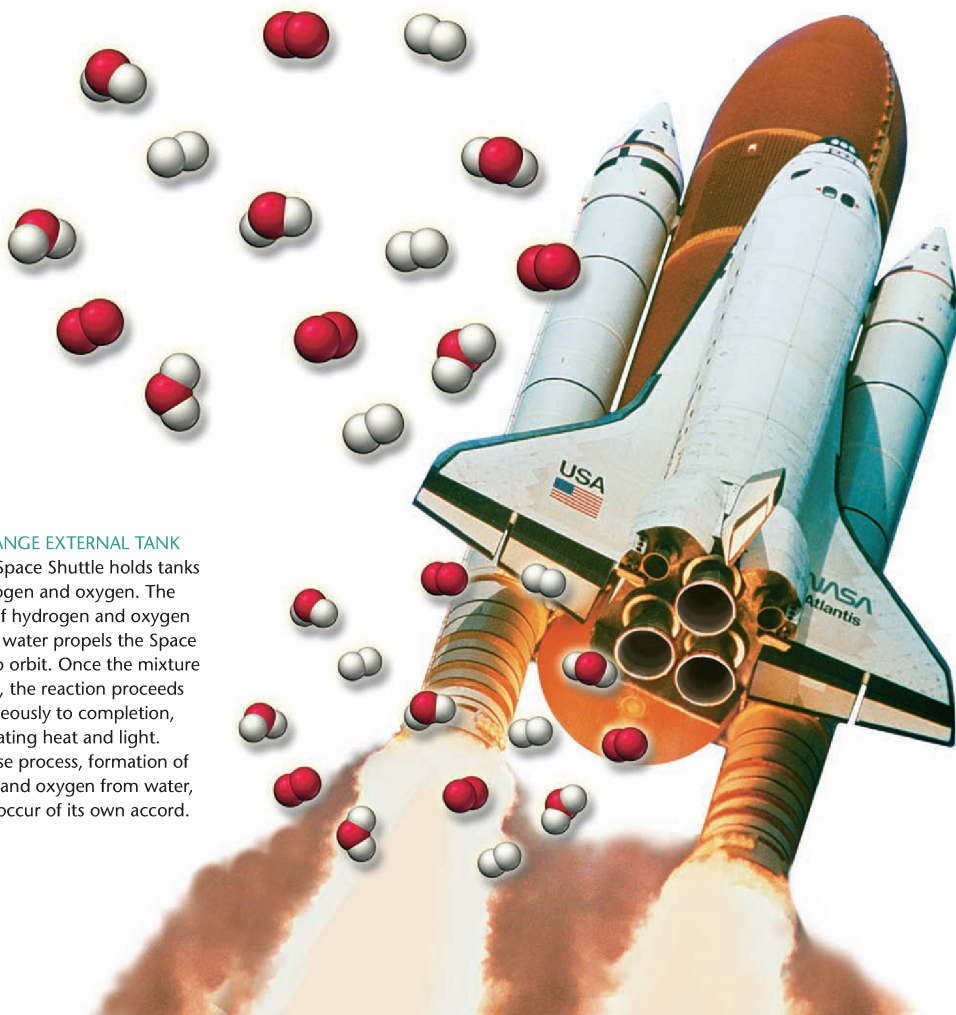


CHAPTER
19

CHEMICAL THERMODYNAMICS

THE ORANGE EXTERNAL TANK
under the Space Shuttle holds tanks of hydrogen and oxygen. The reaction of hydrogen and oxygen producing water propels the Space Shuttle into orbit. Once the mixture is ignited, the reaction proceeds spontaneously to completion, generating heat and light. The reverse process, formation of hydrogen and oxygen from water, does not occur of its own accord.



19.1 Spontaneous Processes

In this chapter we will see why changes that occur in nature have a directional character. They move *spontaneously* in one direction but not in the reverse direction.

19.2 Entropy and the Second Law of Thermodynamics

We will discuss *entropy*, which is a thermodynamic state function that is important in determining whether a process is spontaneous. The *second law of thermodynamics* tells us that in any spontaneous process the entropy of the universe (system plus surroundings) increases.

19.3 The Molecular Interpretation of Entropy

On a molecular level, we will see that an entropy increase is associated with an increase in the number of accessible *microstates*. Entropy change can also be thought of as a measure of a system's randomness at a stated temperature. The *third law of thermodynamics* states that the entropy of a perfect crystalline solid at 0 K is zero.

19.4 Entropy Changes in Chemical Reactions

Using tabulated *standard molar entropies*, we can calculate the standard entropy changes for systems undergoing reaction.

19.5 Gibbs Free Energy

We next encounter another thermodynamic state function, *free energy* (or *Gibbs free energy*), which is a measure of how far removed the system is from equilibrium. Free energy change measures the maximum amount of useful work obtainable from a process and yields information on the direction in which a chemical reaction will proceed spontaneously.

19.6 Free Energy and Temperature

We will consider how the relationship among free-energy change, enthalpy change, and entropy change provides insight into how temperature affects the spontaneity of a process.

19.7 Free Energy and the Equilibrium Constant

Finally, we will consider how the standard free-energy change for a chemical reaction can be used to calculate the equilibrium constant for the process.

THE ENERGY REQUIRED TO PROPEL THE SPACE SHUTTLE INTO SPACE

is obtained from two solid-fuel booster rockets and a rocket engine that relies on the combustion of hydrogen and oxygen to form water. The hydrogen and oxygen are stored as liquids at very low temperatures in tanks mounted below the

Space Shuttle. As the hydrogen and oxygen vapors are ignited, they react very rapidly and virtually completely, producing enormous quantities of water vapor and heat. Two of the most important questions chemists ask when designing and using chemical reactions are "How fast is the reaction?" and "How far does it proceed?" The first question is addressed by the study of chemical kinetics, which we discussed in Chapter 14. The second question involves the equilibrium constant, which was the focus of Chapter 15.

In Chapter 14 we learned that the rates of chemical reactions are controlled largely by a factor related to energy, namely the activation energy of the reaction. ∞ (Section 14.5) In general, the lower the activation energy, the faster a reaction proceeds. In Chapter 15 we saw that equilibrium depends on

the rates of the forward and reverse reactions: Equilibrium is reached when the opposing reactions occur at equal rates. ∞ (Section 15.1) Because reaction rates are closely tied to energy, it is logical that equilibrium also depends in some way on energy.

In this chapter we will explore the connection between energy and the extent of a reaction. Doing so requires us to take a deeper look at *chemical thermodynamics*, the area of chemistry that deals with energy relationships. We first encountered thermodynamics in Chapter 5, where we discussed the nature of energy, the first law of thermodynamics, and the concept of enthalpy. Recall that the enthalpy change is the heat transferred between the system and its surroundings during a constant-pressure process. ∞ (Section 5.3)

Now we will see that reactions involve not only changes in enthalpy but also changes in *entropy*—another important thermodynamic quantity. Our discussion of entropy will lead us to the second law of thermodynamics, which provides insight into why physical and chemical changes tend to favor one direction over another. We drop a brick, for example, and it falls to the ground. We do not expect bricks to spontaneously rise from the ground to our outstretched hand. We light a candle, and it burns down. We do not expect a half-consumed candle to regenerate itself spontaneously, even if we have kept all the gases produced when the candle burned. Thermodynamics helps us understand the significance of this directional character of processes, whether they are exothermic or endothermic.

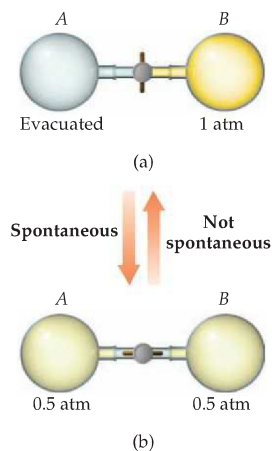
19.1 SPONTANEOUS PROCESSES

The first law of thermodynamics states that *energy is conserved*. ∞ (Section 5.2) In other words, energy is neither created nor destroyed in any process, whether it is the falling of a brick, the burning of a candle, or the melting of an ice cube. Energy can be transferred between a system and the surroundings or can be converted from one form to another, but the total energy remains constant. We expressed the first law of thermodynamics mathematically as $\Delta E = q + w$, where ΔE is the change in the internal energy of a system, q is the heat absorbed by the system from the surroundings, and w is the work done on the system by the surroundings.

The first law helps us balance the books, so to speak, on the heat transferred between a system and its surroundings and the work done by a particular process or reaction. But the first law does not address another important feature of reactions—the extent to which they occur. As we noted in the introduction, our experience tells us that physical and chemical processes have a directional character. For instance, sodium metal and chlorine gas combine readily to form sodium chloride, which we also know as table salt. We never find table salt decomposing of its own accord to form sodium and chlorine. (Have you ever smelled chlorine gas in the kitchen or seen sodium metal on your table salt?) In both processes—the formation of sodium chloride from sodium and chlorine and the decomposition of sodium chloride into sodium and chlorine—energy is conserved, as it must be according to the first law of thermodynamics. Yet one process occurs, and the other does not. A process that occurs of its own accord without any ongoing outside intervention is said to be spontaneous. A **spontaneous process** is one that proceeds on its own without any outside assistance.

A spontaneous process occurs in a definite direction. Imagine you were to see a video clip in which a brick rises from the ground. You would conclude that the video is running in reverse—bricks do not magically rise from the ground! A brick falling is a spontaneous process, whereas the reverse process is *nonspontaneous*.

A gas will expand into a vacuum as shown in Figure 19.1 \blacktriangleleft , but the process will never reverse itself. The expansion of the gas is spontaneous. Likewise, a nail left out in the weather will rust (Figure 19.2 \blacktriangleright). In this process the iron in the nail reacts with oxygen from the air to form an iron oxide. We would never expect the rusty nail to reverse this process and become shiny. The rusting process



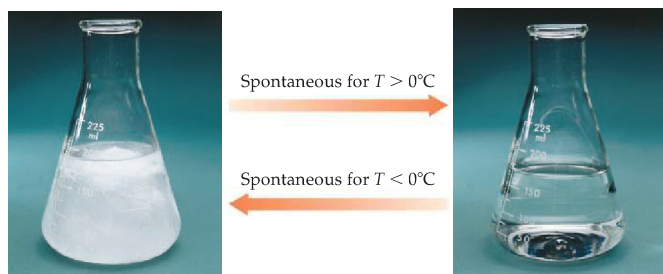
▲ Figure 19.1 Spontaneous expansion of an ideal gas into an evacuated space. In (a) flask B holds an ideal gas at 1 atm pressure and flask A is evacuated. In (b) the stopcock connecting the flasks has been opened. The ideal gas expands to occupy both flasks A and B at a pressure of 0.5 atm. The reverse process—all the gas molecules moving back into flask B—is not spontaneous.

is spontaneous, whereas the reverse process is nonspontaneous. There are countless other examples we could cite that illustrate the same idea: *Processes that are spontaneous in one direction are nonspontaneous in the opposite direction.*

Experimental conditions, such as temperature and pressure, are often important in determining whether a process is spontaneous. Consider, for example, the melting of ice. When the temperature of the surroundings is above $0\text{ }^{\circ}\text{C}$ at ordinary atmospheric pressures, ice melts spontaneously and the reverse process—liquid water turning into ice—is not spontaneous. However, when the surroundings are below $0\text{ }^{\circ}\text{C}$, the opposite is true. Liquid water converts into ice spontaneously, and the conversion of ice into water is *not* spontaneous (Figure 19.3 ▼).

What happens at $T = 0\text{ }^{\circ}\text{C}$, the normal melting point of water, when the flask of Figure 19.3 contains both water and ice? At the normal melting point of a substance, the solid and liquid phases are in equilibrium. \rightleftharpoons (Section 11.5) At this temperature the two phases are interconverting at the same rate and there is no preferred direction for the process.

It is important to realize that the fact that a process is spontaneous does not necessarily mean that it will occur at an observable rate. A chemical reaction is spontaneous if it occurs on its own accord, regardless of its speed. A spontaneous reaction can be very fast, as in the case of acid–base neutralization, or very slow, as in the rusting of iron. Thermodynamics can tell us the *direction* and *extent* of a reaction but tells us nothing about the *speed* of the reaction.



▲ **Figure 19.3 Spontaneity can depend on the temperature.** At $T > 0\text{ }^{\circ}\text{C}$ ice melts spontaneously to liquid water. At $T < 0\text{ }^{\circ}\text{C}$ the reverse process, water freezing to ice, is spontaneous. At $T = 0\text{ }^{\circ}\text{C}$ the two states are in equilibrium.

■ SAMPLE EXERCISE 19.1 | Identifying Spontaneous Processes

Predict whether the following processes are spontaneous as described, spontaneous in the reverse direction, or in equilibrium: (a) When a piece of metal heated to $150\text{ }^{\circ}\text{C}$ is added to water at $40\text{ }^{\circ}\text{C}$, the water gets hotter. (b) Water at room temperature decomposes into $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$. (c) Benzene vapor, $\text{C}_6\text{H}_6(\text{g})$, at a pressure of 1 atm condenses to liquid benzene at the normal boiling point of benzene, $80.1\text{ }^{\circ}\text{C}$.

SOLUTION

Analyze: We are asked to judge whether each process will proceed spontaneously in the direction indicated, in the reverse direction, or in neither direction.

Plan: We need to think about whether each process is consistent with our experience about the natural direction of events or whether we expect the reverse process to occur.

Solve: (a) This process is spontaneous. Whenever two objects at different temperatures are brought into contact, heat is transferred from the hotter object to the colder one. Thus, heat is transferred from the hot metal to the cooler water. The final temperature, after the metal and water achieve the same temperature (thermal equilibrium), will be somewhere between the initial temperatures of the metal and the water. (b) Experience tells us that this process is not spontaneous—we certainly have never seen hydrogen and oxygen gases spontaneously bubbling up out of water! Rather, the



Spontaneous \rightleftharpoons Non-spontaneous



▲ **Figure 19.2 A spontaneous process.** Elemental iron in the shiny nail in the top photograph spontaneously combines with H_2O and O_2 in the surrounding air to form a layer of rust— Fe_2O_3 —on the nail surface.

reverse process—the reaction of H_2 and O_2 to form H_2O —is spontaneous. (c) By definition, the normal boiling point is the temperature at which a vapor at 1 atm is in equilibrium with its liquid. Thus, this is an equilibrium situation. If the temperature were below 80.1°C , condensation would be spontaneous.

