides a useful molecular interpretation of entropy, but is normally not used to calculate the entropy of a system because it is difficult to determine the

Figure 18.4
(a) A diatomic molecule can rotate about the y- and z-axes (the x-axis is along the bond). (b) Vibrational motion of a diatomic molecule. Chemical bonds can be stretched and compressed like a spring.

Stable form

Stretched

Compressed

(a)   (b)
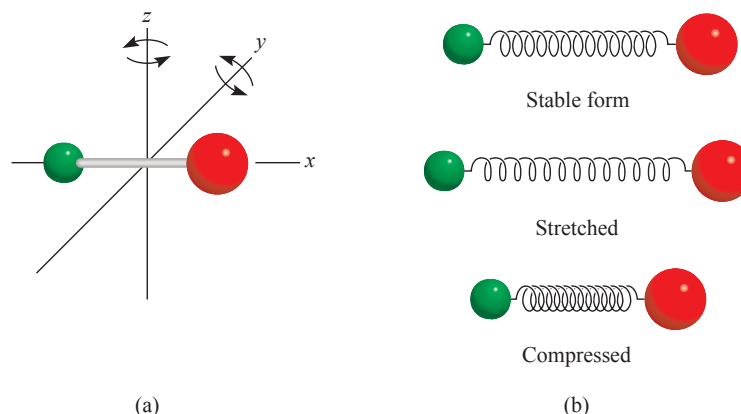
TABLE 18.1

Standard Entropy Values ($S°$) for Some Substances at 25°C

Substance	$S°$ (J/K · mol)
$H_2O(l)$	69.9
$H_2O(g)$	188.7
$Br_2(l)$	152.3
$Br_2(g)$	245.3
$I_2(s)$	116.7
$I_2(g)$	260.6
C (diamond)	2.4
C (graphite)	5.69
CH_4 (methane)	186.2
C_2H_6 (ethane)	229.5
He(g)	126.1
Ne(g)	146.2

number of microstates for a macroscopic system containing many molecules. Instead, entropy is obtained by calorimetric methods. In fact, as we will see shortly, it is possible to determine the absolute value of entropy of a substance, called absolute entropy, something we cannot do for energy or enthalpy. *Standard entropy* is the absolute entropy of a substance at 1 atm and 25°C. (Recall that the standard state refers only to 1 atm. The reason for specifying 25°C is that many processes are carried out at room temperature.) Table 18.1 lists standard entropies of a few elements and compounds; Appendix 2 provides a more extensive listing. The units of entropy are J/K or J/K · mol for 1 mole of the substance. We use joules rather than kilojoules because entropy values are typically quite small. Entropies of elements and compounds are all positive (that is, $S° > 0$). By contrast, the standard enthalpy of formation ($\Delta H_f°$) for elements in their stable form is arbitrarily set equal to zero, and for compounds it may be positive or negative.

Referring to Table 18.1, we see that the standard entropy of water vapor is greater than that of liquid water. Similarly, bromine vapor has a higher standard entropy than liquid bromine, and iodine vapor has a greater standard entropy than solid iodine. For different substances in the same phase, molecular complexity determines which ones have higher entropies. Both diamond and graphite are solids, but diamond has a more ordered structure and hence a smaller number of microstates (see Figure 12.22). Therefore, diamond has a smaller standard entropy than graphite. Consider the natural gases methane and ethane. Ethane has a more complex structure and hence more ways to execute molecular motions, which also increase its microstates. Therefore, ethane has a greater standard entropy than methane. Both helium and neon are monatomic gases, which cannot execute rotational or vibrational motions, but neon has a greater standard entropy than helium because its molar mass is greater. Heavier atoms have more closely spaced energy levels so there is a greater distribution of the atoms' energy among the energy levels. Consequently, there are more microstates associated with these atoms.

Example 18.1

Predict whether the entropy change is greater or less than zero for each of the following processes: (a) freezing ethanol, (b) evaporating a beaker of liquid bromine at room temperature, (c) dissolving glucose in water, (d) cooling nitrogen gas from 80°C to 20°C.

(Continued)

Strategy To determine the entropy change in each case, we examine whether the number of microstates of the system increases or decreases. The sign of ΔS will be positive if there is an increase in the number of microstates and negative if the number of microstates decreases.

Solution (a) Upon freezing, the ethanol molecules are held rigidly in position. This phase transition reduces the number of microstates and therefore the entropy decreases; that is, $\Delta S < 0$.

(b) Evaporating bromine increases the number of microstates because the Br_2 molecules can occupy many more positions in nearly empty space. Therefore $\Delta S > 0$.

(c) Glucose is a nonelectrolyte. The solution process leads to a greater dispersal of matter due to the mixing of glucose and water molecules so we expect $\Delta S > 0$.

(d) The cooling process decreases various molecular motions. This leads to a decrease in microstates and so $\Delta S < 0$.

Practice Exercise How does the entropy of a system change for each of the following processes? (a) condensing water vapor, (b) forming sucrose crystals from a supersaturated solution, (c) heating hydrogen gas from 60°C to 80°C, and (d) subliming dry ice.
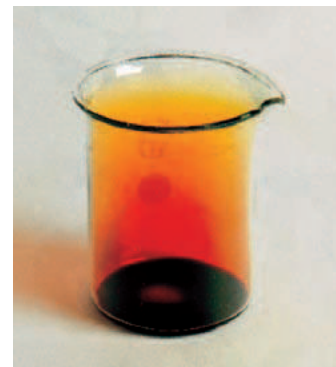
Bromine is a fuming liquid at room temperature.

Similar problem: 18.5.

18.4 The Second Law of Thermodynamics

The connection between entropy and the spontaneity of a reaction is expressed by the *second law of thermodynamics: The entropy of the universe increases in a spontaneous process and remains unchanged in an equilibrium process.* Because the universe is made up of the system and the surroundings, the entropy change in the universe (ΔS_{univ}) for any process is the *sum* of the entropy changes in the system (ΔS_{sys}) and in the surroundings (ΔS_{surr}). Mathematically, we can express the second law of thermodynamics as follows:

Just talking about entropy increases its value in the universe.

For a spontaneous process:
$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0 \qquad (18.4)$$

For an equilibrium process:
$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 0 \qquad (18.5)$$

For a spontaneous process, the second law says that ΔS_{univ} must be greater than zero, but it does not place a restriction on either ΔS_{sys} or ΔS_{surr}. Thus, it is possible for either ΔS_{sys} or ΔS_{surr} to be negative, as long as the sum of these two quantities is greater than zero. For an equilibrium process, ΔS_{univ} is zero. In this case, ΔS_{sys} and ΔS_{surr} must be equal in magnitude, but opposite in sign. What if for some hypothetical process we find that ΔS_{univ} is negative? What this means is that the process is not spontaneous in the direction described. Rather, it is spontaneous in the *opposite* direction.

Entropy Changes in the System

To calculate ΔS_{univ}, we need to know both ΔS_{sys} and ΔS_{surr}. Let us focus first on ΔS_{sys}. Suppose that the system is represented by the following reaction:

Interactivity:
Entropies of Reactions
ARIS, Interactives

$$a\text{A} + b\text{B} \longrightarrow c\text{C} + d\text{D}$$

As is the case for the enthalpy of a reaction [see Equation (6.17)], the *standard entropy of reaction* ΔS_{rxn}° is given by *the difference in standard entropies between products and reactants:*

$$\Delta S_{rxn}^\circ = [cS^\circ(C) + dS^\circ(D)] - [aS^\circ(A) + bS^\circ(B)] \qquad (18.6)$$

or, in general, using Σ to represent summation and m and n for the stoichiometric coefficients in the reaction,

$$\Delta S_{rxn}^\circ = \Sigma nS^\circ(\text{products}) - \Sigma mS^\circ(\text{reactants}) \qquad (18.7)$$

The standard entropy values of a large number of compounds have been measured in $J/K \cdot mol$. To calculate ΔS_{rxn}° (which is ΔS_{sys}), we look up their values in Appendix 2 and proceed according to Example 18.2.

Example 18.2

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 To calculate the standard entropy of a reaction, we look up the standard entropies of reactants and products in Appendix 2 and apply Equation (18.7). As in the calculation of enthalpy of reaction [see Equation (6.18)], the stoichiometric coefficients have no units, so ΔS_{rxn}° is expressed in units of $J/K \cdot mol$.

Solution

(a) $\Delta S_{rxn}^\circ = [S^\circ(CaO) + S^\circ(CO_2)] - [S^\circ(CaCO_3)]$
$= [(39.8 \text{ J/K} \cdot mol) + (213.6 \text{ J/K} \cdot mol)] - (92.9 \text{ J/K} \cdot mol)$
$= 160.5 \text{ J/K} \cdot mol$

Thus, when 1 mole of $CaCO_3$ decomposes to form 1 mole of CaO and 1 mole of gaseous CO_2, there is an increase in entropy equal to 160.5 J/K $\cdot$ mol.

(b) $\Delta S_{rxn}^\circ = [2S^\circ(NH_3)] - [S^\circ(N_2) + 3S^\circ(H_2)]$
$= (2)(193 \text{ J/K} \cdot mol) - [(192 \text{ J/K} \cdot mol) + (3)(131 \text{ J/K} \cdot mol)]$
$= -199 \text{ J/K} \cdot mol$

This result shows that when 1 mole of gaseous nitrogen reacts with 3 moles of gaseous hydrogen to form 2 moles of gaseous ammonia, there is a decrease in entropy equal to -199 J/K $\cdot$ mol.

(c) $\Delta S_{rxn}^\circ = [2S^\circ(HCl)] - [S^\circ(H_2) + S^\circ(Cl_2)]$
$= (2)(187 \text{ J/K} \cdot mol) - [(131 \text{ J/K} \cdot mol) + (223 \text{ J/K} \cdot mol)]$
$= 20 \text{ J/K} \cdot mol$

Thus, the formation of 2 moles of gaseous HCl from 1 mole of gaseous H_2 and 1 mole of gaseous Cl_2 results in a small increase in entropy equal to 20 J/K $\cdot$ mol.

Similar problems: 18.11 and 18.12.

Comment The ΔS_{rxn}° values all apply to the system.

Practice Exercise Calculate the standard entropy change for the following reactions at 25°C:

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

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

(c) $2NaHCO_3(s) \longrightarrow Na_2CO_3(s) + H_2O(l) + CO_2(g)$

The results of Example 18.2 are consistent with those observed for many other reactions. Taken together, they support the following general rules:

- If a reaction produces more gas molecules than it consumes [Example 18.2(a)], $\Delta S°$ is positive.
- If the total number of gas molecules diminishes [Example 18.2(b)], $\Delta S°$ is negative.
- If there is no net change in the total number of gas molecules [Example 18.2(c)], then $\Delta S°$ may be positive or negative, but will be relatively small numerically.