PRACTICE EXERCISE

Under 1 atm pressure $\text{CO}_2(\text{s})$ sublimates at -78°C . Is the transformation of $\text{CO}_2(\text{s})$ to $\text{CO}_2(\text{g})$ a spontaneous process at -100°C and 1 atm pressure?

Answer: No, the reverse process is spontaneous at this temperature.

Seeking a Criterion for Spontaneity

A marble rolling down an incline or a brick falling from your hand loses energy. The loss of energy is a common feature of spontaneous change in mechanical systems. During the 1870s Marcellin Bertholet (1827–1907), a famous chemist of that era, suggested that the direction of spontaneous changes in chemical systems was also determined by the loss of energy. He proposed that all spontaneous chemical and physical changes were exothermic. It takes only a few moments, however, to find exceptions to this generalization. For example, the melting of ice at room temperature is spontaneous even though melting is an endothermic process. Similarly, many spontaneous solution processes, such as the dissolving of NH_4NO_3 , are endothermic, as we discovered in Section 13.1. We conclude therefore that, although the majority of spontaneous reactions are exothermic, there are spontaneous endothermic ones as well. Clearly, some other factor must be at work in determining the natural direction of processes. What is this factor?

To understand why certain processes are spontaneous, we need to consider more closely the ways in which the state of a system can change. Recall that quantities such as temperature, internal energy, and enthalpy are *state functions*, properties that define a state and do not depend on how we reach that state. ∞ (Section 5.2) The heat transferred between a system and its surroundings, q , and the work done by or on the system, w , are *not* state functions. The values of q and w depend on the specific path taken from one state to another. One of the keys to understanding spontaneity is distinguishing between reversible and irreversible paths between states.

GIVE IT SOME THOUGHT

If a process is nonspontaneous, does that mean the process cannot occur under any circumstances?

Reversible and Irreversible Processes

In 1824 a 28-year-old French engineer named Sadi Carnot (1796–1832) published an analysis of the factors that determine how efficiently a steam engine can convert heat to work. Carnot considered what an ideal engine, one with the highest possible efficiency, would be like. He observed that it is impossible to convert the energy content of a fuel completely to work because a significant amount of heat is always lost to the surroundings. Carnot's analysis gave insight into how to build better, more efficient engines, and it was one of the earliest studies in what has developed into the discipline of thermodynamics.

About 40 years later, Rudolph Clausius (1822–1888), a German physicist, extended Carnot's work in an important way. Clausius concluded that a special significance could be ascribed to the ratio of the heat delivered to an ideal engine and the temperature at which it is delivered, q/T . He was so convinced of the importance of this ratio that he gave it a special name, *entropy*. He deliberately selected the name to sound like energy to emphasize his belief that the importance of entropy was comparable to that of energy.

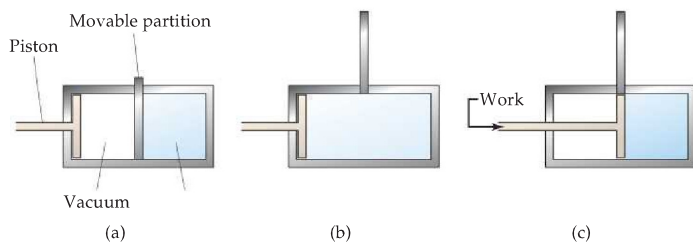
An ideal engine, one with the maximum efficiency, operates under an ideal set of conditions in which all the processes are reversible. In a **reversible process**, a system is changed in such a way that the system and surroundings can be restored to their original state by *exactly* reversing the change. In other words, we can completely restore the system to its original condition with no net change to either the system or its surroundings. An **irreversible process** is one that cannot simply be reversed to restore the system and its surroundings to their original states. What Carnot discovered is that the amount of work we can extract from any spontaneous process depends on the manner in which the process is carried out. A *reversible change produces the maximum amount of work that can be achieved by the system on the surroundings* ($w_{rev} = w_{max}$).

GIVE IT SOME THOUGHT

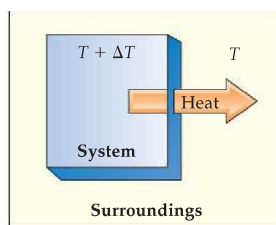
If you evaporate water and then condense it, have you necessarily performed a reversible process?

Let's examine some examples of reversible and irreversible processes. When two objects at different temperatures are in contact, heat will flow spontaneously from the hotter object to the colder one. Because it is impossible to make heat flow in the opposite direction, the flow of heat is irreversible. Given these facts, can we imagine any conditions under which heat transfer can be made reversible? Consider two objects or a system and its surroundings that are at essentially the same temperature, with just an infinitesimal difference (an extremely small temperature difference, ΔT) to make heat flow in the desired direction (Figure 19.4). We can then reverse the direction of heat flow by making an infinitesimal change of temperature in the opposite direction. *Reversible processes are those that reverse direction whenever an infinitesimal change is made in some property of the system.*

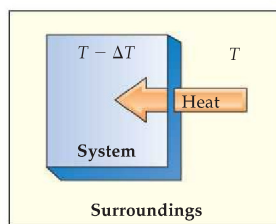
Now consider another example, the expansion of an ideal gas at constant temperature. A constant-temperature process such as this is said to be **isothermal**. To keep the example simple, consider the gas in the cylinder-and-piston arrangement shown in Figure 19.5. When the partition is removed, the gas expands spontaneously to fill the evacuated space. Because the gas is expanding into a vacuum with no external pressure, it does no P - V work on the surroundings ($w = 0$). (Section 5.3) We can use the piston to compress the gas back to its original state, but doing so requires that the surroundings do work on the system ($w > 0$). That is, reversing the process has produced a change in the surroundings as energy is used to do work on the system. The fact that the system and the surroundings are not both returned to their original conditions indicates that the process is irreversible.



▲ **Figure 19.5 An irreversible process.** Restoring the system to its original state after an irreversible process changes the surroundings. In (a) the gas is confined to the right half of the cylinder by a partition. When the partition is removed (b), the gas spontaneously (irreversibly) expands to fill the whole cylinder. No work is done by the system during this expansion. In (c) we can use the piston to compress the gas back to its original state. Doing so requires that the surroundings do work on the system, which changes the surroundings forever.



(a)



(b)

▲ **Figure 19.4 Reversible flow of heat.** Heat can flow reversibly between a system and its surroundings if the two have only an infinitesimally small difference in temperature, ΔT . The direction of heat flow can be changed by increasing or decreasing the temperature of the system by ΔT . (a) Increasing the temperature of the system by ΔT causes heat to flow from the system to the surroundings. (b) Decreasing the temperature of the system by ΔT causes heat to flow from the surroundings into the system.

What might a reversible, isothermal expansion of an ideal gas be like? It will occur only if the external pressure acting on the piston exactly balances the pressure exerted by the gas. Under these conditions, the piston will not move unless the external pressure is reduced infinitely slowly, allowing the pressure of the confined gas to readjust to maintain a balance in the two pressures. This gradual, infinitely slow process in which the external pressure and internal pressure are always in equilibrium is reversible. If we reverse the process and compress the gas in the same infinitely slow manner, we can return the gas to its original volume. The complete cycle of expansion and compression in this hypothetical process, moreover, is accomplished without any net change to the surroundings.

Because real processes can at best only approximate the slow, ever-in-equilibrium change associated with reversible processes, all real processes are irreversible. Further, the reverse of any spontaneous process is a nonspontaneous process. A nonspontaneous process can occur only if the surroundings do work on the system. Thus, *any spontaneous process is irreversible*. Even if we return the system to the original condition, the surroundings will have changed.

19.2 ENTROPY AND THE SECOND LAW OF THERMODYNAMICS

We are now closer to understanding spontaneity because we know that any spontaneous process is irreversible. But how can we use this idea to make predictions about the spontaneity of an unfamiliar process? Understanding spontaneity requires us to examine the thermodynamic quantity called **entropy**. Entropy has been variously associated with the extent of *randomness* in a system or with the extent to which energy is distributed or dispersed among the various motions of the molecules of the system. In fact, entropy is a multifaceted concept whose interpretations are not so quickly summarized by a simple definition. In this section we consider how we can relate entropy changes to heat transfer and temperature. Our analysis will bring us to a profound statement about spontaneity that we call the second law of thermodynamics. In Section 19.3 we examine the molecular significance of entropy.

Entropy Change

The entropy, S , of a system is a state function just like the internal energy, E , and enthalpy, H . As with these other quantities, the value of S is a characteristic of the state of a system. ∞ (Section 5.2) Thus, the change in entropy, ΔS , in a system depends only on the initial and final states of the system and not on the path taken from one state to the other:

$$\Delta S = S_{\text{final}} - S_{\text{initial}} \quad [19.1]$$

For the special case of an isothermal process, ΔS is equal to the heat that would be transferred if the process were reversible, q_{rev} , divided by the temperature at which the process occurs:

$$\Delta S = \frac{q_{\text{rev}}}{T} \quad (\text{constant } T) \quad [19.2]$$

Because S is a state function, we can use Equation 19.2 to calculate ΔS for *any* isothermal process, not just those that are reversible. If a change between two states is irreversible, we calculate ΔS by using a reversible path between the states.

GIVE IT SOME THOUGHT

How do we reconcile the fact that S is a state function but that ΔS depends on q , which is not a state function?

 ΔS for Phase Changes

The melting of a substance at its melting point and the vaporization of a substance at its boiling point are isothermal processes. Consider the melting of ice. At 1 atm pressure, ice and liquid water are in equilibrium with each other at 0 °C. Imagine that we melt one mole of ice at 0 °C, 1 atm to form one mole of liquid water at 0 °C, 1 atm. We can achieve this change by adding a certain amount of heat to the system from the surroundings: $q = \Delta H_{\text{fusion}}$. Now imagine that we carry out the change by adding the heat infinitely slowly, raising the temperature of the surroundings only infinitesimally above 0 °C. When we make the change in this fashion, the process is reversible. We can reverse the process simply by infinitely slowly removing the same amount of heat, ΔH_{fusion} , from the system, using immediate surroundings that are infinitesimally below 0 °C. Thus, $q_{\text{rev}} = \Delta H_{\text{fusion}}$ and $T = 0 \text{ °C} = 273 \text{ K}$.

The enthalpy of fusion for H_2O is $\Delta H_{\text{fusion}} = 6.01 \text{ kJ/mol}$. (The melting is an endothermic process, and so the sign of ΔH is positive.) Thus, we can use Equation 19.2 to calculate ΔS_{fusion} for melting one mole of ice at 273 K:

$$\Delta S_{\text{fusion}} = \frac{q_{\text{rev}}}{T} = \frac{\Delta H_{\text{fusion}}}{T} = \frac{(1 \text{ mol})(6.01 \times 10^3 \text{ J/mol})}{273 \text{ K}} = 22.0 \frac{\text{J}}{\text{K}}$$

Notice that the units for ΔS , J/K , are energy divided by absolute temperature, as we expect from Equation 19.2.

SAMPLE EXERCISE 19.2 | Calculating ΔS for a Phase Change

The element mercury, Hg , is a silvery liquid at room temperature. The normal freezing point of mercury is -38.9 °C , and its molar enthalpy of fusion is $\Delta H_{\text{fusion}} = 2.29 \text{ kJ/mol}$. What is the entropy change of the system when 50.0 g of $\text{Hg}(l)$ freezes at the normal freezing point?

SOLUTION

Analyze: We first recognize that freezing is an *exothermic* process; heat is transferred from the system to the surroundings when a liquid freezes ($q < 0$). The enthalpy of fusion is ΔH for the melting process. Because freezing is the reverse of melting, the enthalpy change that accompanies the freezing of 1 mol of Hg is $-\Delta H_{\text{fusion}} = -2.29 \text{ kJ/mol}$.

Plan: We can use $-\Delta H_{\text{fusion}}$ and the atomic weight of Hg to calculate q for freezing 50.0 g of Hg :

$$q = (50.0 \text{ g Hg}) \left(\frac{1 \text{ mol Hg}}{200.59 \text{ g Hg}} \right) \left(\frac{-2.29 \text{ kJ}}{1 \text{ mol Hg}} \right) \left(\frac{1000 \text{ J}}{1 \text{ kJ}} \right) = -571 \text{ J}$$

We can use this value of q as q_{rev} in Equation 19.2. We must first, however, convert the temperature to K:

$$-38.9 \text{ °C} = (-38.9 + 273.15) \text{ K} = 234.3 \text{ K}$$

Solve: We can now calculate the value of ΔS_{sys}

$$\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T} = \frac{-571 \text{ J}}{234.3 \text{ K}} = -2.44 \text{ J/K}$$

Check: The entropy change is negative because heat flows from the system, making q_{rev} negative.

Comment: The procedure we have used here can be used to calculate ΔS for other isothermal phase changes, such as the vaporization of a liquid at its boiling point.

PRACTICE EXERCISE

The normal boiling point of ethanol, $\text{C}_2\text{H}_5\text{OH}$, is 78.3 °C , and its molar enthalpy of vaporization is 38.56 kJ/mol . What is the change in entropy in the system when 68.3 g of $\text{C}_2\text{H}_5\text{OH}(g)$ at 1 atm condenses to liquid at the normal boiling point?

Answer: -163 J/K

A Closer Look

THE ENTROPY CHANGE WHEN A GAS EXPANDS ISOTHERMALLY

In general, we will see that if a system becomes more spread out, or more random, the system's entropy increases. Thus, we expect the spontaneous expansion of a gas to result in an increase in entropy. To illustrate how the entropy change associated with an expanding gas can be calculated, consider the expansion of an ideal gas that is initially constrained by a piston, as in Figure 19.5(c). If the gas undergoes a reversible isothermal expansion, the work done on the surroundings by the moving piston can be calculated with the aid of calculus:

$$w_{\text{rev}} = -nRT \ln \frac{V_2}{V_1}$$

In this equation, n is the number of moles of gas, R is the gas constant, T is the absolute temperature, V_1 is the initial volume, and V_2 is the final volume. Notice that if $V_2 > V_1$, as it must be in our expansion, then $w_{\text{rev}} < 0$, meaning that the expanding gas does work on the surroundings.

One of the characteristics of an ideal gas is that its internal energy depends only on temperature, not on pressure. Thus, when an ideal gas expands at a constant temperature, $\Delta E = 0$. Because $\Delta E = q_{\text{rev}} + w_{\text{rev}} = 0$, we see that

$q_{\text{rev}} = -w_{\text{rev}} = nRT \ln(V_2/V_1)$. Then, using Equation 19.2, we can calculate the entropy change in the system:

$$\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T} = \frac{nRT \ln \frac{V_2}{V_1}}{T} = nR \ln \frac{V_2}{V_1} \quad [19.3]$$

For 1.00 L of an ideal gas at 1.00 atm and 0 °C, we can calculate the number of moles, $n = 4.46 \times 10^{-2}$ mol. The gas constant, R , can be expressed in units of J/mol-K, 8.314 J/mol-K (Table 10.2). Thus, for the expansion of the gas from 1.00 L to 2.00 L, we have

$$\begin{aligned} \Delta S_{\text{sys}} &= (4.46 \times 10^{-2} \text{ mol}) \left(8.314 \frac{\text{J}}{\text{mol-K}} \right) \left(\ln \frac{2.00 \text{ L}}{1.00 \text{ L}} \right) \\ &= 0.26 \text{ J/K} \end{aligned}$$

In Section 19.3 we will see that this increase in entropy is a measure of the increased randomness of the molecules because of the expansion.

Related Exercises: 19.27 and 19.28

The Second Law of Thermodynamics

The key idea of the first law of thermodynamics is that energy is conserved in any process. Thus, the quantity of energy lost by a system equals the quantity gained by its surroundings. \rightleftharpoons (Section 5.1) We will see, however, that entropy is different because it actually increases in any spontaneous process. Thus, the sum of the entropy change of the system and surroundings for any spontaneous process is always greater than zero. Entropy change is like a signpost indicating whether a process is spontaneous. Let's illustrate this generalization by again considering the melting of ice, designating the ice and water as our system.

Let's calculate the entropy change of the system and the entropy change of the surroundings when a mole of ice (a piece roughly the size of an ordinary ice cube) melts in the palm of your hand. The process is not reversible because the system and surroundings are at different temperatures. Nevertheless, because ΔS is a state function, the entropy change of the system is the same regardless of whether the process is reversible or irreversible. We calculated the entropy change of the system just before Sample Exercise 19.2:

$$\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T} = \frac{(1 \text{ mol})(6.01 \times 10^3 \text{ J/mol})}{273 \text{ K}} = 22.0 \frac{\text{J}}{\text{K}}$$

The surroundings immediately in contact with the ice are your hand, which we will assume is at body temperature, 37 °C = 310 K. The heat lost by your hand is equal in magnitude to the heat gained by the ice but has the opposite sign, -6.01×10^3 J/mol. Hence the entropy change of the surroundings is

$$\Delta S_{\text{surr}} = \frac{q_{\text{rev}}}{T} = \frac{(1 \text{ mol})(-6.01 \times 10^3 \text{ J/mol})}{310 \text{ K}} = -19.4 \frac{\text{J}}{\text{K}}$$

Thus, the total entropy change is positive:

$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \left(22.0 \frac{\text{J}}{\text{K}} \right) + \left(-19.4 \frac{\text{J}}{\text{K}} \right) = 2.6 \frac{\text{J}}{\text{K}}$$

If the temperature of the surroundings were not 310 K but rather some temperature infinitesimally above 273 K, the melting would be reversible instead of irreversible. In that case the entropy change of the surroundings would equal -22.0 J/K and ΔS_{total} would be zero.

In general, any irreversible process results in an overall increase in entropy, whereas a reversible process results in no overall change in entropy. This general statement is known as the **second law of thermodynamics**. The sum of the entropy of a system plus the entropy of the surroundings is everything there is, and so we refer to the total entropy change as the entropy change of the universe, ΔS_{univ} . We can therefore state the second law of thermodynamics in terms of the following equations:

$$\begin{aligned} \text{Reversible process: } \Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0 \\ \text{Irreversible process: } \Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0 \end{aligned} \quad [19.4]$$

All real processes that occur of their own accord are irreversible (with reversible processes being a useful idealization). These processes are also spontaneous. Thus, *the total entropy of the universe increases in any spontaneous process*. This profound generalization is yet another way of expressing the second law of thermodynamics.

GIVE IT SOME THOUGHT

The rusting of iron is accompanied by a decrease in the entropy of the system (the iron and oxygen). What can we conclude about the entropy change of the surroundings?

The second law of thermodynamics tells us the essential character of any spontaneous change—it is always accompanied by an overall increase in entropy. We can, in fact, use this criterion to predict whether processes will be spontaneous. Before beginning to use the second law to predict spontaneity, however, we will find it useful to explore further the meaning of entropy from a molecular perspective.

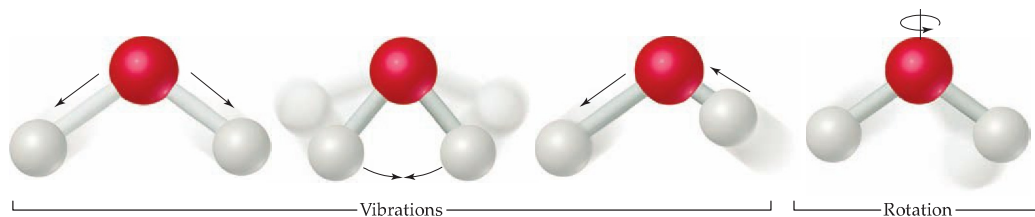
Throughout most of the remainder of this chapter, we will focus mainly on the systems we encounter rather than on their surroundings. To simplify the notation, we will usually refer to the entropy change of the system merely as ΔS rather than explicitly indicating ΔS_{sys} .

19.3 THE MOLECULAR INTERPRETATION OF ENTROPY

As chemists, we are interested in molecules. What does entropy have to do with them and their transformations? What molecular property does entropy reflect? Ludwig Boltzmann (1844–1906) gave conceptual meaning to entropy. To understand Boltzmann's contribution, we need to examine the ways in which molecules can store energy.

Molecular Motions and Energy

When a substance is heated, the motion of its molecules increases. When we studied the kinetic-molecular theory of gases, we found that the average kinetic energy of the molecules of an ideal gas is directly proportional to the absolute temperature of the gas. ∞ (Section 10.7) That means the higher the temperature, the faster the molecules are moving and the more kinetic energy they possess. Moreover, hotter systems have a *broader distribution* of molecular speeds, as you can see by referring back to Figure 10.18. The particles of an ideal gas, however, are merely idealized points with no volume and no bonds, points that we visualize as flitting around through space. Real molecules can undergo more complex kinds of motions.



▲ **Figure 19.6 Vibrational and rotational motions in a water molecule.** Vibrational motions in the molecule involve periodic displacements of the atoms with respect to one another. Rotational motions involve the spinning of a molecule about an axis.

Molecules can undergo three kinds of motion. The entire molecule can move in one direction, as in the motions of the particles of an ideal gas or the motions of larger objects, such as a baseball being thrown around a baseball field. We call such movement **translational motion**. The molecules in a gas have more freedom of translational motion than those in a liquid, which in turn have more translational freedom than the molecules of a solid.

A molecule may also undergo **vibrational motion**, in which the atoms in the molecule move periodically toward and away from one another, much as a tuning fork vibrates about its equilibrium shape. In addition, molecules may possess **rotational motion**, as though they were spinning like tops. Figure 19.6 ▲ shows the vibrational motions and one of the rotational motions possible for the water molecule. These different forms of motion are ways in which a molecule can store energy, and we refer to the various forms collectively as the “motional energy” of the molecule.

GIVE IT SOME THOUGHT

What kinds of motion can a molecule undergo that a single atom cannot?

Boltzmann’s Equation and Microstates

The science of thermodynamics developed as a means of describing the properties of matter in our macroscopic world without regard to the microscopic structure of the matter. In fact, thermodynamics was a well-developed field before the modern views of atomic and molecular structure were even known. The thermodynamic properties of water, for example, addressed the behavior of bulk water (or ice or water vapor) as a substance, without considering any specific properties of individual H_2O molecules.

To connect the microscopic and macroscopic descriptions of matter, scientists have developed the field of *statistical thermodynamics*, which uses the tools of statistics and probability to provide the link between the microscopic and macroscopic worlds. Here we will show how entropy, which is a property of bulk matter, can be connected to the behavior of atoms and molecules. Because the mathematics of statistical thermodynamics is quite complex, our discussion will be largely conceptual.

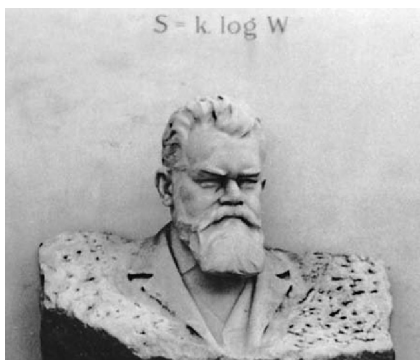
Let’s begin by considering one mole of an ideal gas in a particular thermodynamic state, which we can define by specifying the temperature, T , and volume, V , of the gas. (Remember that the energy, E , of an ideal gas depends only on its temperature and that by fixing the values of n , T , and V , we also fix the value of the pressure, P .) What is happening to our ideal gas sample at the microscopic level, and how does what is going on at the microscopic level relate to the entropy of the sample? To address these questions, we need to consider both the positions of the gas molecules and their individual kinetic energies, which depend on the speeds of the molecules. In our discussion of the kinetic-molecular theory, we considered the gas molecules to be in constant motion within the entire volume of the container. We also saw that the speeds of the gas molecules follow a well-defined distribution at a given temperature, such as that shown in Figure 10.18. ∞ (Section 10.7)

Now imagine that we could take a “snapshot” of the positions and speeds of all of the molecules at a given instant. That particular set of 6×10^{23} positions and energies of the individual gas molecules is what we call a **microstate** of the thermodynamic system. A microstate is a single possible arrangement of the positions and kinetic energies of the gas molecules when the gas is in a specific thermodynamic state. We could envision continuing to take snapshots of our system to see other possible microstates. In fact, as you no doubt see, there would be such a staggeringly large number of microstates that taking individual snapshots of all of them is not feasible. Because we are examining such a large number of particles, however, we can use the tools of statistics and probability to determine the total number of microstates for the thermodynamic state. (That is where the *statistical* part of statistical thermodynamics comes in.) Each thermodynamic state has a characteristic number of microstates associated with it, and we will use the symbol W for that number.

The connection between the number of microstates of a system, W , and its entropy, S , is expressed in a beautifully simple equation developed by Boltzmann:

$$S = k \ln W \quad [19.5]$$

In this equation, k is Boltzmann’s constant, 1.38×10^{-23} J/K. Thus, *entropy is a measure of how many microstates are associated with a particular macroscopic state.* Equation 19.5 appears on Boltzmann’s gravestone (Figure 19.7 ▶).



▲ **Figure 19.7 Ludwig Boltzmann’s gravestone.** Boltzmann’s gravestone in Vienna is inscribed with his famous relationship between the entropy of a state and the number of available microstates. (In Boltzmann’s time, “log” was used to represent the natural logarithm.)

GIVE IT SOME THOUGHT

What is the entropy of a system that has only a single microstate?

The entropy change accompanying any process is

$$\Delta S = k \ln W_{\text{final}} - k \ln W_{\text{initial}} = k \ln \frac{W_{\text{final}}}{W_{\text{initial}}} \quad [19.6]$$

Thus, any change in the system that leads to an increase in the number of microstates leads to a positive value of ΔS : *Entropy increases with the number of microstates of the system.*

Let’s briefly consider two simple changes to our ideal-gas sample and see how the entropy changes in each case. First, suppose we increase the volume of the system, which is analogous to allowing the gas to expand isothermally. A greater volume means that there are a greater number of positions available to the gas atoms. Thus, there will be a greater number of microstates for the system after the increase in volume. The entropy therefore increases as the volume increases, as we saw in the “A Closer Look” box in Section 19.2. Second, suppose we keep the volume fixed but increase the temperature. How will this change affect the entropy of the system? Recall the distribution of molecular speeds presented in Figure 10.18. An increase in temperature increases the average (rms) speed of the molecules and broadens the distribution of speeds. Hence, the molecules have a greater number of possible kinetic energies, and the number of microstates will once again increase. The entropy of the system will therefore increase with increasing temperature.

If we consider real molecules instead of ideal-gas particles, we must also consider the different amounts of vibrational and rotational energies the molecules have in addition to their kinetic energies. A collection of real molecules therefore has a greater number of microstates available than does the same number of ideal-gas particles. In general, *the number of microstates available to a system increases with an increase in volume, an increase in temperature, or an increase in the number of molecules because any of these changes increases the possible positions and energies of the molecules of the system.*

A Closer Look

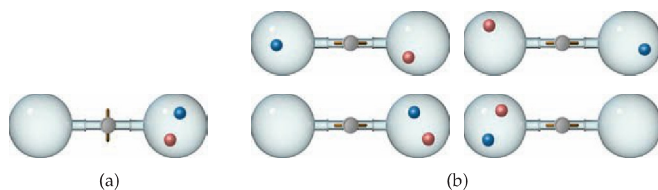
ENTROPY AND PROBABILITY

The game of poker is sometimes used as an analogy to explore the idea of the microstates associated with a particular state. There are about 2.6 million different five-card poker hands that can be dealt, and each of these hands can be viewed as a possible “microstate” for the hand dealt to any one player in a game. Table 19.1 shows two poker hands. The probability that a particular hand will contain five *specific* cards is the same regardless of which five cards are specified. Thus, there is an equal probability of dealing either of the hands shown in Table 19.1. However, the first hand, a royal flush (the ten through ace of a single suit), strikes us as much more highly ordered than the second hand, a “nothing.” The reason for this is clear if we compare the number of five-card arrangements that correspond to a royal flush to the number corresponding to a nothing: only four hands (microstates) for a royal flush but more than 1.3 million for a nothing hand. The nothing state has a higher probability of being dealt from a shuffled deck than the royal-flush state because there are so many more arrangements of cards that correspond to the nothing state. In other words, the value of W in Boltzmann’s equation (Equation 19.5) is much greater for a nothing than for a royal flush. This example teaches us that there is a connection between probability and entropy.