We omit the subscript rxn for simplicity.

These conclusions make sense, given that gases invariably have greater entropy than liquids and solids. For reactions involving only liquids and solids, predicting the sign of $\Delta S°$ is 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.

Example 18.3

Predict whether the entropy change of the system in each of the following reactions is positive or negative.

(a) $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$
(b) $NH_4Cl(s) \longrightarrow NH_3(g) + HCl(g)$
(c) $H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$

Strategy We are asked to predict, not calculate, the sign of entropy change in the reactions. The factors that lead to an increase in entropy are (1) a transition from a condensed phase to the vapor phase and (2) a reaction that produces more product molecules than reactant molecules in the same phase. It is also important to compare the relative complexity of the product and reactant molecules. In general, the more complex the molecular structure, the greater the entropy of the compound.

Solution (a) Two reactant molecules combine to form one product molecule. Even though H_2O is a more complex molecule than either H_2 and O_2, the fact that there is a net decrease of one molecule and gases are converted to liquid ensures that the number of microstates will be diminished and hence $\Delta S°$ is negative.

(b) A solid is converted to two gaseous products. Therefore, $\Delta S°$ is positive.

(c) The same number of molecules is involved in the reactants as in the product. Furthermore, all molecules are diatomic and therefore of similar complexity. As a result, we cannot predict the sign of $\Delta S°$, but we know that the change must be quite small in magnitude.

Similar problems: 18.13 and 18.14.

Practice Exercise Discuss qualitatively the sign of the entropy change expected for each of the following processes:

(a) $I_2(s) \longrightarrow 2I(g)$
(b) $2Zn(s) + O_2(g) \longrightarrow 2ZnO(s)$
(c) $N_2(g) + O_2(g) \longrightarrow 2NO(g)$

Entropy Changes in the Surroundings

Next we see how ΔS_{surr} is calculated. When an exothermic process takes place in the system, the heat transferred to the surroundings enhances motion of the molecules in the surroundings. Consequently, there is an increase in the number of microstates and the entropy of the surroundings increases. Conversely, an endothermic process in the system absorbs heat from the surroundings and so decreases the
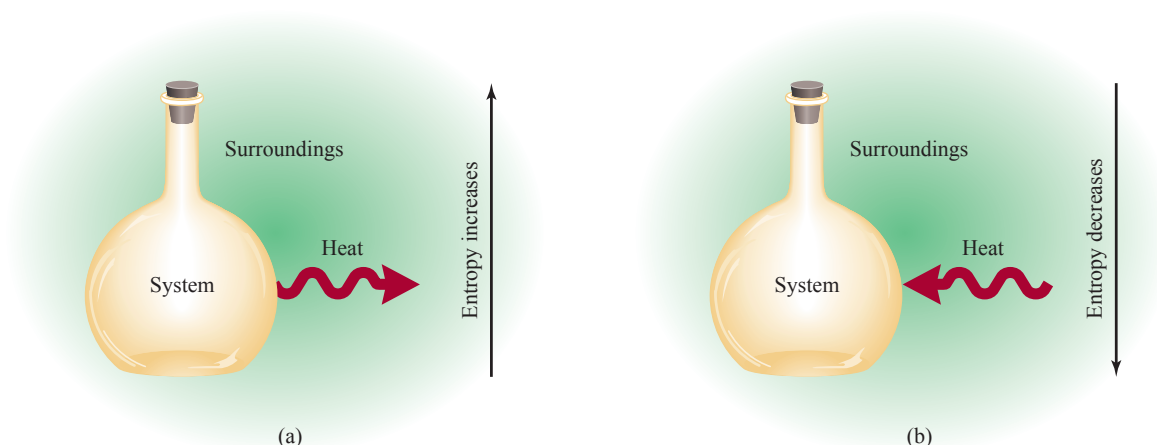
Figure 18.5

(a) An exothermic process transfers heat from the system to the surroundings and results in an increase in the entropy of the surroundings. (b) An endothermic process absorbs heat from the surroundings and thereby decreases the entropy of the surroundings.

entropy of the surroundings because molecular motion decreases (Figure 18.5). For constant-pressure processes, the heat change is equal to the enthalpy change of the system, ΔH_{sys}. Therefore, the change in entropy of the surroundings, ΔS_{surr}, is proportional to ΔH_{sys}:

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

The minus sign is used because if the process is exothermic, ΔH_{sys} is negative and ΔS_{surr} is a positive quantity, indicating an increase in entropy. On the other hand, for an endothermic process, ΔH_{sys} is positive and the negative sign ensures that the entropy of the surroundings decreases.

The change in entropy for a given amount of heat absorbed also depends on the temperature. If the temperature of the surroundings is high, the molecules are already quite energetic. Therefore, the absorption of heat from an exothermic process in the system will have relatively little impact on molecular motion and the resulting increase in entropy of the surroundings will be small. However, if the temperature of the surroundings is low, then the addition of the same amount of heat will cause a more drastic increase in molecular motion and hence a larger increase in entropy. By analogy, someone coughing in a crowded restaurant will not disturb too many people, but someone coughing in a library definitely will. From the inverse relationship between ΔS_{surr} and temperature T (in kelvins)—that is, the higher the temperature, the smaller the ΔS_{surr} and vice versa—we can rewrite the preceding relationship as

This equation, which can be derived from the laws of thermodynamics, assumes that both the system and the surroundings are at temperature T.

$$\Delta S_{surr} = \frac{-\Delta H_{sys}}{T} \tag{18.8}$$

Let us now apply the procedure for calculating ΔS_{sys} and ΔS_{surr} to the synthesis of ammonia and ask whether the reaction is spontaneous at 25°C:

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g) \qquad \Delta H^\circ_{rxn} = -92.6 \text{ kJ/mol}$$
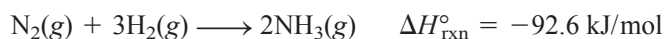
From Example 18.2(b) we have $\Delta S_{sys} = -199$ J/K · mol, and substituting ΔH_{sys} (-92.6 kJ/mol) in Equation (18.8), we obtain

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

The change in entropy of the universe is

$$\begin{aligned}\Delta S_{univ} &= \Delta S_{sys} + \Delta S_{surr} \\ &= -199 \text{ J/K} \cdot \text{mol} + 311 \text{ J/K} \cdot \text{mol} \\ &= 112 \text{ J/K} \cdot \text{mol}\end{aligned}$$

Because ΔS_{univ} is positive, we predict that the reaction is spontaneous at 25°C. It is important to keep in mind 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 a reaction will occur spontaneously under specific conditions, but it does not say how fast it will occur. Reaction rates are the subject of chemical kinetics (see Chapter 14).
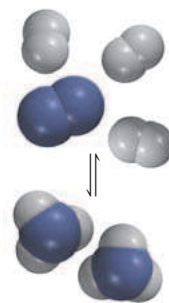
The Third Law of Thermodynamics and Absolute Entropy

Finally, it is appropriate to consider the *third law of thermodynamics* briefly in connection with the determination of entropy values. So far we have related entropy to microstates—the greater the number of microstates a system possesses, the larger is the entropy of the system. Consider a perfect crystalline substance at absolute zero (0 K). Under these conditions, molecular motions are kept at a minimum and the number of microstates (W) is one (there is only one way to arrange the atoms or molecules to form a perfect crystal). From Equation (18.1) we write

$$\begin{aligned}S &= k \ln W \\ &= k \ln 1 = 0\end{aligned}$$

According to the **third law of thermodynamics,** *the entropy of a perfect crystalline substance is zero at the absolute zero of temperature*. As the temperature increases, the freedom of motion increases and hence also the number of microstates. Thus, the entropy of any substance at a temperature above 0 K is greater than zero. Note also that if the crystal is impure or if it has defects, then its entropy is greater than zero even at 0 K because it would not be perfectly ordered and the number of microstates would be greater than one.

The important point about the third law of thermodynamics is that it enables us to determine the *absolute* entropies of substances. Starting with the knowledge that the entropy of a pure crystalline substance is zero at absolute zero, we can measure the increase in entropy of the substance when it is heated from 0 K to, say, 298 K. The change in entropy, ΔS, is given by

$$\begin{aligned}\Delta S &= S_f - S_i \\ &= S_f\end{aligned}$$

because S_i is zero. The entropy of the substance at 298 K, then, is given by ΔS or S_f, which is called the absolute entropy because this is the *true* value and not a value derived using some arbitrary reference as in the case of standard enthalpy of formation. Thus, the entropy values quoted so far and those listed in Appendix 2
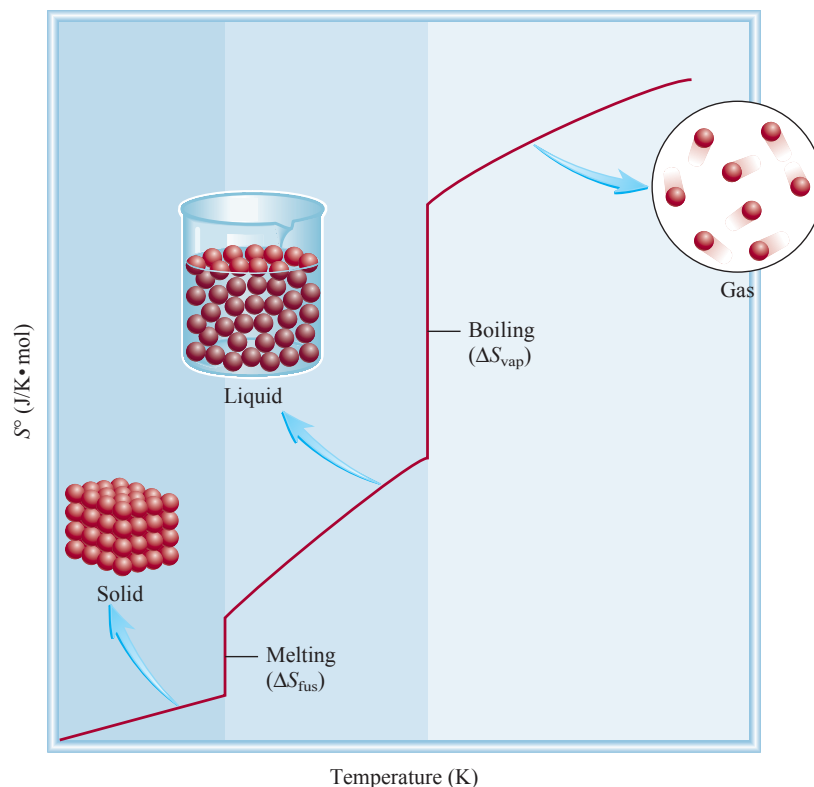
Interactivity:
Entropy vs. Temperature
ARIS, Interactives

The entropy increase can be calculated from the temperature change and heat capacity of the substance, plus any phase changes.