The entropy of any system has a natural tendency to increase, because increased entropy represents a movement toward a state of higher probability. Let’s use this reasoning to explain the isothermal expansion of a gas,



such as that depicted in Figure 19.1. When the stopcock is opened, the gas molecules are less constrained, and there are more possible arrangements for them (more microstates) in the larger volume. The various microstates are depicted in a schematic way in Figure 19.8. In this figure, we make no attempt to describe the motion of the particles, focusing instead only on their locations. The spreading of the molecules over the larger volume represents movement to the more probable state.

When we use the terms randomness and disorder to describe entropy, we have to be careful not to carry an aesthetic sense of what we mean. What we must remember is that the fundamental connection to entropy is not tied directly with randomness, disorder, or energy dispersal, but with the number of available microstates.



▲ **Figure 19.8 Probability and the locations of gas molecules.** The two molecules are colored red and blue to keep track of them. (a) Before the stopcock is opened, both molecules are in the right-hand flask. (b) After the stopcock is opened, there are four possible arrangements of the two molecules. Only one of the four arrangements corresponds to both molecules being in the right-hand flask. The greater number of possible arrangements corresponds to greater disorder in the system. In general, the probability that the molecules will stay in the original flask is $(\frac{1}{2})^n$, where n is the number of molecules.

TABLE 19.1 ■ A Comparison of the Number of Combinations that Can Lead to a Royal Flush and to a “Nothing” Hand in Poker

Hand	State	Number of Hands that Lead to This State
	Royal flush	4
	“Nothing”	1,302,540

Chemists use several different ways to describe an increase in the number of microstates and therefore an increase in the entropy for a system. Each of these ways seeks to capture a sense of the increased freedom of motion that causes molecules to spread out if not restrained by physical barriers or chemical bonds.

Some say the increase in entropy represents an increase in the *randomness* or *disorder* of the system. Others liken an increase in entropy to an increased *dispersion* (*spreading out*) of energy because there is an increase in the number of ways the positions and energies of the molecules can be distributed throughout the system. Each of these descriptions (randomness, disorder, and energy dispersal) is conceptually helpful if applied correctly. Indeed, you will find it useful to keep these descriptions in mind as you evaluate entropy changes.

Making Qualitative Predictions About ΔS

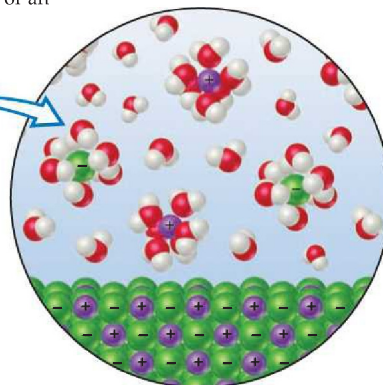
It is usually not difficult to construct a mental picture to estimate qualitatively how the entropy of a system changes during a simple process. In most instances, an increase in the number of microstates, and hence an increase in entropy, parallels an increase in

1. temperature
2. volume
3. number of independently moving particles

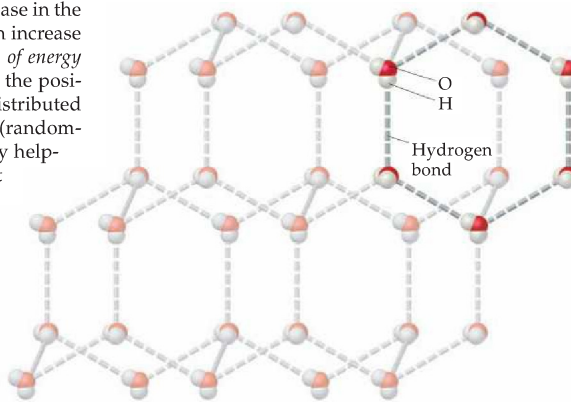
Thus, we can usually make qualitative predictions about entropy changes by focusing on these factors. For example, when water vaporizes, the molecules spread out into a larger volume. Because they occupy a larger space, there is an increase in their freedom of motion, giving rise to more accessible microstates and hence to an increase in entropy.

Consider the melting of ice. The rigid structure of the water molecules, shown in Figure 19.9▲, restricts motion to only tiny vibrations throughout the crystal. In contrast, the molecules in liquid water are free to move about with respect to one another (translation) and to tumble around (rotation) as well as vibrate. During melting, therefore, the number of accessible microstates increases and so does the entropy.

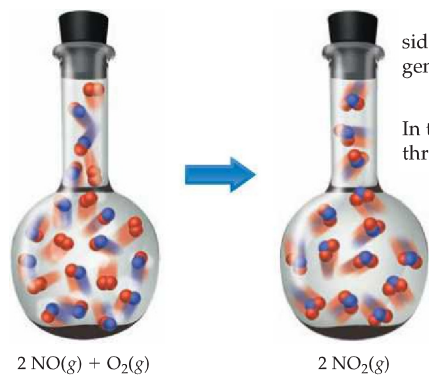
When an ionic solid, such as KCl, dissolves in water, a mixture of water and ions replaces the pure solid and pure water (Figure 19.10▼). The ions now move in a larger volume and possess more motional energy than in the rigid solid. We have to be careful, however, because water molecules are held around the ions as water of hydration. ∞(Section 13.1) These water molecules have less motional energy than before because they are now confined to the immediate environment of the ions. The greater the charge of an ion, the greater are the ion-dipole attractions that hold the ion and the water together, thereby restricting motions. Thus, even though the solution process is normally accompanied by a net increase in entropy, the dissolving of salts with highly charged ions can result in a net *decrease* in entropy.



► **Figure 19.10 Dissolving an ionic solid in water.** The ions become more spread out and random in their motions, but the water molecules that hydrate the ions become less random.



▲ **Figure 19.9 Structure of ice.** The intermolecular attractions in the three-dimensional lattice restrict the molecules to vibrational motion only.



▲ Figure 19.11 Entropy change for a reaction. A decrease in the number of gaseous molecules leads to a decrease in the entropy of the system. When the $\text{NO}(g)$ and $\text{O}_2(g)$ (left) react to form the $\text{NO}_2(g)$ (right), the number of gaseous molecules decreases. The atoms have fewer degrees of freedom because new N—O bonds form and the entropy decreases.

The same ideas apply to systems involving chemical reactions. Consider the reaction between nitric oxide gas and oxygen gas to form nitrogen dioxide gas:



In this case the reaction results in a decrease in the number of molecules—three molecules of gaseous reactants form two molecules of gaseous products (Figure 19.11 ◀). The formation of new N—O bonds reduces the motions of the atoms in the system. The formation of new bonds decreases the *number of degrees of freedom*, or forms of motion, available to the atoms. That is, the atoms are less free to move in random fashion because of the formation of new bonds. The decrease in the number of molecules and the resultant decrease in motion result in fewer accessible microstates and therefore a decrease in the entropy of the system.

In summary, we generally expect the entropy of the system to increase for processes in which

1. Gases are formed from either solids or liquids.
2. Liquids or solutions are formed from solids.
3. The number of gas molecules increases during a chemical reaction.

■ SAMPLE EXERCISE 19.3 | Predicting the Sign of ΔS

Predict whether ΔS is positive or negative for each of the following processes, assuming each occurs at constant temperature:

- (a) $\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(g)$
- (b) $\text{Ag}^+(aq) + \text{Cl}^-(aq) \longrightarrow \text{AgCl}(s)$
- (c) $4 \text{Fe}(s) + 3 \text{O}_2(g) \longrightarrow 2 \text{Fe}_2\text{O}_3(s)$
- (d) $\text{N}_2(g) + \text{O}_2(g) \longrightarrow 2 \text{NO}(g)$

SOLUTION

Analyze: We are given four equations and asked to predict the sign of ΔS for each chemical reaction.

Plan: The sign of ΔS will be positive if there is an increase in temperature, an increase in the volume in which the molecules move, or an increase in the number of gas particles in the reaction. The question states that the temperature is constant. Thus, we need to evaluate each equation with the other two factors in mind.

Solve:

- (a) The evaporation of a liquid is accompanied by a large increase in volume. One mole of water (18 g) occupies about 18 mL as a liquid and if it could exist as a gas at STP it would occupy 22.4 L. Because the molecules are distributed throughout a much larger volume in the gaseous state than in the liquid state, an increase in motional freedom accompanies vaporization. Therefore, ΔS is positive.
- (b) In this process the ions, which are free to move throughout the volume of the solution, form a solid in which they are confined to a smaller volume and restricted to more highly constrained positions. Thus, ΔS is negative.
- (c) The particles of a solid are confined to specific locations and have fewer ways to move (fewer microstates) than do the molecules of a gas. Because O_2 gas is converted into part of the solid product Fe_2O_3 , ΔS is negative.
- (d) The number of moles of gases is the same on both sides of the equation, and so the entropy change will be small. The sign of ΔS is impossible to predict based on our discussions thus far, but we can predict that ΔS will be close to zero.

■ PRACTICE EXERCISE

Indicate whether each of the following processes produces an increase or decrease in the entropy of the system:

- (a) $\text{CO}_2(s) \longrightarrow \text{CO}_2(g)$
- (b) $\text{CaO}(s) + \text{CO}_2(g) \longrightarrow \text{CaCO}_3(s)$
- (c) $\text{HCl}(g) + \text{NH}_3(g) \longrightarrow \text{NH}_4\text{Cl}(s)$
- (d) $2 \text{SO}_2(g) + \text{O}_2(g) \longrightarrow 2 \text{SO}_3(g)$

Answers: (a) increase, (b) decrease, (c) decrease, (d) decrease

SAMPLE EXERCISE 19.4 Predicting Which Sample of Matter Has the Higher Entropy

Choose the sample of matter that has greater entropy in each pair, and explain your choice: (a) 1 mol of NaCl(s) or 1 mol of HCl(g) at 25 °C, (b) 2 mol of HCl(g) or 1 mol of HCl(g) at 25 °C, (c) 1 mol of HCl(g) or 1 mol of Ar(g) at 298 K.

SOLUTION

Analyze: We need to select the system in each pair that has the greater entropy.

Plan: To do this, we examine the state of the system and the complexity of the molecules it contains.

Solve: (a) Gaseous HCl has the higher entropy because gases have more available motions than solids. (b) The sample containing 2 mol of HCl has twice the number of molecules as the sample containing 1 mol. Thus, the 2-mol sample has twice the number of microstates and twice the entropy when they are at the same pressure. (c) The HCl sample has the higher entropy because the HCl molecule is capable of storing energy in more ways than is Ar. HCl molecules can rotate and vibrate; Ar atoms cannot.

PRACTICE EXERCISE

Choose the substance with the greater entropy in each case: (a) 1 mol of H₂(g) at STP or 1 mol of H₂(g) at 100 °C and 0.5 atm, (b) 1 mol of H₂O(s) at 0 °C or 1 mol of H₂O(l) at 25 °C, (c) 1 mol of H₂(g) at STP or 1 mol of SO₂(g) at STP, (d) 1 mol of N₂O₄(g) at STP or 2 mol of NO₂(g) at STP.

Answers: (a) 1 mol of H₂(g) at 100 °C and 0.5 atm, (b) 1 mol of H₂O(l) at 25 °C, (c) 1 mol of SO₂(g) at STP, (d) 2 mol of NO₂(g) at STP

Chemistry and Life

ENTROPY AND LIFE

The ginkgo leaf shown in Figure 19.12(a) reveals beautiful patterns of form and color. Both plant systems and animal systems, including those of humans, are incredibly complex structures in which a host of substances come together in organized ways to form cells, tissue, organ systems, and so on. These various components must operate in synchrony for the organism as a whole to be viable. If even one key system strays far from its optimal state, the organism as a whole may die.

To make a living system from its component molecules—such as a ginkgo leaf from sugar molecules, cellulose molecules, and the other substances present in the leaf—requires a very large reduction in entropy. It would seem, then, that living systems might violate the second law of thermodynamics. They seem spontaneously to become more, not less, organized as they develop. To get the full picture, however, we must take into account the surroundings.

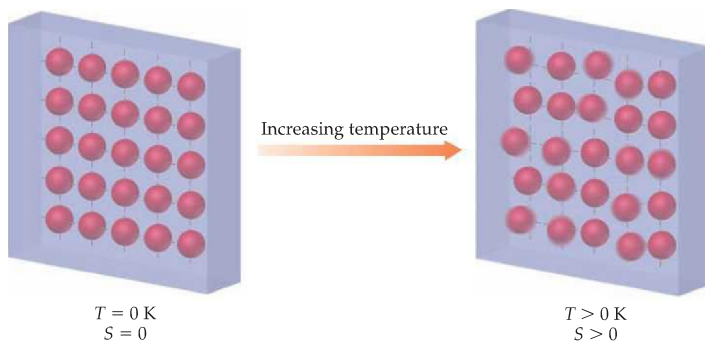
We know that a system can move toward lower entropy if we do work on it. (That is, if we supply energy to the system in a very specific way.) When we do work on a gas, for example, by compressing it isothermally, the entropy of the gas is lowered. The energy for the work done is provided by the surroundings, and in the process the net entropy change in the universe is positive.

The striking thing about living systems is that they are organized to recruit energy from their surroundings spontaneously. Some single-celled organisms, called *autotrophs*, capture energy from sunlight and store it in molecules such as sugars and fats [Figure 19.12(b)]. Others, called *heterotrophs*, absorb food molecules from their surroundings and then break down the molecules to provide needed energy. Whatever their mode of existence, however, living systems gain their order at the expense of the surroundings. Each cell exists at the expense of an increase in the entropy of the universe.



▲ **Figure 19.12 Entropy and life.** (a) This ginkgo leaf represents a highly organized living system. (b) Cyanobacteria absorb light energy and utilize it to synthesize the substances needed for growth.

► **Figure 19.13** A perfectly ordered crystalline solid at and above 0 K. At absolute zero (left), all lattice units are in their lattice sites, devoid of thermal motion. As the temperature rises above 0 K (right), the atoms or molecules gain energy and their vibrational motion increases.

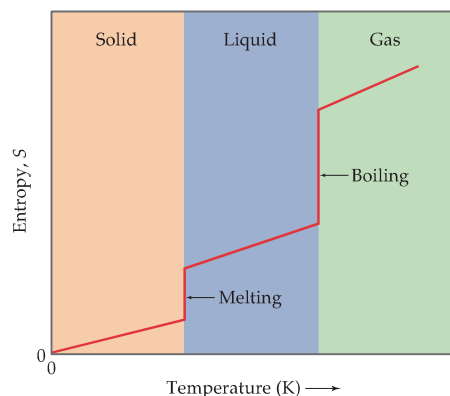


The Third Law of Thermodynamics

If we decrease the thermal energy of a system by lowering the temperature, the energy stored in translational, vibrational, and rotational forms of motion decreases. As less energy is stored, the entropy of the system decreases. If we keep lowering the temperature, do we reach a state in which these motions are essentially shut down, a point described by a single microstate? This question is addressed by the **third law of thermodynamics**, which states that *the entropy of a pure crystalline substance at absolute zero is zero: $S(0 \text{ K}) = 0$* .

Figure 19.13 ▲ shows schematically a pure crystalline solid. At absolute zero all the units of the lattice have no thermal motion. There is, therefore, only one microstate. As a result $S = k \ln W = k \ln 1 = 0$. As the temperature is increased from absolute zero, the atoms or molecules in the crystal gain energy in the form of vibrational motion about their lattice positions. Thus, the degrees of freedom of the crystal increase. The entropy of the lattice therefore increases with temperature because vibrational motion causes the atoms or molecules to have a greater number of accessible microstates.

What happens to the entropy of the substance as we continue to heat it? Figure 19.14 ◀ is a plot of how the entropy of a typical substance varies with temperature. We see that the entropy of the solid continues to increase steadily with



increasing temperature up to the melting point of the solid. When the solid melts, the bonds holding the atoms or molecules are broken and the particles are free to move about the entire volume of the substance. The added degrees of freedom for the individual molecules allow greater dispersal of the substance's energy thereby increasing its entropy. We therefore see a sharp increase in the entropy at the melting point. After all the solid has melted to liquid, the temperature again increases and with it, the entropy.

At the boiling point of the liquid, another abrupt increase in entropy occurs. We can understand this increase as resulting from the increased volume in which the molecules may be found. When the gas is heated further, the entropy increases steadily as more energy is stored in the translational motion of the gas molecules. At higher temperatures, the distribution of molecular speeds is spread out toward higher values. ∞ (Figure 10.18) More of the molecules have speeds that differ greatly from the most probable value. The expansion of the range of speeds of the gas molecules leads to an increased entropy.

The general conclusions we reach in examining Figure 19.14 are consistent with what we noted earlier: Entropy generally increases with increasing temperature because the increased motional energy can be dispersed in more ways. Further, the entropies of the phases of a given substance follow the order $S_{\text{solid}} < S_{\text{liquid}} < S_{\text{gas}}$. This ordering fits in nicely with our picture of the number of microstates available to solids, liquids, and gases.

▲ **Figure 19.14** Entropy as a function of temperature. Entropy increases as the temperature of a crystalline solid is increased from absolute zero. The vertical jumps in entropy correspond to phase changes.

GIVE IT SOME THOUGHT

If you are told that the entropy of a certain system is zero, what do you know about the system?

19.4 ENTROPY CHANGES IN CHEMICAL REACTIONS

In Section 5.5 we discussed how calorimetry can be used to measure ΔH for chemical reactions. No comparable, easy method exists for measuring ΔS for a reaction. By using experimental measurements of the variation of heat capacity with temperature, however, we can determine the absolute value of the entropy, S , for many substances at any temperature. (The theory and the methods used for these measurements and calculations are beyond the scope of this text.) Absolute entropies are based on the reference point of zero entropy for perfect crystalline solids at 0 K (the third law). Entropies are usually tabulated as molar quantities, in units of joules per mole-kelvin (J/mol-K).

The molar entropy values of substances in their standard states are known as **standard molar entropies** and are denoted S° . The standard state for any substance is defined as the pure substance at 1 atm pressure.* Table 19.2 lists the values of S° for several substances at 298 K; Appendix C gives a more extensive list.

We can make several observations about the S° values in Table 19.2:

1. Unlike enthalpies of formation, the standard molar entropies of elements at the reference temperature of 298 K are *not* zero.
2. The standard molar entropies of gases are greater than those of liquids and solids, consistent with our interpretation of experimental observations, as represented in Figure 19.14
3. Standard molar entropies generally increase with increasing molar mass. [Compare Li(s), Na(s), and K(s).]
4. Standard molar entropies generally increase with an increasing number of atoms in the formula of a substance.

Point 4 is related to molecular motion (Section 19.3). In general, the number of degrees of freedom for a molecule increases with increasing number of atoms, and thus the number of accessible microstates also increases. Figure 19.15 compares the standard molar entropies of three hydrocarbons. Notice how the entropy increases as the number of atoms in the molecule increases.

The entropy change in a chemical reaction equals the sum of the entropies of the products less the sum of the entropies of the reactants:

$$\Delta S^\circ = \sum nS^\circ(\text{products}) - \sum mS^\circ(\text{reactants}) \quad [19.8]$$

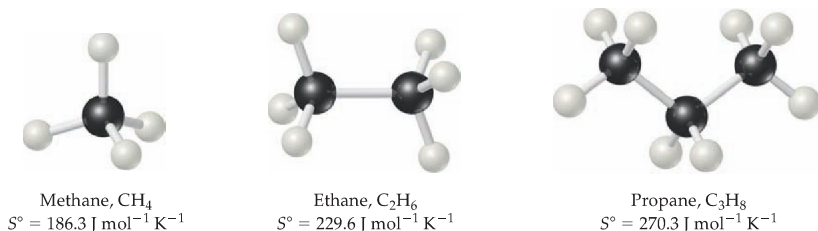
As in Equation 5.31, the coefficients n and m are the coefficients in the chemical equation, as illustrated in Sample Exercise 19.5.

TABLE 19.2 Standard Molar Entropies of Selected Substances at 298 K

Substance	S° , J/mol-K
Gases	
H ₂ (g)	130.6
N ₂ (g)	191.5
O ₂ (g)	205.0
H ₂ O(g)	188.8
NH ₃ (g)	192.5
CH ₃ OH(g)	237.6
C ₆ H ₆ (g)	269.2
Liquids	
H ₂ O(l)	69.9
CH ₃ OH(l)	126.8
C ₆ H ₆ (l)	172.8
Solids	
Li(s)	29.1
Na(s)	51.4
K(s)	64.7
Fe(s)	27.23
FeCl ₃ (s)	142.3
NaCl(s)	72.3

▼ Figure 19.15 Molar entropies.

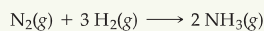
In general, the more complex a molecule (that is, the greater the number of atoms present), the greater the molar entropy of the substance, as illustrated here by the molar entropies of three simple hydrocarbons.



*The standard pressure used in thermodynamics is no longer 1 atm but is based on the SI unit for pressure, the pascal (Pa). The standard pressure is 10⁵ Pa, a quantity known as a bar: 1 bar = 10⁵ Pa = 0.987 atm. Because 1 bar differs from 1 atm by only 1.3%, we will continue to refer to the standard pressure as 1 atm.

SAMPLE EXERCISE 19.5 | Calculating ΔS from Tabulated Entropies

Calculate ΔS° for the synthesis of ammonia from $\text{N}_2(\text{g})$ and $\text{H}_2(\text{g})$ at 298 K:

**SOLUTION**

Analyze: We are asked to calculate the entropy change for the synthesis of $\text{NH}_3(\text{g})$ from its constituent elements.

Plan: We can make this calculation using Equation 19.8 and the standard molar entropy values for the reactants and the products that are given in Table 19.2 and in Appendix C.

Solve: Using Equation 19.8, we have $\Delta S^\circ = 2S^\circ(\text{NH}_3) - [S^\circ(\text{N}_2) + 3S^\circ(\text{H}_2)]$

Substituting the appropriate S° values from Table 19.2 yields $\Delta S^\circ = (2 \text{ mol})(192.5 \text{ J/mol}\cdot\text{K}) - [(1 \text{ mol})(191.5 \text{ J/mol}\cdot\text{K}) + (3 \text{ mol})(130.6 \text{ J/mol}\cdot\text{K})]$
 $= -198.3 \text{ J/K}$

Check: The value for ΔS° is negative, in agreement with our qualitative prediction based on the decrease in the number of molecules of gas during the reaction.

PRACTICE EXERCISE

Using the standard entropies in Appendix C, calculate the standard entropy change, ΔS° , for the following reaction at 298 K:



Answer: 180.39 J/K

Entropy Changes in the Surroundings

We can use tabulated absolute entropy values to calculate the standard entropy change in a system, such as a chemical reaction, as just described. But what about the entropy change in the surroundings? We encountered this situation in Section 19.2, but it is good to revisit it now that we are examining chemical reactions.

We should recognize that the surroundings serve essentially as a large, constant-temperature heat source (or heat sink if the heat flows from the system to the surroundings). The change in entropy of the surroundings will depend on how much heat is absorbed or given off by the system. For an isothermal process, the entropy change of the surroundings is given by

$$\Delta S_{\text{surr}} = \frac{-q_{\text{sys}}}{T}$$

For a reaction occurring at constant pressure, q_{sys} is simply the enthalpy change for the reaction, ΔH . Thus, we can write

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T} \quad [19.9]$$

For the reaction in Sample Exercise 19.5, the formation of ammonia from $\text{H}_2(\text{g})$ and $\text{N}_2(\text{g})$ at 298 K, q_{sys} is the enthalpy change for reaction under standard conditions, ΔH° . ∞ (Section 5.7) Using the procedures described in Section 5.7, we have

$$\begin{aligned} \Delta H_{\text{rxn}}^\circ &= 2\Delta H_f^\circ[\text{NH}_3(\text{g})] - 3\Delta H_f^\circ[\text{H}_2(\text{g})] - \Delta H_f^\circ[\text{N}_2(\text{g})] \\ &= 2(-46.19 \text{ kJ}) - 3(0 \text{ kJ}) - (0 \text{ kJ}) = -92.38 \text{ kJ} \end{aligned}$$

Thus at 298 K the formation of ammonia from $\text{H}_2(\text{g})$ and $\text{N}_2(\text{g})$ is exothermic. Absorption of the heat given off by the system results in an increase in the entropy of the surroundings:

$$\Delta S_{\text{surr}}^\circ = \frac{92.38 \text{ kJ}}{298 \text{ K}} = 0.310 \text{ kJ/K} = 310 \text{ J/K}$$

Notice that the magnitude of the entropy gained by the surroundings is greater than that lost by the system (as calculated in Sample Exercise 19.5):

$$\Delta S_{\text{univ}}^{\circ} = \Delta S_{\text{sys}}^{\circ} + \Delta S_{\text{surr}}^{\circ} = -198.3 \text{ J/K} + 310 \text{ J/K} = 112 \text{ J/K}$$

Because $\Delta S_{\text{univ}}^{\circ}$ is positive for any spontaneous reaction, this calculation indicates that when $\text{NH}_3(\text{g})$, $\text{H}_2(\text{g})$, and $\text{N}_2(\text{g})$ are together at 298 K in their standard states (each at 1 atm pressure), the reaction system will move spontaneously toward formation of $\text{NH}_3(\text{g})$. Keep in mind that while the thermodynamic calculations indicate that formation of ammonia is spontaneous, they do not tell us anything about the rate at which ammonia is formed. Establishing equilibrium in this system within a reasonable period requires a catalyst, as discussed in Section 15.7.

GIVE IT SOME THOUGHT

If a process is exothermic, does the entropy of the surroundings (1) always increase, (2) always decrease, or (3) sometimes increase and sometimes decrease, depending on the process?

19.5 GIBBS FREE ENERGY

We have seen examples of endothermic processes that are spontaneous, such as the dissolution of ammonium nitrate in water. ∞ (Section 13.1) We learned in our discussion of the solution process that a spontaneous, endothermic process must be accompanied by an increase in the entropy of the system. However, we have also encountered processes that are spontaneous and yet proceed with a *decrease* in the entropy of the system, such as the highly exothermic formation of sodium chloride from its constituent elements. ∞ (Section 8.2) Spontaneous processes that result in a decrease in the system's entropy are always exothermic. Thus, the spontaneity of a reaction seems to involve two thermodynamic concepts, enthalpy and entropy.

There should be a way to use ΔH and ΔS to predict whether a given reaction occurring at constant temperature and pressure will be spontaneous. The means for doing so was first developed by the American mathematician J. Willard Gibbs (1839–1903). Gibbs (Figure 19.16) proposed a new state function, now called the **Gibbs free energy** (or just **free energy**). The Gibbs free energy, G , of a state is defined as

$$G = H - TS \quad [19.10]$$

where T is the absolute temperature. For a process occurring at constant temperature, the change in free energy of the system, ΔG , is given by the expression

$$\Delta G = \Delta H - T\Delta S \quad [19.11]$$

Under standard conditions, this equation becomes

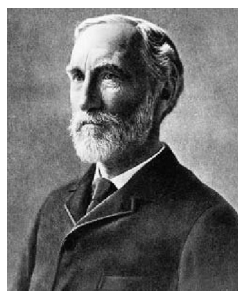
$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \quad [19.12]$$

To see how the state function G relates to reaction spontaneity, recall that for a reaction occurring at constant temperature and pressure

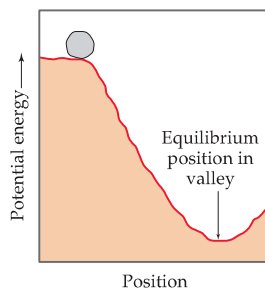
$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} + \left(\frac{-\Delta H_{\text{sys}}}{T} \right)$$

Multiplying both sides by $(-T)$ gives us

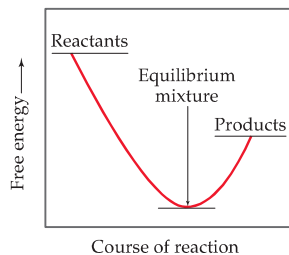
$$-T\Delta S_{\text{univ}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}} \quad [19.13]$$



▲ **Figure 19.16 Josiah Willard Gibbs (1839–1903).** Gibbs was the first person to be awarded a Ph.D. in science from an American university (Yale, 1863). From 1871 until his death, he held the chair of mathematical physics at Yale. He developed much of the theoretical foundation that led to the development of chemical thermodynamics.



(a)



(b)

▲ Figure 19.17 Potential energy and free energy. An analogy is shown between the gravitational potential-energy change of a boulder rolling down a hill (a) and the free-energy change in a spontaneous reaction (b). The equilibrium position in (a) is given by the minimum gravitational potential energy available to the system. The equilibrium position in (b) is given by the minimum free energy available to the system.