Figure 18.6
Entropy increase of a substance as the temperature rises from absolute zero.

are all absolute entropies. Because measurements are carried out at 1 atm, we usually refer to absolute entropies as standard entropies. In contrast, we cannot have the absolute energy or enthalpy of a substance because the zero of energy or enthalpy is undefined. Figure 18.6 shows the change (increase) in entropy of a substance with temperature. At absolute zero, it has a zero entropy value (assuming that it is a perfect crystalline substance). As it is heated, its entropy increases gradually because of greater molecular motion. At the melting point, there is a sizable increase in entropy as the liquid state is formed. Further heating increases the entropy of the liquid again due to enhanced 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 rise with increasing temperature.

18.5 Gibbs Free Energy

The second law of thermodynamics tells us that a spontaneous reaction increases the entropy of the universe; that is, $\Delta S_{univ} > 0$. In order to determine the sign of ΔS_{univ} for a reaction, however, we would need to calculate both ΔS_{sys} and ΔS_{surr}. In general, we are usually concerned only with what happens in a particular system. Therefore, we need another thermodynamic function to help us determine whether a reaction will occur spontaneously if we consider only the system itself.

From Equation (18.4), we know that for a spontaneous process, we have

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

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

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

Multiplying both sides of the equation by T gives

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

Now we have a criterion for a spontaneous reaction that is expressed only in terms of the properties of the system (ΔH_{sys} and ΔS_{sys}) and we can ignore the surroundings. For convenience, we can change the preceding equation by multiplying it throughout by -1 and replacing the $>$ sign with $<$:

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

The change in unequal sign when we multiply the equation by -1 follows from the fact that $1 > 0$ and $-1 < 0$.

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

In order to express the spontaneity of a reaction more directly, we introduce another thermodynamic function called **Gibbs free energy (G),** or simply **free energy** (after the American physicist Josiah Willard Gibbs):

$$G = H - TS \tag{18.9}$$

A commemorative stamp honoring Gibbs.

All quantities in Equation (18.9) pertain to the system, and T is the temperature of the system. You can see that G has units of energy (both H and TS are in energy units). Like H and S, G is a state function.

The change in free energy (ΔG) of a system for a *constant-temperature* process is

$$\Delta G = \Delta H - T\Delta S \tag{18.10}$$

We omit the subscript sys for simplicity.

In this context free energy is *the energy available to do work.* Thus, if a particular reaction is accompanied by a release of usable energy (that is, if ΔG is negative), this fact alone guarantees that it is spontaneous, and there is no need to worry about what happens to the rest of the universe.
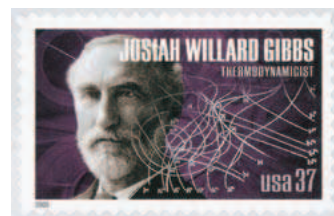
The word "free" in the term "free energy" does not mean without cost.

Note that we have merely organized the expression for the entropy change of the universe and equating the free-energy change of the system (ΔG) with $-T\Delta S_{univ}$, so that we can focus on changes in the system. We can now summarize the conditions for spontaneity and equilibrium at constant temperature and pressure in terms of ΔG as follows:

$\Delta G < 0$ The reaction is spontaneous in the forward direction.
$\Delta G > 0$ The reaction is nonspontaneous. The reaction is spontaneous in the opposite direction.
$\Delta G = 0$ The system is at equilibrium. There is no net change.

Standard Free-Energy Changes

The **standard free-energy of reaction (ΔG°_{rxn})** is *the free-energy change for a reaction when it occurs under standard-state conditions, when reactants in their standard states are converted to products in their standard states.* Table 18.2 summarizes the

conventions used by chemists to define the standard states of pure substances as well as solutions. To calculate (ΔG_{rxn}°) we start with the 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

$$\Delta G_{rxn}^\circ = [c\Delta G_f^\circ(\text{C}) + d\Delta G_f^\circ(\text{D})] - [a\Delta G_f^\circ(\text{A}) + b\Delta G_f^\circ(\text{B})] \qquad (18.11)$$

or, in general,

$$\Delta G_{rxn}^\circ = \Sigma n\Delta G_f^\circ(\text{products}) - \Sigma m\Delta G_f^\circ(\text{reactants}) \qquad (18.12)$$

where m and n are stoichiometric coefficients. The term ΔG_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 elements in their standard states*. For the combustion of graphite:

$$\text{C(graphite)} + \text{O}_2(g) \longrightarrow \text{CO}_2(g)$$
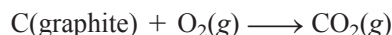
the standard free-energy change [from Equation (18.12)] is

$$\Delta G_{rxn}^\circ = \Delta G_f^\circ(\text{CO}_2) - [\Delta G_f^\circ(\text{C, graphite}) + \Delta G_f^\circ(\text{O}_2)]$$

As in the case of the standard enthalpy of formation (p. 192), we define the standard free energy of formation of any element in its stable allotropic form at 1 atm and 25°C as zero. Thus,

$$\Delta G_f^\circ(\text{C, graphite}) = 0 \qquad \text{and} \qquad \Delta G_f^\circ(\text{O}_2) = 0$$
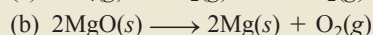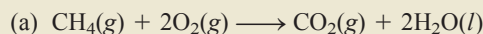
Therefore, the standard free-energy change for the reaction in this case is equal to the standard free energy of formation of CO_2:

$$\Delta G_{rxn}^\circ = \Delta G_f^\circ(\text{CO}_2)$$

Appendix 2 lists the values of ΔG_f° for a number of compounds.

Example 18.4

Calculate the standard free-energy changes for the following reactions at 25°C.
(a) $\text{CH}_4(g) + 2\text{O}_2(g) \longrightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l)$
(b) $2\text{MgO}(s) \longrightarrow 2\text{Mg}(s) + \text{O}_2(g)$

Strategy To calculate the standard free-energy change of a reaction, we look up the standard free energies of formation of reactants and products in Appendix 2 and apply Equation (18.12). Note that all the stoichiometric coefficients have no units so ΔG_{rxn}° is expressed in units of kJ/mol, and ΔG_f° for O_2 is zero because it is the stable allotropic element at 1 atm and 25°C.

Solution (a) According to Equation (18.12), we write

$$\Delta G_{rxn}^\circ = [\Delta G_f^\circ(\text{CO}_2) + 2\Delta G_f^\circ(\text{H}_2\text{O})] - [\Delta G_f^\circ(\text{CH}_4) + 2\Delta G_f^\circ(\text{O}_2)]$$

(Continued)

We insert the appropriate values from Appendix 2:

$$\Delta G^{\circ}_{\text{rxn}} = [(-394.4 \text{ kJ/mol}) + (2)(-237.2 \text{ kJ/mol})] -$$
$$[(-50.8 \text{ kJ/mol}) + (2)(0 \text{ kJ/mol})]$$
$$= -818.0 \text{ kJ/mol}$$

(b) The equation is

$$\Delta G^{\circ}_{\text{rxn}} = [2\Delta G^{\circ}_{\text{f}}(\text{Mg}) + \Delta G^{\circ}_{\text{f}}(\text{O}_2)] - [2\Delta G^{\circ}_{\text{f}}(\text{MgO})]$$

From data in Appendix 2 we write

$$\Delta G^{\circ}_{\text{rxn}} = [(2)(0 \text{ kJ/mol}) + (0 \text{ kJ/mol})] - [(2)(-569.6 \text{ kJ/mol})]$$
$$= 1139 \text{ kJ/mol}$$

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

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

(b) $2C_2H_6(g) + 7O_2(g) \longrightarrow 4CO_2(g) + 6H_2O(l)$

Applications of Equation (18.10)

In order to predict the sign of ΔG, according to Equation (18.10) we need to know both ΔH and ΔS. A negative ΔH (an exothermic reaction) and a positive ΔS (a reaction that results in an increase in the microstates of the system) tend to make ΔG negative, although temperature may also influence the *direction* of a spontaneous reaction. The four possible outcomes of this relationship are:

- If both ΔH and ΔS are positive, then ΔG will be negative only when the $T\Delta S$ term is greater in magnitude than ΔH. This condition is met when T is large.
- If ΔH is positive and ΔS is negative, ΔG will always be positive, regardless of temperature.
- If ΔH is negative and ΔS is positive, then ΔG will always be negative regardless of temperature.
- If ΔH is negative and ΔS is negative, then ΔG will be negative only when $T\Delta S$ is smaller in magnitude than ΔH. This condition is met when T is small.

The temperatures that will cause ΔG to be negative for the first and last cases depend on the actual values of ΔH and ΔS of the system. Table 18.3 summarizes the effects of the possibilities just described.

Before we apply the change in free energy to predict reaction spontaneity, it is useful to distinguish between ΔG and ΔG°. Suppose we carry out a reaction in solution with all the reactants in their standard states (that is, all at 1 *M* concentration). As soon as the reaction starts, the standard-state condition no longer exists for the reactants or the products because their concentrations are different from 1 *M*. Under nonstandard state conditions, we must use the sign of ΔG rather than that of ΔG° to predict the direction of the reaction. The sign of ΔG°, on the other hand, tells us whether the products or the reactants are favored when the reacting system reaches equilibrium. Thus, a negative value of ΔG° indicates that the reaction favors product formation whereas a positive value of ΔG° indicates that there will be more reactants than products at equilibrium.

TABLE 18.3		Factors Affecting the Sign of ΔG in the Relationship $\Delta G = \Delta H - T\Delta S$	
ΔH	ΔS	ΔG	Example
$+$	$+$	Reaction proceeds spontaneously at high temperatures. At low temperatures, reaction is spontaneous in the reverse direction.	$2HgO(s) \longrightarrow 2Hg(l) + O_2(g)$
$+$	$-$	ΔG is always positive. Reaction is spontaneous in the reverse direction at all temperatures.	$3O_2(g) \longrightarrow 2O_3(g)$
$-$	$+$	ΔG is always negative. Reaction proceeds spontaneously at all temperatures.	$2H_2O_2(l) \longrightarrow 2H_2O(l) + O_2(g)$
$-$	$-$	Reaction proceeds spontaneously at low temperatures. At high temperatures, the reverse reaction becomes spontaneous.	$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$

We will now consider two specific applications of Equation (18.10).