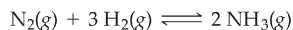
Comparing Equation 19.13 with Equation 19.11, we see that the free-energy change in a process occurring at constant temperature and pressure, ΔG , is equal to $-T\Delta S_{\text{univ}}$. We know that for spontaneous processes, ΔS_{univ} is always positive, and therefore $-T\Delta S_{\text{univ}}$ will be negative. Thus, the sign of ΔG provides us with extremely valuable information about the spontaneity of processes that occur at constant temperature and pressure. If both T and P are constant, the relationship between the sign of ΔG and the spontaneity of a reaction is as follows:

1. If ΔG is negative, the reaction is spontaneous in the forward direction.
2. If ΔG is zero, the reaction is at equilibrium.
3. If ΔG is positive, the reaction in the forward direction is nonspontaneous; work must be supplied from the surroundings to make it occur. However, the reverse reaction will be spontaneous.

It is more convenient to use ΔG as a criterion for spontaneity than to use ΔS_{univ} , because ΔG relates to the system alone and avoids the complication of having to examine the surroundings.

An analogy is often drawn between the free-energy change during a spontaneous reaction and the potential-energy change when a boulder rolls down a hill. Potential energy in a gravitational field “drives” the boulder until it reaches a state of minimum potential energy in the valley [Figure 19.17(a)]. Similarly, the free energy of a chemical system decreases until it reaches a minimum value [Figure 19.17(b)]. When this minimum is reached, a state of equilibrium exists. *In any spontaneous process at constant temperature and pressure, the free energy always decreases.*

As a specific illustration of these ideas, let’s return to the Haber process for the synthesis of ammonia from nitrogen and hydrogen, which we discussed extensively in Chapter 15:



Imagine that we have a reaction vessel that allows us to maintain a constant temperature and pressure and that we have a catalyst that allows the reaction to proceed at a reasonable rate. What will happen if we charge the vessel with a certain number of moles of N_2 and three times that number of moles of H_2 ? As we saw in Figure 15.3(a), the N_2 and H_2 will react spontaneously to form NH_3 until equilibrium is achieved. Similarly, Figure 15.3(b) demonstrates that if we charge the vessel with pure NH_3 , it will decompose spontaneously to form N_2 and H_2 until equilibrium is reached. In each case the free energy of the system is lowered on the way to equilibrium, which represents a minimum in the free energy. We illustrate these cases in Figure 19.18.

GIVE IT SOME THOUGHT

Give the criterion for spontaneity first in terms of entropy and then in terms of free energy.

This is a good time to remind ourselves of the significance of the reaction quotient, Q , for a system that is not at equilibrium. ∞ (Section 15.6) Recall that when $Q < K$, there is an excess of reactants relative to products. The reaction will proceed spontaneously in the forward direction to reach equilibrium. When $Q > K$, the reaction will proceed spontaneously in the reverse direction. At equilibrium $Q = K$. We have illustrated these points in Figure 19.18. In Section 19.7 we will see how to use the value of Q to calculate the value of ΔG for systems that are not at equilibrium.

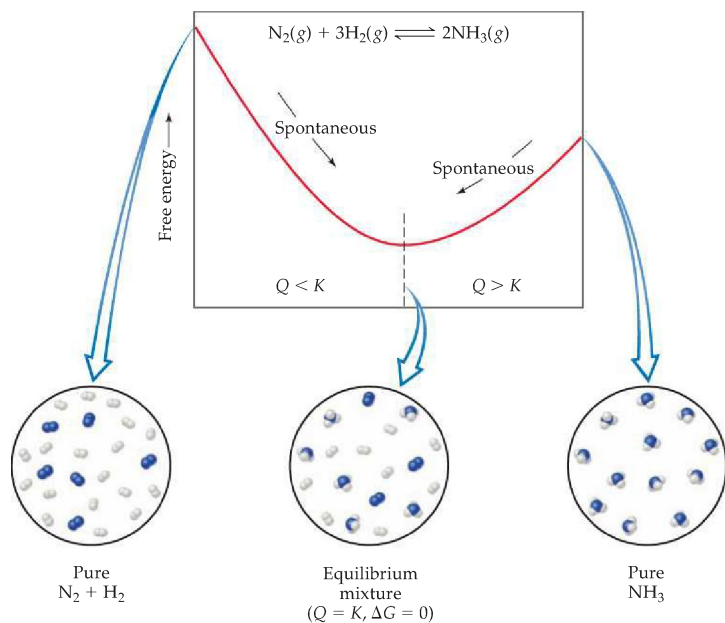
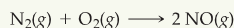


Figure 19.18 Free energy and equilibrium. In the reaction $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$, if the reaction mixture has too much N_2 and H_2 relative to NH_3 (left), the equilibrium lies too far to the left ($Q < K$) and NH_3 forms spontaneously. If there is too much NH_3 in the mixture (right), the equilibrium lies too far to the right ($Q > K$) and the NH_3 decomposes spontaneously into N_2 and H_2 . Both of these spontaneous processes are “downhill” in free energy. At equilibrium (center), $Q = K$ and the free energy is at a minimum ($\Delta G = 0$).

SAMPLE EXERCISE 19.6 Calculating Free-Energy Change from ΔH° , T , and ΔS°

Calculate the standard free energy change for the formation of $\text{NO}(\text{g})$ from $\text{N}_2(\text{g})$ and $\text{O}_2(\text{g})$ at 298 K:



given that $\Delta H^\circ = 180.7 \text{ kJ}$ and $\Delta S^\circ = 24.7 \text{ J/K}$. Is the reaction spontaneous under these circumstances?

SOLUTION

Analyze: We are asked to calculate ΔG° for the indicated reaction (given ΔH° , ΔS° , and T) and to predict whether the reaction is spontaneous under standard conditions at 298 K.

Plan: To calculate ΔG° , we use Equation 19.12, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. To determine whether the reaction is spontaneous under standard conditions, we look at the sign of ΔG° .

Solve:

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= 180.7 \text{ kJ} - (298 \text{ K})(24.7 \text{ J/K})\left(\frac{1 \text{ kJ}}{10^3 \text{ J}}\right) \\ &= 180.7 \text{ kJ} - 7.4 \text{ kJ} \\ &= 173.3 \text{ kJ} \end{aligned}$$

Because ΔG° is positive, the reaction is not spontaneous under standard conditions at 298 K.

Comment: Notice that we had to convert the units of the $T\Delta S^\circ$ term to kJ so that they could be added to the ΔH° term, whose units are kJ.

PRACTICE EXERCISE

A particular reaction has $\Delta H^\circ = 24.6 \text{ kJ}$ and $\Delta S^\circ = 132 \text{ J/K}$ at 298 K. Calculate ΔG° . Is the reaction spontaneous under these conditions?

Answer: $\Delta G^\circ = -14.7 \text{ kJ}$; the reaction is spontaneous.

TABLE 19.3 Conventions Used in Establishing Standard Free Energies

State of Matter	Standard State
Solid	Pure solid
Liquid	Pure liquid
Gas	1 atm pressure
Solution	1 M concentration
Elements	Standard free energy of formation of an element in its standard state is defined as zero

Standard Free Energy of Formation

Free energy is a state function, like enthalpy. We can tabulate **standard free energies of formation** for substances, just as we can tabulate standard enthalpies of formation. ∞ (Section 5.7) It is important to remember that standard values for these functions imply a particular set of conditions, or standard states. The standard state for gaseous substances is 1 atm pressure. For solid substances, the standard state is the pure solid; for liquids, the pure liquid. For substances in solution, the standard state is normally a concentration of 1 M. (In very accurate work it may be necessary to make certain corrections, but we need not worry about these.) The temperature usually chosen for purposes of tabulating data is 25 °C, but we will calculate ΔG° at other temperatures as well. Just as for the standard heats of formation, the free energies of elements in their standard states are set to zero. This arbitrary choice of a reference point has no effect on the quantity in which we are interested, namely, the *difference* in free energy between reactants and products. The rules about standard states are summarized in Table 19.3. A listing of standard free energies of formation, denoted ΔG_f° , appears in Appendix C.

GIVE IT SOME THOUGHT

What does the superscript $^\circ$ indicate when associated with a thermodynamic quantity, as in ΔH° , ΔS° , or ΔG° ?

The standard free energies of formation are useful in calculating the *standard free-energy change* for chemical processes. The procedure is analogous to the calculation of ΔH° (Equation 5.31) and ΔS° (Equation 19.8):

$$\Delta G^\circ = \sum n\Delta G_f^\circ(\text{products}) - \sum m\Delta G_f^\circ(\text{reactants}) \quad [19.14]$$

A Closer Look

WHAT'S "FREE" ABOUT FREE ENERGY?

The Gibbs free energy is a remarkable thermodynamic quantity. Because so many chemical reactions are carried out under conditions of near-constant pressure and temperature, chemists, biochemists, and engineers use the sign and magnitude of ΔG as exceptionally useful tools in the design and implementation of chemical and biochemical reactions. We will see examples of the usefulness of ΔG throughout the remainder of this chapter and this text. But what is "free" about free energy?

We have seen that we can use the sign of ΔG to conclude whether a reaction is spontaneous, nonspontaneous, or at equilibrium. The magnitude of ΔG is also significant. A reaction for which ΔG is large and negative, such as the burning of gasoline, is much more capable of doing work on the surroundings than is a reaction for which ΔG is small and negative, such as ice melting at room temperature. In fact, thermodynamics tells us that *the change in free energy for a process, ΔG , equals the maximum useful work that can be done by the system on its surroundings in a spontaneous process occurring at constant temperature and pressure:*

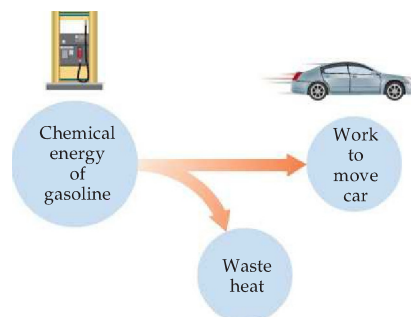
$$\Delta G = -w_{\text{max}} \quad [19.15]$$

In other words, ΔG gives the theoretical limit to how much work can be done by a process. This relationship explains why ΔG is called the *free energy*. It is the portion of the energy change of a spontaneous reaction that is free to do useful work. The remainder of the energy enters the environment as heat.

For example, when we burn gasoline to move a car, only part of the energy of the gasoline is used to drive the car forward, performing useful work. The rest of the energy is

dissipated to the surroundings as heat, accomplishing no useful work, as illustrated in Figure 19.19. The efficiency of energy conversion is given by the ratio of the work accomplished compared to the total energy used.

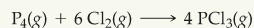
For processes that are not spontaneous ($\Delta G > 0$), the free-energy change is a measure of the *minimum* amount of work that must be done to cause the process to occur. In actual cases we always need to do more than this theoretical minimum amount because of the inefficiencies in the way the changes occur.



▲ Figure 19.19 Energy conversion. All conversions of energy are accompanied by production of heat, which enters the surroundings without accomplishing useful work.

SAMPLE EXERCISE 19.7 | Calculating Standard Free-Energy Change from Free Energies of Formation

(a) Use data from Appendix C to calculate the standard free-energy change for the following reaction at 298 K:



(b) What is ΔG° for the reverse of the above reaction?

SOLUTION

Analyze: We are asked to calculate the free-energy change for the indicated reaction and then to determine the free-energy change of its reverse.

Plan: To accomplish our task, we look up the free-energy values for the products and reactants and use Equation 19.14: We multiply the molar quantities by the coefficients in the balanced equation, and subtract the total for the reactants from that for the products.

Solve:

(a) $\text{Cl}_2(\text{g})$ is in its standard state, so ΔG_f° is zero for this reactant. $\text{P}_4(\text{g})$, however, is not in its standard state, so ΔG_f° is not zero for this reactant. From the balanced equation and using Appendix C, we have:

$$\begin{aligned} \Delta G_{\text{rxn}}^\circ &= 4 \Delta G_f^\circ[\text{PCl}_3(\text{g})] - \Delta G_f^\circ[\text{P}_4(\text{g})] - 6 \Delta G_f^\circ[\text{Cl}_2(\text{g})] \\ &= (4 \text{ mol})(-269.6 \text{ kJ/mol}) - (1 \text{ mol})(24.4 \text{ kJ/mol}) - 0 \\ &= -1102.8 \text{ kJ} \end{aligned}$$

The fact that ΔG° is negative tells us that a mixture of $\text{P}_4(\text{g})$, $\text{Cl}_2(\text{g})$, and $\text{PCl}_3(\text{g})$ at 25 °C, each present at a partial pressure of 1 atm, would react spontaneously in the forward direction to form more PCl_3 . Remember, however, that the value of ΔG° tells us nothing about the rate at which the reaction occurs.

(b) Remember that $\Delta G = G(\text{products}) - G(\text{reactants})$. If we reverse the reaction, we reverse the roles of the reactants and products. Thus, reversing the reaction changes the sign of ΔG , just as reversing the reaction changes the sign of ΔH (Section 5.4). Hence, using the result from part (a):

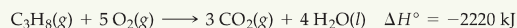
**PRACTICE EXERCISE**

By using data from Appendix C, calculate ΔG° at 298 K for the combustion of methane: $\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{g})$.

Answer: -800.7 kJ

SAMPLE EXERCISE 19.8 | Estimating and Calculating ΔG°

In Section 5.7 we used Hess's law to calculate ΔH° for the combustion of propane gas at 298 K:



(a) Without using data from Appendix C, predict whether ΔG° for this reaction is more negative or less negative than ΔH° . (b) Use data from Appendix C to calculate the standard free-energy change for the reaction at 298 K. Is your prediction from part (a) correct?

SOLUTION

Analyze: In part (a) we must predict the value for ΔG° relative to that for ΔH° on the basis of the balanced equation for the reaction. In part (b) we must calculate the value for ΔG° and compare with our qualitative prediction.

Plan: The free-energy change incorporates both the change in enthalpy and the change in entropy for the reaction (Equation 19.11), so under standard conditions:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

To determine whether ΔG° is more negative or less negative than ΔH° , we need to determine the sign of the term $T\Delta S^\circ$. T is the absolute temperature, 298 K, so it is a positive number. We can predict the sign of ΔS° by looking at the reaction.

Solve:

(a) We see that the reactants consist of six molecules of gas, and the products consist of three molecules of gas and four molecules of liquid. Thus, the number of molecules of gas has decreased significantly during the reaction. By using the general rules we discussed in Section 19.3, we would expect a decrease in the number of gas molecules to lead to a decrease in the entropy of the system—the products have fewer accessible microstates than the reactants. We therefore expect ΔS° and therefore $T\Delta S^\circ$ to be negative numbers. Because we are subtracting $T\Delta S^\circ$, which is a negative number, we would predict that ΔG° is *less negative* than ΔH° .

(b) Using Equation 19.14 and values from Appendix C, we can calculate the value of ΔG°

$$\begin{aligned}\Delta G^\circ &= 3\Delta G_f^\circ[\text{CO}_2(\text{g})] + 4\Delta G_f^\circ[\text{H}_2\text{O}(\text{l})] - \Delta G_f^\circ[\text{C}_3\text{H}_8(\text{g})] - 5\Delta G_f^\circ[\text{O}_2(\text{g})] \\ &= 3 \text{ mol}(-394.4 \text{ kJ/mol}) + 4 \text{ mol}(-237.13 \text{ kJ/mol}) - \\ &\quad 1 \text{ mol}(-23.47 \text{ kJ/mol}) - 5 \text{ mol}(0 \text{ kJ/mol}) = -2108 \text{ kJ}\end{aligned}$$

Notice that we have been careful to use the value of ΔG_f° for $\text{H}_2\text{O}(\text{l})$, as in the calculation of ΔH values, the phases of the reactants and products are important. As we predicted, ΔG° is less negative than ΔH° because of the decrease in entropy during the reaction.

PRACTICE EXERCISE

Consider the combustion of propane to form $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ at 298 K: $\text{C}_3\text{H}_8(\text{g}) + 5 \text{ O}_2(\text{g}) \longrightarrow 3 \text{ CO}_2(\text{g}) + 4 \text{ H}_2\text{O}(\text{g})$. Would you expect ΔG° to be more negative or less negative than ΔH° ?

Answer: more negative

19.6 FREE ENERGY AND TEMPERATURE

We have seen that tabulations of ΔG_f° , such as those in Appendix C, make it possible to calculate ΔG° for reactions at the standard temperature of 25°C. However, we are often interested in examining reactions at other temperatures. How is the change in free energy affected by the change in temperature? Let's look again at Equation 19.11:

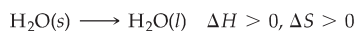
$$\Delta G = \Delta H - T\Delta S = \underbrace{\Delta H}_{\text{Enthalpy term}} + \underbrace{(-T\Delta S)}_{\text{Entropy term}}$$

Notice that we have written the expression for ΔG as a sum of two contributions, an enthalpy term, ΔH , and an entropy term, $-T\Delta S$. Because the value of $-T\Delta S$ depends directly on the absolute temperature T , ΔG will vary with temperature. T is a positive number at all temperatures other than absolute zero. We know that the enthalpy term, ΔH , can be positive or negative. The entropy term, $-T\Delta S$, can also be positive or negative. When ΔS is positive, which means that the final state has greater randomness (a greater number of microstates) than the initial state, the term $-T\Delta S$ is negative. When ΔS is negative, the term $-T\Delta S$ is positive.

The sign of ΔG , which tells us whether a process is spontaneous, will depend on the signs and magnitudes of ΔH and $-T\Delta S$. When both ΔH and $-T\Delta S$ are negative, ΔG will always be negative and the process will be spontaneous at all temperatures. Likewise, when both ΔH and $-T\Delta S$ are positive, ΔG will always be positive and the process will be nonspontaneous at all temperatures (the reverse process will be spontaneous at all temperatures). When ΔH and $-T\Delta S$ have opposite signs, however, the sign of ΔG will depend on the magnitudes of these two terms. In these instances temperature is an important consideration. Generally, ΔH and ΔS change very little with temperature.

However, the value of T directly affects the magnitude of $-T\Delta S$. As the temperature increases, the magnitude of the term $-T\Delta S$ increases and it will become relatively more important in determining the sign and magnitude of ΔG .

For example, let's consider once more the melting of ice to liquid water at 1 atm pressure:



This process is endothermic, which means that ΔH is positive. We also know that the entropy increases during this process, so ΔS is positive and $-T\Delta S$ is negative. At temperatures below 0°C (273 K) the magnitude of ΔH is greater than that of $-T\Delta S$. Hence, the positive enthalpy term dominates, leading to a positive value for ΔG . The positive value of ΔG means that the melting of ice is not spontaneous at $T < 0^\circ\text{C}$; rather, the reverse process, the freezing of liquid water into ice, is spontaneous at these temperatures.

What happens at temperatures greater than 0°C ? As the temperature increases, so does the magnitude of the entropy term $-T\Delta S$. When $T > 0^\circ\text{C}$, the magnitude of $-T\Delta S$ is greater than the magnitude of ΔH . At these temperatures the negative entropy term dominates, which leads to a negative value for ΔG . The negative value of ΔG tells us that the melting of ice is spontaneous at $T > 0^\circ\text{C}$. At the normal melting point of water, $T = 0^\circ\text{C}$, the two phases are in equilibrium. Recall that $\Delta G = 0$ at equilibrium; at $T = 0^\circ\text{C}$, ΔH and $-T\Delta S$, are equal in magnitude and opposite in sign, so they cancel one another and give $\Delta G = 0$.

GIVE IT SOME THOUGHT

The normal boiling point of benzene is 80°C . At 100°C and 1 atm, which term is greater for the vaporization of benzene, ΔH or $T\Delta S$?

The possible situations for the relative signs of ΔH and ΔS are given in Table 19.4, along with examples of each. By applying the concepts we have developed for predicting entropy changes, we often can predict how ΔG will change with temperature.

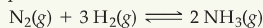
Our discussion of the temperature dependence of ΔG is also relevant to standard free-energy changes. As we saw earlier in Equation 19.12, we can calculate ΔG° from ΔH° and $T\Delta S^\circ$: $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. We can readily calculate the values of ΔH° and ΔS° at 298 K from the data tabulated in Appendix C. If we assume that the values of ΔH° and ΔS° do not change with temperature, we can then use Equation 19.12 to estimate the value of ΔG° at temperatures other than 298 K.

TABLE 19.4 ■ Effect of Temperature on the Spontaneity of Reactions

ΔH	ΔS	$-T\Delta S$	$\Delta G = \Delta H - T\Delta S$	Reaction Characteristics	Example
–	+	–	–	Spontaneous at all temperatures	$2 \text{O}_3(g) \longrightarrow 3 \text{O}_2(g)$
+	–	+	+	Nonspontaneous at all temperatures	$3 \text{O}_2(g) \longrightarrow 2 \text{O}_3(g)$
–	–	+	+ or –	Spontaneous at low T ; nonspontaneous at high T	$\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(s)$
+	+	–	+ or –	Spontaneous at high T ; nonspontaneous at low T	$\text{H}_2\text{O}(s) \longrightarrow \text{H}_2\text{O}(l)$

■ SAMPLE EXERCISE 19.9 | Determining the Effect of Temperature on Spontaneity

The Haber process for the production of ammonia involves the equilibrium



Assume that ΔH° and ΔS° for this reaction do not change with temperature. (a) Predict the direction in which ΔG° for this reaction changes with increasing temperature. (b) Calculate the values of ΔG° for the reaction at 25 °C and 500 °C.

SOLUTION

Analyze: In part (a) we are asked to predict the direction in which ΔG° for the ammonia synthesis reaction changes as temperature increases. In part (b) we need to determine ΔG° for the reaction at two different temperatures.

Plan: In part (a) we can make this prediction by determining the sign of ΔS for the reaction and then using that information to analyze Equation 19.12. In part (b) we need to calculate ΔH° and ΔS° for the reaction by using the data in Appendix C. We can then use Equation 19.12 to calculate ΔG° .

Solve:

(a) Equation 19.12 tells us that ΔG° is the sum of the enthalpy term ΔH° and the entropy term $-T\Delta S^\circ$. The temperature dependence of ΔG° comes from the entropy term. We expect ΔS° for this reaction to be negative because the number of molecules of gas is smaller in the products. Because ΔS° is negative, the term $-T\Delta S^\circ$ is positive and grows larger with increasing temperature. As a result, ΔG° becomes less negative (or more positive) with increasing temperature. Thus, the driving force for the production of NH_3 becomes smaller with increasing temperature.

(b) We calculated the value of ΔH° in Sample Exercise 15.14, and the value of ΔS° was determined in Sample Exercise 19.5: $\Delta H^\circ = -92.38 \text{ kJ}$ and $\Delta S^\circ = -198.3 \text{ J/K}$. If we assume that these values do not change with temperature, we can calculate ΔG° at any temperature by using Equation 19.12. At $T = 298 \text{ K}$ we have:

$$\begin{aligned} \Delta G^\circ &= -92.38 \text{ kJ} - (298 \text{ K})(-198.3 \text{ J/K})\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right) \\ &= -92.38 \text{ kJ} + 59.1 \text{ kJ} = -33.3 \text{ kJ} \end{aligned}$$

At $T = 500 + 273 = 773 \text{ K}$ we have

$$\begin{aligned} \Delta G^\circ &= -92.38 \text{ kJ} - (773 \text{ K})\left(-198.3 \frac{\text{J}}{\text{K}}\right)\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right) \\ &= -92.38 \text{ kJ} + 153 \text{ kJ} = 61 \text{ kJ} \end{aligned}$$

Notice that we have been careful to convert $-T\Delta S^\circ$ into units of kJ so that it can be added to ΔH° , which has units of kJ.

Comment: Increasing the temperature from 298 K to 773 K changes ΔG° from -33.3 kJ to $+61 \text{ kJ}$. Of course, the result at 773 K depends on the assumption that ΔH° and ΔS° do not change with temperature. In fact, these values do change slightly with temperature. Nevertheless, the result at 773 K should be a reasonable approximation. The positive increase in ΔG° with increasing T agrees with our prediction in part (a) of this exercise. Our result indicates that a mixture of $\text{N}_2(\text{g})$, $\text{H}_2(\text{g})$, and $\text{NH}_3(\text{g})$, each present at a partial pressure of 1 atm, will react spontaneously at 298 K to form more $\text{NH}_3(\text{g})$. In contrast, at 773 K the positive value of ΔG° tells us that the reverse reaction is spontaneous. Thus, when the mixture of three gases, each at a partial pressure of 1 atm, is heated to 773 K, some of the $\text{NH}_3(\text{g})$ spontaneously decomposes into $\text{N}_2(\text{g})$ and $\text{H}_2(\text{g})$.

■ PRACTICE EXERCISE

(a) Using standard enthalpies of formation and standard entropies in Appendix C, calculate ΔH° and ΔS° at 298 K for the following reaction: $2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2 \text{SO}_3(\text{g})$. (b) Using the values obtained in part (a), estimate ΔG° at 400 K.

Answers: (a) $\Delta H^\circ = -196.6 \text{ kJ}$, $\Delta S^\circ = -189.6 \text{ J/K}$; (b) $\Delta G^\circ = -120.8 \text{ kJ}$

19.7 FREE ENERGY AND THE EQUILIBRIUM CONSTANT

In Section 19.5 we saw a special relationship between ΔG and equilibrium: For a system at equilibrium, $\Delta G = 0$. We have also seen how we can use tabulated thermodynamic data, such as those in Appendix C, to calculate values of the standard free-energy change, ΔG° . In this final section of this chapter, we will

learn two more ways in which we can use free energy as a powerful tool in our analysis of chemical reactions. First, we will learn how to use the value of ΔG° to calculate the value of ΔG under *nonstandard* conditions. Second, we will see how we can directly relate the value of ΔG° for a reaction to the value of the equilibrium constant for the reaction.

The set of standard conditions for which ΔG° values pertain are given in Table 19.3. Most chemical reactions occur under nonstandard conditions. For any chemical process the general relationship between the standard free-energy change, ΔG° , and the free-energy change under any other conditions, ΔG , is given by the expression

$$\Delta G = \Delta G^\circ + RT \ln Q \quad [19.16]$$

In this equation R is the ideal-gas constant, $8.314 \text{ J/mol}\cdot\text{K}$, T is the absolute temperature; and Q is the reaction quotient that corresponds to the particular reaction mixture of interest. ∞ (Section 15.6) Recall that the expression for Q is identical to the equilibrium-constant expression except that the reactants and products need not necessarily be at equilibrium.

Under standard conditions the concentrations of all the reactants and products are equal to 1. Thus, under standard conditions $Q = 1$ and therefore $\ln Q = 0$. We see that Equation 19.16 therefore reduces to $\Delta G = \Delta G^\circ$ under standard conditions, as it should.

SAMPLE EXERCISE 19.10 | Relating ΔG to a Phase Change at Equilibrium

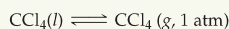
As we saw in Section 11.5, the *normal boiling point* is the temperature at which a pure liquid is in equilibrium with its vapor at a pressure of 1 atm. (a) Write the chemical equation that defines the normal boiling point of liquid carbon tetrachloride, $\text{CCl}_4(l)$. (b) What is the value of ΔG° for the equilibrium in part (a)? (c) Use thermodynamic data in Appendix C and Equation 19.12 to estimate the normal boiling point of CCl_4 .

SOLUTION

Analyze: (a) We must write a chemical equation that describes the physical equilibrium between liquid and gaseous CCl_4 at the normal boiling point. (b) We must determine the value of ΔG° for CCl_4 , in equilibrium with its vapor at the normal boiling point. (c) We must estimate the normal boiling point of CCl_4 , based on available thermodynamic data.

Plan: (a) The chemical equation will merely show the change of state of CCl_4 from liquid to solid. (b) We need to analyze Equation 19.16 at equilibrium ($\Delta G = 0$). (c) We can use Equation 19.12 to calculate T when $\Delta G = 0$.

Solve: (a) The normal boiling point of CCl_4 is the temperature at which pure liquid CCl_4 is in equilibrium with its vapor at a pressure of 1 atm:



(b) At equilibrium $\Delta G = 0$. In any normal boiling-point equilibrium both the liquid and the vapor are in their standard states (Table 19.2). Consequently, $Q = 1$, $\ln Q = 0$, and $\Delta G = \Delta G^\circ$ for this process. Thus, we conclude that $\Delta G^\circ = 0$ for the equilibrium involved in the normal boiling point of any liquid. We would also find that $\Delta G^\circ = 0$ for the equilibria relevant to normal melting points and normal sublimation points of solids.