Temperature and Chemical Reactions

Calcium oxide (CaO), also called quicklime, is an extremely valuable inorganic substance used in steelmaking, production of calcium metal, the paper industry, water treatment, and pollution control. It is prepared by decomposing limestone ($CaCO_3$) in a kiln at a high temperature (Figure 18.7):

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

Le Châtelier's principle predicts that the forward, endothermic reaction is favored by heating.

The reaction is reversible, and CaO readily combines with CO_2 to form $CaCO_3$. The pressure of CO_2 in equilibrium with $CaCO_3$ and CaO increases with temperature. In the industrial preparation of quicklime, the system is never maintained at equilibrium; rather, CO_2 is constantly removed from the kiln to shift the equilibrium from left to right, promoting the formation of calcium oxide.

The important information for the practical chemist is the temperature at which the decomposition of $CaCO_3$ becomes appreciable (that is, the temperature at which the reaction begins to favor products). 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 (6.17):

$$\begin{aligned}\Delta H° &= [\Delta H_f°(CaO) + \Delta H_f°(CO_2)] - [\Delta H_f°(CaCO_3)] \\ &= [(-635.6 \text{ kJ/mol}) + (-393.5 \text{ kJ/mol})] - (-1206.9 \text{ kJ/mol}) \\ &= 177.8 \text{ kJ/mol}\end{aligned}$$

Next we apply Equation (18.6) to find $\Delta S°$

$$\begin{aligned}\Delta S° &= [S°(CaO) + S°(CO_2)] - S°(CaCO_3) \\ &= [(39.8 \text{ J/K} \cdot \text{mol}) + (213.6 \text{ J/K} \cdot \text{mol})] - (92.9 \text{ J/K} \cdot \text{mol}) \\ &= 160.5 \text{ J/K} \cdot \text{mol}\end{aligned}$$

From Equation (18.10)

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

we obtain

Figure 18.7
The production of CaO from $CaCO_3$ in a rotatory kiln.

$$\begin{aligned}\Delta G° &= 177.8 \text{ kJ/mol} - (298 \text{ K})(160.5 \text{ J/K} \cdot \text{mol})\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right) \\ &= 130.0 \text{ kJ/mol}\end{aligned}$$

Because $\Delta G°$ is a large positive quantity, we conclude that the reaction is not favored for product formation at 25°C (or 298 K). Indeed, the pressure of CO_2 is so low at room temperature that it cannot be measured. In order to make $\Delta G°$ negative, we first have to find the temperature at which $\Delta G°$ is zero; that is,

$$0 = \Delta H° - T\Delta S°$$

or

$$T = \frac{\Delta H°}{\Delta S°}$$

$$= \frac{(177.8 \text{ kJ/mol})(1000 \text{ J/1 kJ})}{160.5 \text{ J/K} \cdot \text{mol}}$$

$$= 1108 \text{ K or } 835°C$$

At a temperature higher than 835°C, $\Delta G°$ becomes negative, indicating that the reaction now favors the formation of CaO and CO_2. For example, at 840°C, or 1113 K,

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

$$= 177.8 \text{ kJ/mol} - (1113 \text{ K})(160.5 \text{ J/K} \cdot \text{mol})\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right)$$

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

Two points are worth making about such a calculation. First, we used the $\Delta H°$ and $\Delta S°$ values at 25°C to calculate changes that occur at a much higher temperature. Because both $\Delta H°$ and $\Delta S°$ change with temperature, this approach will not give us an accurate value of $\Delta G°$, but it is good enough for "ball park" estimates. Second, we should not be misled into thinking that nothing happens below 835°C and that at 835°C $CaCO_3$ suddenly begins to decompose. Far from it. The fact that $\Delta G°$ is a positive value at some temperature below 835°C does not mean that no CO_2 is produced, but rather that the pressure of the CO_2 gas formed at that temperature will be below 1 atm (its standard-state value; see Table 18.2). As Figure 18.8 shows, the pressure of CO_2 at first increases very slowly with temperature; it becomes easily measurable above 700°C. The significance of 835°C is that this is the temperature at which the equilibrium pressure of CO_2 reaches 1 atm. Above 835°C, the equilibrium pressure of CO_2 exceeds 1 atm.

> The equilibrium constant of this reaction is $K_P = P_{CO_2}$.

Phase Transitions

At the temperature at which a phase transition occurs (that is, at the melting point or boiling point) the system is at equilibrium ($\Delta G = 0$), so Equation (18.10) becomes

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

or

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

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

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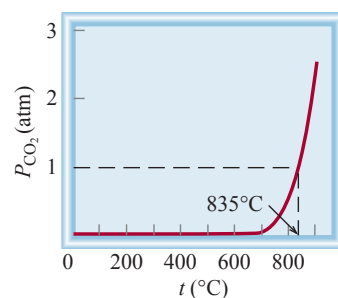
$$= 22.0 \text{ J/K} \cdot \text{mol}$$

Figure 18.8
Equilibrium pressure of CO_2 from the decomposition of $CaCO_3$, as a function of temperature. This curve is calculated by assuming that $\Delta H°$ and $\Delta S°$ of the reaction do not change with temperature.

Thus, when 1 mole of ice melts at 0°C, there is an increase in entropy of 22.0 J/K · mol. The increase in entropy is consistent with the increase in microstates from solid to liquid. Conversely, for the water → ice transition, the decrease in entropy is given by

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

In the laboratory we normally carry out unidirectional changes, that is, either ice to water or water to ice transition. We can calculate entropy change in each case using the equation $\Delta S = \Delta H/T$ as long as the temperature remains at 0°C. The same procedure can be applied to the water → steam transition. In this case ΔH is the heat of vaporization and T is the boiling point of water.

Example 18.5

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

Liquid and solid benzene in equilibrium at 5.5°C.

Strategy At the melting point, liquid and solid benzene are at equilibrium, so $\Delta G = 0$. From Equation (18.10) we have $\Delta G = 0 = \Delta H - T\Delta S$ or $\Delta S = \Delta H/T$. To calculate the entropy change for the solid benzene → liquid benzene transition, we write $\Delta S_{\text{fus}} = \Delta H_{\text{fus}}/T_{\text{f}}$. Here ΔH_{fus} is positive for an endothermic process, so ΔS_{fus} is also positive, as expected for a solid to liquid transition. The same procedure applies to the liquid benzene → vapor benzene transition. What temperature unit should be used?

Solution The entropy change for melting 1 mole of benzene at 5.5°C is

$$\Delta S_{\text{fus}} = \frac{\Delta H_{\text{fus}}}{\Delta T_{\text{f}}}$$
$$= \frac{(10.9 \text{ kJ/mol})(1000 \text{ J/1 kJ})}{(5.5 + 273) \text{ K}}$$
$$= 39.1 \text{ J/K} \cdot \text{mol}$$

Similarly, the entropy change for boiling 1 mole of benzene at 80.1°C is

$$\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_{\text{bp}}}$$
$$= \frac{(31.0 \text{ kJ/mol})(1000 \text{ J/1 kJ})}{(80.1 + 273) \text{ K}}$$
$$= 87.8 \text{ J/K} \cdot \text{mol}$$

Check Because vaporization creates more microstates than the melting process, $\Delta S_{\text{vap}} > \Delta S_{\text{fus}}$.

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

18.6 Free Energy and Chemical Equilibrium

As mentioned earlier, during the course of a chemical reaction not all the reactants and products will be at their standard states. Under this condition, the relationship between ΔG and $\Delta G°$, which can be derived from thermodynamics, is

$$\Delta G = \Delta G° + RT \ln Q \tag{18.13}$$

where R is the gas constant (8.314 J/K · mol), T is the absolute temperature of the reaction, and Q is the reaction quotient (see p. 507). We see that ΔG depends on two quantities: $\Delta G°$ and $RT \ln Q$. For a given reaction at temperature T the value of $\Delta G°$ is fixed but that of $RT \ln Q$ is not, because Q varies according to the composition of the reaction mixture. Let us consider two special cases:

Case 1: A large negative value of $\Delta G°$ will tend to make ΔG also negative. Thus, the net reaction will proceed from left to right until a significant amount of product has been formed. At that point, the $RT \ln Q$ term will become positive enough to match the negative $\Delta G°$ term.

Case 2: A large positive $\Delta G°$ term will tend to make ΔG also positive. Thus, the net reaction will proceed from right to left until a significant amount of reactant has been formed. At that point, the $RT \ln Q$ term will become negative enough to match the positive $\Delta G°$ term.

At equilibrium, by definition, $\Delta G = 0$ and $Q = K$, where K is the equilibrium constant. Thus,

Sooner or later a reversible reaction will reach equilibrium.

$$0 = \Delta G° + RT \ln K$$

or

$$\Delta G° = -RT \ln K \tag{18.14}$$

In this equation, K_P is used for gases and K_c for reactions in solution. Note that the larger the K is, the more negative $\Delta G°$ is. For chemists, Equation (18.14) is one of the most important equations in thermodynamics because it enables us to find the equilibrium constant of a reaction if we know the change in standard free energy and vice versa.

It is significant that Equation (18.14) relates the equilibrium constant to the *standard* free energy change $\Delta G°$ rather than to the *actual* free energy change ΔG. The actual free energy change of the system varies as the reaction progresses and becomes zero at equilibrium. On the other hand, $\Delta G°$ is a constant for a particular reaction at a given temperature. Figure 18.9 shows plots of the free energy of a reacting system versus the extent of the reaction for two types of reactions. As you can see, if $\Delta G° < 0$, the products are favored over reactants at equilibrium. Conversely, if $\Delta G° > 0$, there will be more reactants than products at equilibrium. Table 18.4 summarizes the three possible relations between $\Delta G°$ and K, as predicted by Equation (18.14). Remember this important distinction: It is the sign of ΔG and not that of $\Delta G°$ that determines the direction of reaction spontaneity. The sign of $\Delta G°$ tells us only the relative amounts of products and reactants when equilibrium is reached, not the direction of the net reaction.

Interactivity:
Free Energy—Equilibrium
ARIS, Interactives

For reactions having very large or very small equilibrium constants, it is generally very difficult, if not impossible, to measure the K values by monitoring the
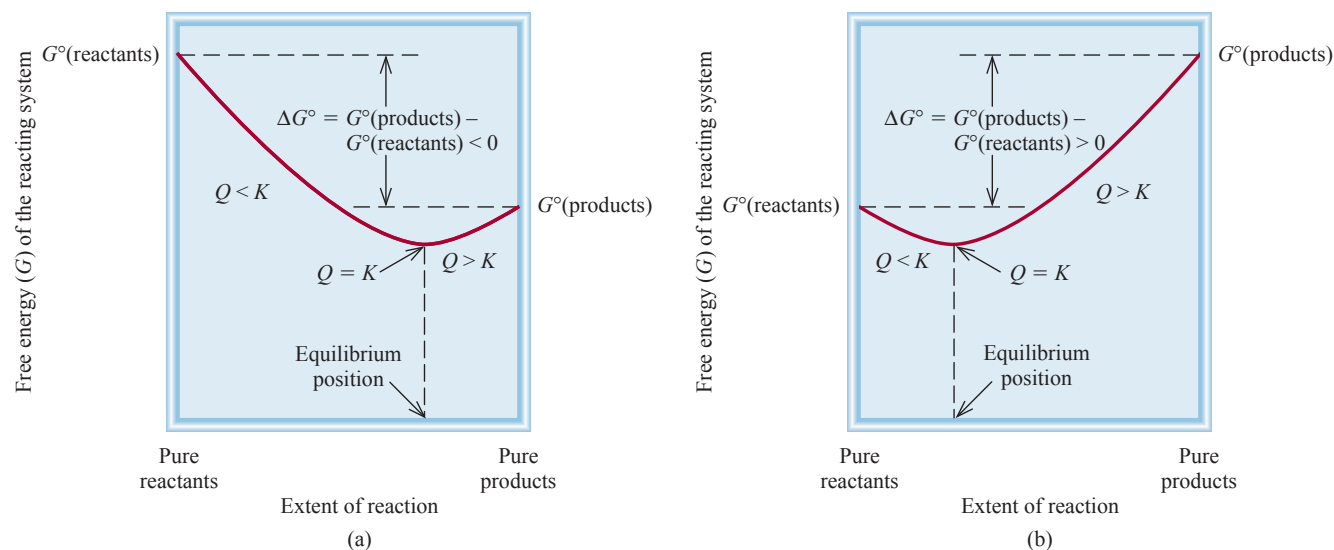
Figure 18.9
(a) $\Delta G° < 0$. At equilibrium, there is a significant conversion of reactants to products. (b) $\Delta G° > 0$. At equilibrium, reactants are favored over products. In both cases, the net reaction toward equilibrium is from left to right (reactants to products) if $Q < K$ and right to left (products to reactants) if $Q > K$.

concentrations of all the reacting species. Consider, for example, the formation of nitric oxide from molecular nitrogen and molecular oxygen:

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$
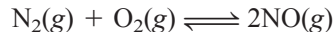
At 25°C, the equilibrium constant K_P is

$$K_P = \frac{P_{NO}^2}{P_{N_2}P_{O_2}} = 4.0 \times 10^{-31}$$

The very small value of K_P means that the concentration of NO at equilibrium will be exceedingly low. In such a case the equilibrium constant is more conveniently obtained from $\Delta G°$. (As we have seen, $\Delta G°$ can be calculated from $\Delta H°$ and $\Delta S°$.) On the other hand, the equilibrium constant for the formation of hydrogen iodide from molecular hydrogen and molecular iodine is near unity at room temperature:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$
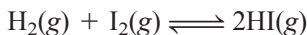
For this reaction it is easier to measure K_P and then calculate $\Delta G°$ using Equation (18.14) than to measure $\Delta H°$ and $\Delta S°$ and use Equation (18.10).

TABLE 18.4	Relation Between $\Delta G°$ and K as Predicted by the Equation $\Delta G° = -RT \ln K$		
K	**ln K**	**$\Delta G°$**	**Comments**
> 1	Positive	Negative	Products are favored over reactants at equilibrium.
= 1	0	0	Products and reactants are equally favored at equilibrium.
< 1	Negative	Positive	Reactants are favored over products at equilibrium.

Example 18.6

Using data listed in Appendix 2, calculate the equilibrium constant (K_P) for the following reaction at 25°C:
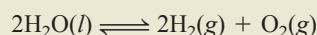
$$2H_2O(l) \rightleftharpoons 2H_2(g) + O_2(g)$$

Strategy According to Equation (18.14), the equilibrium constant for the reaction is related to the standard free energy change; that is, $\Delta G° = -RT \ln K$. Therefore, we first need to calculate $\Delta G°$ by following the procedure in Example 18.4. Then we can calculate K_P. What temperature unit should be used?

Solution According to Equation (18.12),

$$\begin{aligned}\Delta G°_{rxn} &= [2\Delta G°_f(H_2) + \Delta G°_f(O_2)] - [2\Delta G°_f(H_2O)]\\ &= [(2)(0 \text{ kJ/mol}) + (0 \text{ kJ/mol})] - [(2)(-237.2 \text{ kJ/mol})]\\ &= 474.4 \text{ kJ/mol}\end{aligned}$$

Using Equation (18.14)

$$\Delta G°_{rxn} = -RT \ln K_P$$

$$474.4 \text{ kJ/mol} \times \frac{1000 \text{ J}}{1 \text{ kJ}} = -(8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K}) \ln K_P$$

$$\ln K_P = -191.5$$

$$K_P = e^{-191.5} = \boxed{7 \times 10^{-84}}$$

To calculate K_P, enter −191.5 on your calculator and then press the key labeled "e" or "inv(erse) ln x."

Comment This extremely small equilibrium constant is consistent with the fact that water does not decompose into hydrogen and oxygen gases at 25°C. Thus, a large positive $\Delta G°$ favors reactants over products at equilibrium.

Similar problems: 18.23 and 18.26.

Practice Exercise Calculate the equilibrium constant (K_P) for the reaction at 25°C

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

Example 18.7

In Chapter 17 we discussed the solubility product of slightly soluble substances. Using the solubility product of silver chloride at 25°C (1.6×10^{-10}), calculate $\Delta G°$ for the process
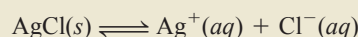
$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

Strategy According to Equation (18.14), the equilibrium constant for the reaction is related to standard free energy change; that is, $\Delta G° = -RT \ln K$. Because this is a heterogeneous equilibrium, the solubility product (K_{sp}) is the equilibrium constant. We calculate the standard free energy change from the K_{sp} value of AgCl. What temperature unit should be used?

Solution The solubility equilibrium for AgCl is

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$
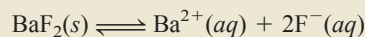$$K_{sp} = [Ag^+][Cl^-] = 1.6 \times 10^{-10}$$
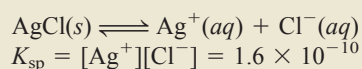
Using Equation (18.14) we obtain

$$\begin{aligned}\Delta G° &= -(8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K}) \ln (1.6 \times 10^{-10})\\ &= 5.6 \times 10^4 \text{ J/mol}\\ &= \boxed{56 \text{ kJ/mol}}\end{aligned}$$

(Continued)

Check The large, positive $\Delta G°$ indicates that AgCl is slightly soluble and that the equilibrium lies mostly to the left.

Practice Exercise Calculate $\Delta G°$ for the following process at 25°C:

$$BaF_2(s) \rightleftharpoons Ba^{2+}(aq) + 2F^-(aq)$$

The K_{sp} of BaF_2 is 1.7×10^{-6}.

Example 18.8

The equilibrium constant (K_P) for the reaction

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

is 0.113 at 298 K, which corresponds to a standard free-energy change of 5.40 kJ/mol. In a certain experiment, the initial pressures are $P_{NO_2} = 0.122$ atm and $P_{N_2O_4} = 0.453$ atm. Calculate ΔG for the reaction at these pressures and predict the direction of the net reaction.

Strategy From the information given we see that neither the reactant nor the product is at its standard state of 1 atm. To determine the direction of the net reaction, we need to calculate the free-energy change under nonstandard-state conditions (ΔG) using Equation (18.13) and the given $\Delta G°$ value. Note that the partial pressures are expressed as dimensionless quantities in the reaction quotient Q_P.

Solution Equation (18.13) can be written as

$$
\begin{aligned}
\Delta G &= \Delta G° + RT \ln Q_P \\
&= \Delta G° + RT \ln \frac{P_{NO_2}^2}{P_{N_2O_4}} \\
&= 5.40 \times 10^3 \text{ J/mol} + (8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K}) \times \ln \frac{(0.122)^2}{0.453} \\
&= 5.40 \times 10^3 \text{ J/mol} - 8.46 \times 10^3 \text{ J/mol} \\
&= -3.06 \times 10^3 \text{ J/mol} = -3.06 \text{ kJ/mol}
\end{aligned}
$$

Because $\Delta G < 0$, the net reaction proceeds from left to right to reach equilibrium.

Check Note that although $\Delta G° > 0$, the reaction can be made to favor product formation initially by having a small concentration (pressure) of the product compared to that of the reactant. Confirm the prediction by showing that $Q_P < K_P$.

Practice Exercise The $\Delta G°$ for the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$
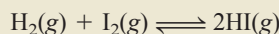
is 2.60 kJ/mol at 25°C. In one experiment, the initial pressures are $P_{H_2} = 4.26$ atm, $P_{I_2} = 0.024$ atm, and $P_{HI} = 0.23$ atm. Calculate ΔG for the reaction and predict the direction of the net reaction.

18.7 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*
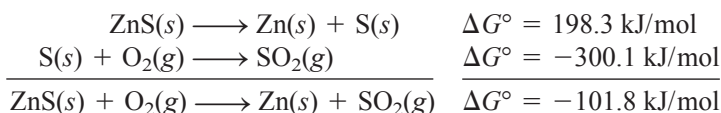
reactions is based on a simple concept: we can use a thermodynamically favorable reaction to drive an unfavorable one. Consider an industrial process. Suppose we wish to extract zinc from the ore sphalerite (ZnS). The following reaction will not work because it has a large positive $\Delta G°$ value:

$$ZnS(s) \longrightarrow Zn(s) + S(s) \qquad \Delta G° = 198.3 \text{ kJ/mol}$$

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:

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

A mechanical analog for coupled reactions. We can make the smaller weight move upward (a nonspontaneous process) by coupling it with the falling of a larger weight.

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

$$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l) \quad \Delta G° = -2880 \text{ kJ/mol}$$
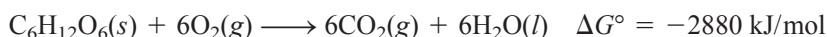
In a living cell, this reaction does not take place in a single step (as burning glucose in a flame would); rather, the glucose molecule is broken down with the aid of enzymes in a series of steps. Much of the free energy released along the way is used to synthesize adenosine triphosphate (ATP) from adenosine diphosphate (ADP) and phosphoric acid (Figure 18.10):

$$ADP + H_3PO_4 \longrightarrow ATP + H_2O \qquad \Delta G° = +31 \text{ kJ/mol}$$

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 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
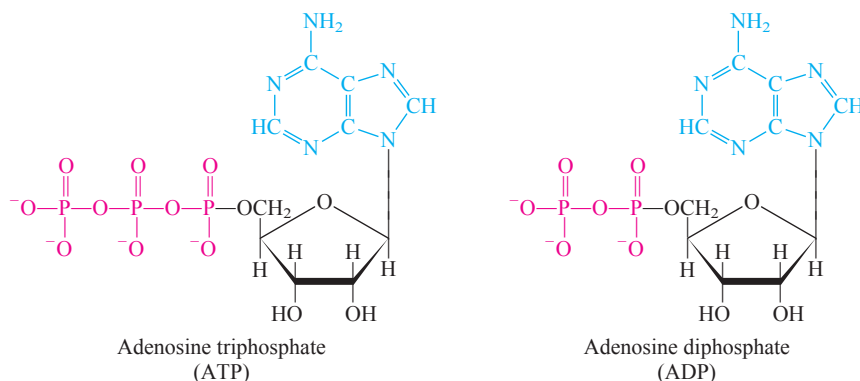

Figure 18.10
Structure of ATP and ADP in ionized forms. The adenine group is in blue, the ribose group in black, and the phosphate group in red. Note that ADP has one fewer phosphate group than ATP.

Adenosine triphosphate
(ATP)

Adenosine diphosphate
(ADP)

Figure 18.11
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 into ATP. The ATP molecules are then used as an energy source to drive unfavorable reactions, such as protein synthesis from amino acids.
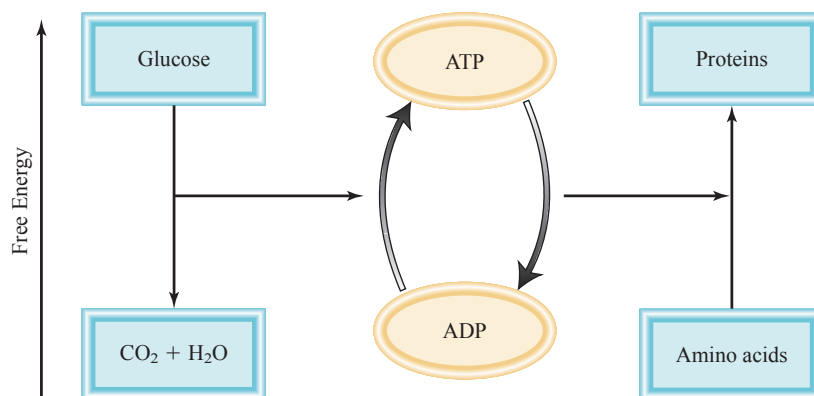
the dipeptide (a two-amino-acid unit) alanylglycine from alanine and glycine. This reaction represents the first step in the synthesis of a protein molecule:

$$\text{Alanine} + \text{Glycine} \longrightarrow \text{Alanylglycine} \quad \Delta G° = +29 \text{ kJ/mol}$$

As you can see, this reaction does not favor the formation of product, and so only a little of the dipeptide would be formed at equilibrium. However, with the aid of an enzyme, the reaction is coupled to the hydrolysis of ATP as follows:

$$\text{ATP} + \text{H}_2\text{O} + \text{Alanine} + \text{Glycine} \longrightarrow \text{ADP} + \text{H}_3\text{PO}_4 + \text{Alanylglycine}$$
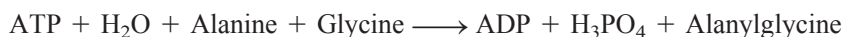
The overall free-energy change is given by $\Delta G° = -31 \text{ kJ/mol} + 29 \text{ kJ/mol} = -2 \text{ kJ/mol}$, which means that the coupled reaction now favors the formation of product, and an appreciable amount of alanylglycine will be formed under this condition. Figure 18.11 shows the ATP-ADP interconversions that act as energy storage (from metabolism) and free energy release (from ATP hydrolysis) to drive essential reactions.

KEY EQUATIONS

$S = k \ln W$	(18.1)	Relating entropy to number of microstates.
$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$	(18.4)	The second law of thermodynamics (spontaneous process).
$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$	(18.5)	The second law of thermodynamics (equilibrium process).
$\Delta S°_{\text{rxn}} = \Sigma n S°(\text{products}) - \Sigma m S°(\text{reactants})$	(18.7)	Standard entropy change of a reaction.
$G = H - TS$	(18.9)	Definition of Gibbs free energy.
$\Delta G = \Delta H - T\Delta S$	(18.10)	Free-energy change at constant temperature.
$\Delta G°_{\text{rxn}} = \Sigma n \Delta G°_{\text{f}}(\text{products}) - \Sigma m \Delta G°_{\text{f}}(\text{reactants})$	(18.12)	Standard free-energy change of a reaction.
$\Delta G = \Delta G° + RT \ln Q$	(18.13)	Relationship between free-energy change and standard free-energy change and reaction quotient.
$\Delta G° = -RT \ln K$	(18.14)	Relationship between standard free-energy change and the equilibrium constant.

SUMMARY OF FACTS AND CONCEPTS

1. Entropy is usually described as a measure of the disorder of a system. Any spontaneous process must lead to a net increase in entropy in the universe (second law of thermodynamics).

2. The standard entropy of a chemical reaction can be calculated from the absolute entropies of reactants and products.

3. The third law of thermodynamics states that the entropy of a perfect crystalline substance is zero at 0 K. This law enables us to measure the absolute entropies of substances.

4. Under conditions of constant temperature and pressure, the free-energy change ΔG is less than zero for a spontaneous process and greater than zero for a nonspontaneous process. For an equilibrium process, $\Delta G = 0$.

5. For a chemical or physical process at constant temperature and pressure, $\Delta G = \Delta H - T\Delta S$. This equation can be used to predict the spontaneity of a process.

6. The standard free-energy change for a reaction, $\Delta G°$, can be calculated from the standard free energies of formation of reactants and products.

7. The equilibrium constant of a reaction and the standard free-energy change of the reaction are related by the equation $\Delta G° = -RT \ln K$.

8. Many biological reactions are nonspontaneous. They are driven by the hydrolysis of ATP, for which $\Delta G°$ is negative.

KEY WORDS

Entropy (S), p. 612
Free energy (G), p. 623
Gibbs free energy (G), p. 623

Second law of thermodynamics, p. 617
Standard entropy of reaction ($\Delta S°_{rxn}$), p. 618

Standard free energy of formation ($\Delta G°_f$), p. 624
Standard free energy of reaction ($\Delta G°_{rxn}$), p. 623

Third law of thermodynamics, p. 621

QUESTIONS AND PROBLEMS

Spontaneous Processes and Entropy

Review Questions

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

18.2 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

18.3 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

18.4 Define entropy. What are the units of entropy?

18.5 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) Urea dissolves in water.

Problems

18.6 Consider the situation shown in Figure 18.1(a). After the valve is opened, the probability of finding one molecule in either bulb is $\frac{1}{2}$ (because the bulbs have the same volume) and that of finding the molecule in the total volume is one. The probability of finding two molecules in the same bulb is the product of the individual probabilities; that is, $\frac{1}{2} \times \frac{1}{2}$ or $\frac{1}{4}$. Extend

the calculation to finding 100 molecules in the same bulb. Based on your results, explain why it is highly improbable for the process shown in Figure 18.1(b) to occur spontaneously when the number of molecules becomes very large, say, 6×10^{23}.

The Second Law of Thermodynamics

Review Questions

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

18.8   State the third law of thermodynamics and explain its usefulness in calculating entropy values.

Problems

18.9   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 $N_2O_4(g)$

18.10   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.

18.11   Using the data in Appendix 2, calculate the standard entropy changes for the following reactions at 25°C:

(a) $S(s) + O_2(g) \longrightarrow SO_2(g)$

(b) $MgCO_3(s) \longrightarrow MgO(s) + CO_2(g)$

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

18.13   Without consulting Appendix 2, 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) $N_2(g) \longrightarrow 2N(g)$

18.14   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) $PCl_3(l) + Cl_2(g) \longrightarrow PCl_5(s)$

(b) $2HgO(s) \longrightarrow 2Hg(l) + O_2(g)$

(c) $H_2(g) \longrightarrow 2H(g)$

(d) $U(s) + 3F_2(g) \longrightarrow UF_6(s)$

Gibbs Free Energy

Review Questions

18.15   Define free energy. What are its units?

18.16   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?

Problems

18.17   Calculate $\Delta G°$ 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.)

18.18   Calculate $\Delta G°$ 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.

18.19   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?

18.20   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.

Free Energy and Chemical Equilibrium

Review Questions

18.21   Explain the difference between ΔG and $\Delta G°$.

18.22   Explain why Equation (18.14) is of great importance in chemistry.

Problems

18.23   Calculate K_P for the following reaction at 25°C:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \quad \Delta G° = 2.60 \text{ kJ/mol}$$

18.24   For the autoionization of water at 25°C,

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

K_w is 1.0×10^{-14}. What is $\Delta G°$ for the process?

18.25   Consider the following reaction at 25°C:

$$Fe(OH)_2(s) \rightleftharpoons Fe^{2+}(aq) + 2OH^-(aq)$$

Calculate $\Delta G°$ for the reaction. K_{sp} for $Fe(OH)_2$ is 1.6×10^{-14}.

18.26 Calculate $\Delta G°$ and K_P for the following equilibrium reaction at 25°C.

$$2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$$
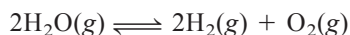
18.27 (a) Calculate $\Delta G°$ and K_P for the following equilibrium reaction at 25°C. The $\Delta G_f°$ values are 0 for $Cl_2(g)$, -286 kJ/mol for $PCl_3(g)$, and -325 kJ/mol for $PCl_5(g)$.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

(b) Calculate ΔG for the reaction if the partial pressures of the initial mixture are $P_{PCl_5} = 0.0029$ atm, $P_{PCl_3} = 0.27$ atm, and $P_{Cl_2} = 0.40$ atm.

18.28 The equilibrium constant (K_P) for the reaction

$$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$$
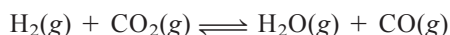
is 4.40 at 2000 K. (a) Calculate $\Delta G°$ for the reaction. (b) Calculate ΔG for the reaction when the partial pressures are $P_{H_2} = 0.25$ atm, $P_{CO_2} = 0.78$ atm, $P_{H_2O} = 0.66$ atm, and $P_{CO} = 1.20$ atm.

18.29 Consider the decomposition of calcium carbonate:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

Calculate the pressure in atm of CO_2 in an equilibrium process (a) at 25°C and (b) at 800°C. Assume that $\Delta H° = 177.8$ kJ/mol and $\Delta S° = 160.5$ J/K · mol for the temperature range.

18.30 The equilibrium constant K_P for the reaction

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$
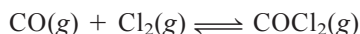
is 5.62×10^{35} at 25°C. Calculate $\Delta G_f°$ for $COCl_2$ at 25°C.

18.31 At 25°C, $\Delta G°$ for the process

$$H_2O(l) \rightleftharpoons H_2O(g)$$

is 8.6 kJ/mol. Calculate the vapor pressure of water at this temperature.

18.32 Calculate $\Delta G°$ for the process

$$C(diamond) \longrightarrow C(graphite)$$

Is the formation of graphite from diamond favored at 25°C? If so, why is it that diamonds do not become graphite on standing?

## Thermodynamics in Living Systems

Review Questions

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

18.34 What is the role of ATP in biological reactions?

Problems

18.35 Referring to the metabolic process involving glucose on p. 633, calculate the maximum number of moles of ATP that can be synthesized from ADP from the breakdown of one mole of glucose.

**18.36** In the metabolism of glucose, the first step is the conversion of glucose to glucose 6-phosphate:

$$glucose + H_3PO_4 \longrightarrow glucose\ 6\text{-}phosphate + H_2O$$
$$\Delta G° = 13.4\ kJ/mol$$
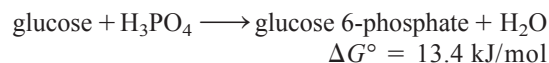
Because $\Delta G°$ is positive, this reaction does not favor the formation of products. Show how this reaction can be made to proceed by coupling it with the hydrolysis of ATP. Write an equation for the coupled reaction and estimate the equilibrium constant for the coupled process.

Additional Problems

18.37 Explain the following nursery rhyme in terms of the second law of thermodynamics.

Humpty Dumpty sat on a wall;
Humpty Dumpty had a great fall.
All the King's horses and all the King's men
Couldn't put Humpty together again.

18.38 Calculate ΔG for the reaction

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$
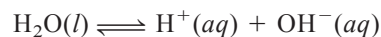
at 25°C for the following conditions:

(a) $[H^+] = 1.0 \times 10^{-7}\ M$, $[OH^-] = 1.0 \times 10^{-7}\ M$
(b) $[H^+] = 1.0 \times 10^{-3}\ M$, $[OH^-] = 1.0 \times 10^{-4}\ M$
(c) $[H^+] = 1.0 \times 10^{-12}\ M$, $[OH^-] = 2.0 \times 10^{-8}\ M$
(d) $[H^+] = 3.5\ M$, $[OH^-] = 4.8 \times 10^{-4}\ M$

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

18.40 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.

18.41 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.

18.42 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.)

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

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

18.45 Calculate the equilibrium pressure of CO_2 due to the decomposition of barium carbonate ($BaCO_3$) at 25°C.

18.46 (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.

18.47 Referring to Problem 18.46, explain why the ratio is considerably smaller than 90 J/K · mol for liquid HF.

18.48 Carbon monoxide (CO) and nitric oxide (NO) are pol-luting gases contained in automobile exhaust. Under suitable conditions, these gases can be made to react to form nitrogen (N_2) and the less harmful carbon diox-ide (CO_2). (a) Write an equation for this reaction. (b) Identify the oxidizing and reducing agents. (c) Cal-culate the K_P for the reaction at 25°C. (d) Under nor-mal atmospheric conditions, the partial pressures are $P_{N_2} = 0.80$ atm, $P_{CO_2} = 3.0 \times 10^{-4}$ atm, $P_{CO} = 5.0 \times 10^{-5}$ atm, and $P_{NO} = 5.0 \times 10^{-7}$ atm. Calcu-late Q_P and predict the direction toward which the reaction will proceed. (e) Will raising the tempera-ture favor the formation of N_2 and CO_2?

18.49 For reactions carried out under standard-state condi-tions, Equation (18.10) takes the form $\Delta G° = \Delta H° - T\Delta S°$. (a) Assuming $\Delta H°$ and $\Delta S°$ are independent of temperature, derive the equation

$$\ln \frac{K_2}{K_1} = \frac{\Delta H°}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

where K_1 and K_2 are the equilibrium constants at T_1 and T_2, respectively. (b) Given that at 25°C K_c is 4.63×10^{-3} for the reaction

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \quad \Delta H° = 58.0 \text{ kJ/mol}$$
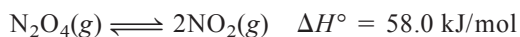
calculate the equilibrium constant at 65°C.

18.50 The K_{sp} of AgCl is given in Table 17.2. What is its value at 60°C? [*Hint:* You need the result of Prob-lem 18.49(a) and the data in Appendix 2 to calcu-late $\Delta H°$.]

18.51 Under what conditions does a substance have a stan-dard entropy of zero? Can a substance ever have a negative standard entropy?

18.52 Water gas, a mixture of H_2 and CO, is a fuel made by reacting steam with red-hot coke (a by-product of coal distillation):

$$H_2O(g) + C(s) \rightleftharpoons CO(g) + H_2(g)$$

From the data in Appendix 2, estimate the tempera-ture at which the reaction begins to favor the forma-tion of products.

18.53 Consider the following Brønstead acid-base reaction at 25°C:

$$HF(aq) + Cl^-(aq) \rightleftharpoons HCl(aq) + F^-(aq)$$

(a) Predict whether K will be greater or smaller than unity. (b) Does $\Delta S°$ or $\Delta H°$ make a greater contribution to $\Delta G°$? (c) Is $\Delta H°$ likely to be positive or negative?

18.54 Crystallization of sodium acetate from a supersatu-rated solution occurs spontaneously (see p. 426). What can you deduce about the signs of ΔS and ΔH?
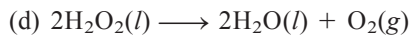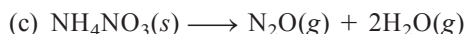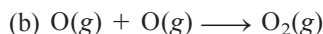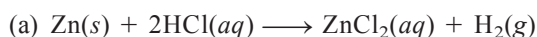
18.55 Consider the thermal decomposition of $CaCO_3$:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

The equilibrium vapor pressures of CO_2 are 22.6 mmHg at 700°C and 1829 mmHg at 950°C. Calculate the standard enthalpy of the reaction. [*Hint:* See Problem 18.49(a).]
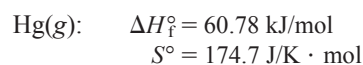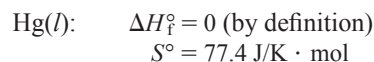
18.56 A certain reaction is spontaneous at 72°C. If the en-thalpy change for the reaction is 19 kJ/mol, what is the *minimum* value of ΔS (in (J/K · mol) for the reaction?

18.57 Predict whether the entropy change is positive or negative for each of these reactions:

(a) $Zn(s) + 2HCl(aq) \longrightarrow ZnCl_2(aq) + H_2(g)$
(b) $O(g) + O(g) \longrightarrow O_2(g)$
(c) $NH_4NO_3(s) \longrightarrow N_2O(g) + 2H_2O(g)$
(d) $2H_2O_2(l) \longrightarrow 2H_2O(l) + O_2(g)$

18.58 The reaction $NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$ pro-ceeds spontaneously at 25°C even though there is a de-crease in the number of microstates of the system (gases are converted to a solid). Explain.

18.59 Use the following data to determine the normal boil-ing point, in kelvins, of mercury. What assumptions must you make in order to do the calculation?

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

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

18.60 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 mol ethanol.

18.61 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?

18.62 In the Mond process for the purification of nickel, carbon monoxide is reacted with heated nickel to produce $Ni(CO)_4$, which is a gas and can therefore be separated from solid impurities:

$$Ni(s) + 4CO(g) \rightleftharpoons Ni(CO)_4(g)$$
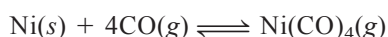
Given that the standard free energies of formation of $CO(g)$ and $Ni(CO)_4(g)$ are -137.3 kJ/mol and -587.4 kJ/mol, respectively, calculate the equilibrium constant of the reaction at 80°C. Assume that $\Delta G_f°$ is temperature independent.

18.63 Calculate $\Delta G°$ and K_P for the following processes at 25°C:

(a) $H_2(g) + Br_2(l) \rightleftharpoons 2HBr(g)$
(b) $\frac{1}{2}H_2(g) + \frac{1}{2}Br_2(l) \rightleftharpoons HBr(g)$
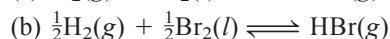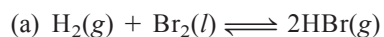
Account for the differences in $\Delta G°$ and K_P obtained for (a) and (b).

18.64 Calculate the pressure of O_2 (in atm) over a sample of NiO at 25°C if $\Delta G° = 212$ kJ/mol for the reaction

$$NiO(s) \rightleftharpoons Ni(s) + \frac{1}{2}O_2(g)$$

18.65 Comment on the statement: "Just talking about entropy increases its value in the universe."

18.66 For a reaction with a negative $\Delta G°$ value, which of the following statements is false? (a) The equilibrium constant K is greater than one, (b) the reaction is spontaneous when all the reactants and products are in their standard states, and (c) the reaction is always exothermic.

18.67 Consider the reaction

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$
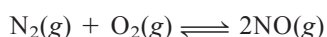
Given that $\Delta G°$ for the reaction at 25°C is 173.4 kJ/mol, (a) calculate the standard free energy of formation of NO, and (b) calculate K_P of the reaction. (c) One of the starting substances in smog formation is NO. Assuming that the temperature in a running automobile engine is 1100°C, estimate K_P for the above reaction. (d) As farmers know, lightning helps to produce a better crop. Why?

18.68 Heating copper(II) oxide at 400°C does not produce any appreciable amount of Cu:

$$CuO(s) \rightleftharpoons Cu(s) + \frac{1}{2}O_2(g) \quad \Delta G° = 127.2 \text{ kJ/mol}$$
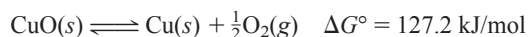
However, if this reaction is coupled to the conversion of graphite to carbon monoxide, it becomes spontaneous. Write an equation for the coupled process and calculate the equilibrium constant for the coupled reaction.

18.69 The internal combustion engine of a 1200-kg car is designed to run on octane (C_8H_{18}), whose enthalpy of combustion is 5510 kJ/mol. If the car is moving up a slope, calculate the maximum height (in meters) to which the car can be driven on 1.0 gallon of the fuel. Assume that the engine cylinder temperature is 2200°C and the exit temperature is 760°C, and neglect all forms of friction. The mass of 1 gallon of fuel is 3.1 kg. [*Hint:* The efficiency of the internal combustion engine, defined as work performed by the engine divided by the energy input, is given by $(T_2 - T_1)/T_2$, where T_2 and T_1 are the engine's operating temperature and exit temperature (in kelvins). The work done in moving the car over a vertical distance is mgh, where m is the mass of the car in kg, g the acceleration due to gravity (9.81 m/s^2), and h the height in meters.]

18.70 A carbon monoxide (CO) crystal is found to have entropy greater than zero at absolute zero of temperature. Give two possible explanations for this observation.

18.71 (a) Over the years there have been numerous claims about "perpetual motion machines," machines that will produce useful work with no input of energy. Explain why the first law of thermodynamics prohibits the possibility of such a machine existing. (b) Another kind of machine, sometimes called a "perpetual motion of the second kind," operates as follows. Suppose an ocean liner sails by scooping up water from the ocean and then extracting heat from the water, converting the heat to electric power to run the ship, and dumping the water back into the ocean. This process does not violate the first law of thermodynamics, for no energy is created—energy from the ocean is just converted to electrical energy. Show that the second law of thermodynamics prohibits the existence of such a machine.

18.72 The activity series in Section 4.4 shows that reaction (a) is spontaneous while reaction (b) is nonspontaneous at 25°C:

(a) $Fe(s) + 2H^+ \longrightarrow Fe^{2+}(aq) + H_2(g)$
(b) $Cu(s) + 2H^+ \longrightarrow Cu^{2+}(aq) + H_2(g)$
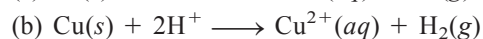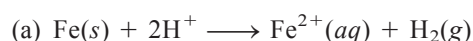
Use the data in Appendix 2 to calculate the equilibrium constant for these reactions and hence confirm that the activity series is correct.

18.73 The rate constant for the elementary reaction

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$
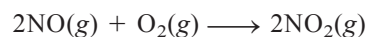
is $7.1 \times 10^9/M^2 \cdot s$ at 25°C. What is the rate constant for the reverse reaction at the same temperature?

18.74 The following reaction was described as the cause of sulfur deposits formed at volcanic sites:

$$2H_2S(g) + SO_2(g) \rightleftharpoons 3S(s) + 2H_2O(g)$$
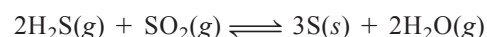
It may also be used to remove SO_2 from powerplant stack gases. (a) Identify the type of redox reaction it is. (b) Calculate the equilibrium constant (K_P) at 25°C and comment on whether this method is feasible for removing SO_2. (c) Would this procedure become more or less effective at a higher temperature?

18.75 Describe two ways that you could measure $\Delta G°$ of a reaction.

18.76 The following reaction represents the removal of ozone in the stratosphere:

$$2O_3(g) \rightleftharpoons 3O_2(g)$$

Calculate the equilibrium constant (K_P) for the reaction. In view of the magnitude of the equilibrium constant, explain why this reaction is not considered a major cause of ozone depletion in the absence of man-made pollutants such as the nitrogen oxides and CFCs? Assume the temperature of the stratosphere to be $-30°C$ and $\Delta G_f°$ to be temperature independent.

18.77 A 74.6-g ice cube floats in the Arctic Sea. The temperature and pressure of the system and surroundings are at 1 atm and 0°C. 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.)

18.78 Comment on the feasibility of extracting copper from its ore chalcocite (Cu_2S) by heating:

$$Cu_2S(s) \longrightarrow 2Cu(s) + S(s)$$
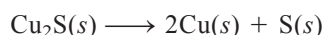
Calculate the $\Delta G°$ for the overall reaction if the above process is coupled to the conversion of sulfur to sulfur dioxide, given that $\Delta G_f°(Cu_2S) = -86.1$ kJ/mol.

18.79 Active transport is the process in which a substance is transferred from a region of lower concentration to one of higher concentration. This is a nonspontaneous process and must be coupled to a spontaneous process, such as the hydrolysis of ATP. The concentrations of K^+ ions in the blood plasma and in nerve cells are 15 mM and 400 mM, respectively (1 mM = 1×10^{-3} M). Use Equation (18.13) to calculate ΔG for the process at the physiological temperature of 37°C:

$$K^+(15 \text{ m}M) \longrightarrow K^+(400 \text{ m}M)$$
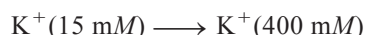
In this calculation, the $\Delta G°$ term can be set to zero. What is the justification for this step?

18.80 Large quantities of hydrogen are needed for the synthesis of ammonia. One preparation of hydrogen involves the reaction between carbon monoxide and steam at 300°C in the presence of a copper-zinc catalyst:

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

Calculate the equilibrium constant (K_P) for the reaction and the temperature at which the reaction favors the formation of CO and H_2O. Will a larger K_P be attained at the same temperature if a more efficient catalyst is used?

18.81 Consider two carboxylic acids (acids that contain the —COOH group): CH_3COOH (acetic acid, $K_a = 1.8 \times 10^{-5}$) and $CH_2ClCOOH$ (chloroacetic acid, $K_a = 1.4 \times 10^{-3}$). (a) Calculate $\Delta G°$ for the ionization of these acids at 25°C (b) From the equation $\Delta G° = \Delta H° - T\Delta S°$, we see that the contributions to the $\Delta G°$ term are an enthalpy term ($\Delta H°$) and a temperature times entropy term ($T\Delta S°$). These contributions are listed below for the two acids:

	$\Delta H°$(kJ/mol)	$T\Delta S°$(kJ/mol)
CH_3COOH	-0.57	-27.6
$CH_2ClCOOH$	-4.7	-21.1

Which is the dominant term in determining the value of $\Delta G°$ (and hence K_a of the acid)? (c) What processes contribute to $\Delta H°$? (Consider the ionization of the acids as a Brønsted acid-base reaction.) (d) Explain why the $T\Delta S°$ term is more negative for CH_3COOH.

18.82 One of the steps in the extraction of iron from its ore (FeO) is the reduction of iron(II) oxide by carbon monoxide at 900°C:

$$FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g)$$

If CO is allowed to react with an excess of FeO, calculate the mole fractions of CO and CO_2 at equilibrium. State any assumptions.

18.83 Derive the following equation

$$\Delta G = RT \ln (Q/K)$$

where Q is the reaction quotient and describe how you would use it to predict the spontaneity of a reaction.

**18.84** The sublimation of carbon dioxide at $-78°C$ is given by

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

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

18.85 Entropy has sometimes been described as "time's arrow" because it is the property that determines the forward direction of time. Explain.

18.86 Referring to Figure 18.1, we see that the probability of finding all 100 molecules in the same flask is 8×10^{-31} (see Problem 18.6). Assuming that the age of the universe is 13 billion years, calculate the time in seconds during which this event can be observed.

18.87 A student looked up the $\Delta G_f°$, $\Delta H_f°$, and $S°$ values for CO_2 in Appendix 2. Plugging these values into Equation (18.10), he found that $\Delta G_f° \neq \Delta H_f° - TS°$ at 298 K. What is wrong with his approach?

18.88 Consider the following reaction at 298 K:

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$
$$\Delta H° = -571.6 \text{ kJ/mol}$$
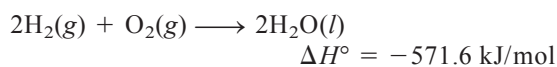
Calculate ΔS_{sys}, ΔS_{surr}, and ΔS_{univ} for the reaction.

18.89 As an approximation, we can assume that proteins exist either in the native (or physiologically functioning) state and the denatured state

native $\Longleftrightarrow$ denatured

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 process favors the denatured state.

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

18.91 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.

18.92 Hydrogenation reactions (for example, the process of converting C=C bonds to C—C bonds in 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.

SPECIAL PROBLEMS

18.93 The standard free energies of formation (ΔG_f°) of the three isomers of pentane (see p. 358) in the gas phase are: *n*-pentane: -8.37 kJ/mol; 2-methylbutane: -14.8 kJ/mol; 2,2-dimethylpropane: -15.2 kJ/mol. (a) Determine the mole percent of these molecules in an equilibrium mixture at 25°C. (b) How does the stability of these molecules depend on the extent of branching?

18.94 Carry out the following experiments: Quickly stretch a rubber band (at least 0.5 cm wide) and press it against your lips. You will feel a warming effect. Next, carry out the reverse procedure; that is, first stretch a rubber band and hold it in position for a few seconds. Now quickly release the tension and press the rubber band against your lips. You will feel a cooling effect. (a) Apply Equation (18.7) to these processes to determine the signs of ΔG, ΔH, and hence ΔS in each case. (b) From the signs of ΔS, what can you conclude about the structure of rubber molecules?

18.95 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 (a) and 4.2 J/K · mol [*Hint:* Assume that each CO molecule has two choices for orientation and use Equation (18.1) to calculate the residual entropy.]

18.96 Comment on the correctness of the analogy sometimes used to relate a student's dormitory room becoming untidy to an increase in entropy.

18.97 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 ΔH°, ΔS°, and ΔG° for the process at 25°C. Comment on your answers.

$$C_6H_6(l) \longrightarrow C_6H_6(g)$$

18.98 The following diagram shows the variation of the equilibrium constant with temperature for the reaction

$$I_2(g) \Longleftrightarrow 2I(g)$$
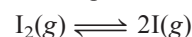
Calculate ΔG°, ΔH°, and ΔS° for the reaction at 872 K. (*Hint:* See Problem 18.49.)
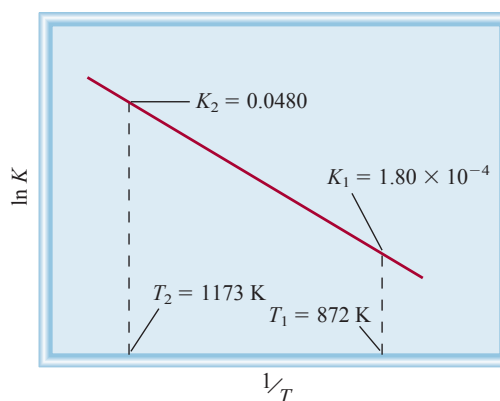
ANSWERS TO PRACTICE EXERCISES

18.1 (a) Entropy decreases, (b) entropy decreases, (c) entropy increases, (d) entropy increases.
18.2 (a) -173.6 J/K · mol, (b) -139.8 J/K · mol, (c) 215.3 J/K · mol.   **18.3** (a) $\Delta S > 0$, (b) $\Delta S < 0$, (c) $\Delta S \approx 0$.

18.4 (a) -106.4 kJ/mol, (b) -2935.0 kJ/mol.
18.5 $\Delta S_{fus} = 16$ J/K · mol; $\Delta S_{vap} = 72$ J/K · mol.
18.6 2×10^{57}.   **18.7** 33 kJ/mol.   **18.8** $\Delta G = 0.97$ kJ/mol; direction is from right to left.