(c) Combining Equation 19.12 with the result from part (b), we see that the equality at the normal boiling point, T_b , of $\text{CCl}_4(l)$ or any other pure liquid is

$$\Delta G^\circ = \Delta H^\circ - T_b \Delta S^\circ = 0$$

Solving the equation for T_b , we obtain

$$T_b = \Delta H^\circ / \Delta S^\circ$$

Strictly speaking, we would need the values of ΔH° and ΔS° for the equilibrium between $\text{CCl}_4(l)$ and $\text{CCl}_4(g)$ at the normal boiling point to do this calculation. However, we can *estimate* the boiling point by using the values of ΔH° and ΔS° for CCl_4 at 298 K, which we can obtain from the data in Appendix C and Equations 5.31 and 19.8:

$$\Delta H^\circ = (1 \text{ mol})(-106.7 \text{ kJ/mol}) - (1 \text{ mol})(-139.3 \text{ kJ/mol}) = +32.6 \text{ kJ}$$

$$\Delta S^\circ = (1 \text{ mol})(309.4 \text{ J/mol}\cdot\text{K}) - (1 \text{ mol})(214.4 \text{ J/mol}\cdot\text{K}) = +95.0 \text{ J/K}$$

Notice that, as expected, the process is endothermic ($\Delta H > 0$) and produces a gas in which energy can be more spread out ($\Delta S > 0$). We can now use these values to estimate T_b for $\text{CCl}_4(l)$:

$$T_b = \frac{\Delta H^\circ}{\Delta S^\circ} = \left(\frac{32.6 \text{ kJ}}{95.0 \text{ J/K}} \right) \left(\frac{1000 \text{ J}}{1 \text{ kJ}} \right) = 343 \text{ K} = 70^\circ \text{C}$$

Note also that we have used the conversion factor between J and kJ to make sure that the units of ΔH° and ΔS° match.

Check: The experimental normal boiling point of $\text{CCl}_4(l)$ is 76.5°C . The small deviation of our estimate from the experimental value is due to the assumption that ΔH° and ΔS° do not change with temperature.

■ PRACTICE EXERCISE

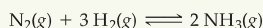
Use data in Appendix C to estimate the normal boiling point, in K, for elemental bromine, $\text{Br}_2(l)$. (The experimental value is given in Table 11.3.)

Answer: 330 K

When the concentrations of reactants and products are nonstandard, we must calculate the value of Q to determine the value of ΔG . We illustrate how this is done in Sample Exercise 19.11. At this stage in our discussion, it becomes important to note the units associated with Q in Equation 19.16. The convention used for standard states imposes itself into the way Q is expressed: In Equation 19.16 the concentrations of gases are always expressed by their partial pressures in atmospheres, and solutes are expressed by their concentrations in molarity.

■ SAMPLE EXERCISE 19.11 | Calculating the Free-Energy Change under Nonstandard Conditions

We will continue to explore the Haber process for the synthesis of ammonia:



Calculate ΔG at 298 K for a reaction mixture that consists of 1.0 atm N_2 , 3.0 atm H_2 , and 0.50 atm NH_3 .

SOLUTION

Analyze: We are asked to calculate ΔG under nonstandard conditions.

Plan: We can use Equation 19.16 to calculate ΔG . Doing so requires that we calculate the value of the reaction quotient Q for the specified partial pressures of the gases and evaluate ΔG° , using a table of standard free energies of formation.

Solve: Solving for the reaction quotient gives:

$$Q = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} P_{\text{H}_2}^3} = \frac{(0.50)^2}{(1.0)(3.0)^3} = 9.3 \times 10^{-3}$$

In Sample Exercise 19.9 we calculated $\Delta G^\circ = -33.3 \text{ kJ}$ for this reaction. We will have to change the units of this quantity in applying Equation 19.16, however. For the units in Equation 19.16 to work out, we will use kJ/mol as our units for ΔG° , where “per mole” means “per mole of the reaction as written.” Thus, $\Delta G^\circ = -33.3 \text{ kJ/mol}$ implies per 1 mol of N_2 , per 3 mol of H_2 , and per 2 mol of NH_3 .

We can now use Equation 19.16 to calculate ΔG for these nonstandard conditions:

$$\begin{aligned} \Delta G &= \Delta G^\circ + RT \ln Q \\ &= (-33.3 \text{ kJ/mol}) + (8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})(1 \text{ kJ}/1000 \text{ J}) \ln(9.3 \times 10^{-3}) \\ &= (-33.3 \text{ kJ/mol}) + (-11.6 \text{ kJ/mol}) = -44.9 \text{ kJ/mol} \end{aligned}$$

Comment: We see that ΔG becomes more negative, changing from -33.3 kJ/mol to -44.9 kJ/mol , as the pressures of N_2 , H_2 , and NH_3 are changed from 1.0 atm each (standard conditions, ΔG°) to 1.0 atm, 3.0 atm, and 0.50 atm, respectively. The larger negative value for ΔG indicates a larger “driving force” to produce NH_3 .

We would have made the same prediction based on Le Châtelier’s principle. ∞ (Section 15.7) Relative to standard conditions, we have increased the pressure of a reactant (H_2) and decreased the pressure of the product (NH_3). Le Châtelier’s principle predicts that both of these changes should shift the reaction more to the product side, thereby forming more NH_3 .

■ PRACTICE EXERCISE

Calculate ΔG at 298 K for the reaction of nitrogen and hydrogen to form ammonia if the reaction mixture consists of 0.50 atm N_2 , 0.75 atm H_2 , and 2.0 atm NH_3 .

Answer: -26.0 kJ/mol

We can now use Equation 19.16 to derive the relationship between ΔG° and the equilibrium constant, K . At equilibrium $\Delta G = 0$. Further, recall that the reaction quotient, Q , equals the equilibrium constant, K , when the system is at equilibrium. Thus, at equilibrium, Equation 19.16 transforms as follows:

$$\begin{aligned}\Delta G &= \Delta G^\circ + RT \ln Q \\ 0 &= \Delta G^\circ + RT \ln K \\ \Delta G^\circ &= -RT \ln K\end{aligned}\quad [19.17]$$

Equation 19.17 also allows us to calculate the value of K if we know the value of ΔG° . If we solve the equation for K , we obtain

$$K = e^{-\Delta G^\circ/RT}\quad [19.18]$$

As we pointed out in discussing Equation 19.16, some care is necessary in the choice of units. Thus, in Equations 19.17 and 19.18 we again express ΔG° in kJ/mol. For the reactants and products in the equilibrium-constant expression, we use the following conventions: Gas pressures are given in atm; solution concentrations are given in moles per liter (molarity); and solids, liquids, and solvents do not appear in the expression. ∞ (Section 15.4) Thus, for gas-phase reactions the equilibrium constant is K_p , whereas for reactions in solution it is K_c . ∞ (Section 15.2)

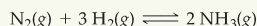
From Equation 19.17 we can see that if ΔG° is negative, then $\ln K$ must be positive. A positive value for $\ln K$ means $K > 1$. Therefore, the more negative ΔG° is, the larger the equilibrium constant, K . Conversely, if ΔG° is positive, then $\ln K$ is negative, which means that $K < 1$. Table 19.5 summarizes these conclusions by comparing ΔG° and K for both positive and negative values of ΔG° .

TABLE 19.5 Relationship between ΔG° and K at 298 K

ΔG° , kJ/mol	K
+200	8.7×10^{-36}
+100	3.0×10^{-18}
+50	1.7×10^{-9}
+10	1.8×10^{-2}
+1.0	6.7×10^{-1}
0	1.0
-1.0	1.5
-10	5.7×10^1
-50	5.8×10^8
-100	3.4×10^{17}
-200	1.1×10^{35}

SAMPLE EXERCISE 19.12 | Calculating an Equilibrium Constant from ΔG°

Use standard free energies of formation to calculate the equilibrium constant, K , at 25 °C for the reaction involved in the Haber process:



The standard free-energy change for this reaction was calculated in Sample Exercise 19.9: $\Delta G^\circ = -33.3 \text{ kJ/mol} = -33,300 \text{ J/mol}$.

SOLUTION

Analyze: We are asked to calculate K for a reaction, given ΔG° .

Plan: We can use Equation 19.18 to evaluate the equilibrium constant, which in this case takes the form

$$K = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} P_{\text{H}_2}^3}$$

In this expression the gas pressures are expressed in atmospheres. (Remember that we use kJ/mol as the units of ΔG° when using Equations 19.16, 19.17, or 19.18.)

Solve: Solving Equation 19.17 for the exponent $-\Delta G^\circ/RT$, we have

$$\frac{-\Delta G^\circ}{RT} = \frac{-(-33,300 \text{ J/mol})}{(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})} = 13.4$$

We insert this value into Equation 19.18 to obtain K :

$$K = e^{-\Delta G^\circ/RT} = e^{13.4} = 7 \times 10^5$$

Comment: This is a large equilibrium constant, which indicates that the product, NH_3 , is greatly favored in the equilibrium mixture at 25 °C. The equilibrium constants for temperatures in the range of 300 °C to 600 °C, given in Table 15.2, are much smaller than the value at 25 °C. Clearly, a low-temperature equilibrium favors the production of ammonia more than a high-temperature one. Nevertheless, the Haber process is carried out at high temperatures because the reaction is extremely slow at room temperature.

Remember: Thermodynamics can tell us the direction and extent of a reaction, but tells us nothing about the rate at which it will occur. If a catalyst were found that would permit the reaction to proceed at a rapid rate at room temperature, high pressures would not be needed to force the equilibrium toward NH_3 .

PRACTICE EXERCISE

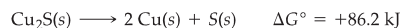
Use data from Appendix C to calculate the standard free-energy change, ΔG° , and the equilibrium constant, K , at 298 K for the reaction $\text{H}_2(\text{g}) + \text{Br}_2(\text{l}) \rightleftharpoons 2 \text{HBr}(\text{g})$.

Answer: $\Delta G^\circ = -106.4 \text{ kJ/mol}$, $K = 4 \times 10^{18}$

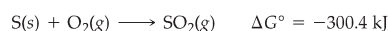
Chemistry and Life

DRIVING NONSPONTANEOUS REACTIONS

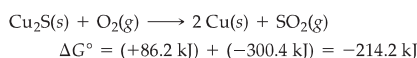
Many desirable chemical reactions, including a large number that are central to living systems, are nonspontaneous as written. For example, consider the extraction of copper metal from the mineral *chalcocite*, which contains Cu_2S . The decomposition of Cu_2S to its elements is nonspontaneous:



Because ΔG° is very positive, we cannot obtain $\text{Cu}(s)$ directly via this reaction. Instead, we must find some way to “do work” on the reaction to force it to occur as we wish. We can do this by coupling the reaction to another one so that the overall reaction is spontaneous. For example, we can envision the $\text{S}(s)$ reacting with $\text{O}_2(g)$ to form $\text{SO}_2(g)$:



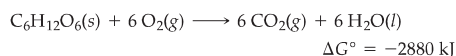
By coupling these reactions, we can extract much of the copper metal via a spontaneous reaction:



In essence, we have used the spontaneous reaction of $\text{S}(s)$ with $\text{O}_2(g)$ to provide the free energy needed to extract the copper metal from the mineral.

Biological systems employ the same principle of using spontaneous reactions to drive nonspontaneous ones. Many of the biochemical reactions that are essential for the formation and maintenance of highly ordered biological structures are not spontaneous. These necessary reactions are made to

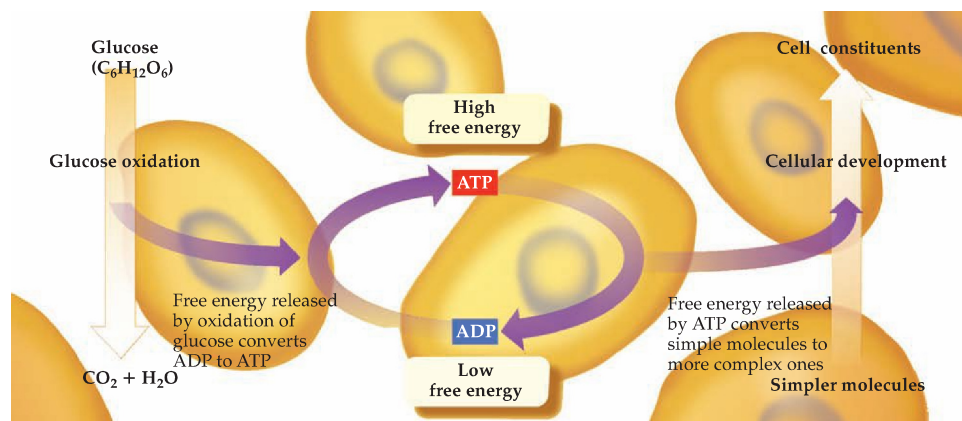
occur by coupling them with spontaneous reactions that release energy. The metabolism of food is the usual source of the free energy needed to do the work of maintaining biological systems. For example, complete oxidation of the sugar *glucose*, $\text{C}_6\text{H}_{12}\text{O}_6$, to CO_2 and H_2O yields substantial free energy:



This energy can be used to drive nonspontaneous reactions in the body. However, a means is necessary to transport the energy released by glucose metabolism to the reactions that require energy. One way, shown in Figure 19.20, involves the interconversion of adenosine triphosphate (ATP) and adenosine diphosphate (ADP), molecules that are related to the building blocks of nucleic acids. The conversion of ATP to ADP releases free energy ($\Delta G^\circ = -30.5 \text{ kJ}$) that can be used to drive other reactions.

In the human body the metabolism of glucose occurs via a complex series of reactions, most of which release free energy. The free energy released during these steps is used in part to reconvert lower-energy ADP back to higher-energy ATP. Thus, the ATP–ADP interconversions are used to store energy during metabolism and to release it as needed to drive nonspontaneous reactions in the body. If you take a course in biochemistry, you will have the opportunity to learn more about the remarkable sequence of reactions used to transport free energy throughout the human body.

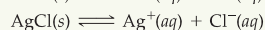
Related Exercises: 19.94 and 19.95



▲ Figure 19.20 Free energy and cell metabolism. This schematic representation shows part of the free-energy changes that occur in cell metabolism. The oxidation of glucose to CO_2 and H_2O produces free energy that is then used to convert ADP into the more energetic ATP. The ATP is then used, as needed, as an energy source to convert simple molecules into more complex cell constituents. When it releases its stored free energy, ATP is converted back into ADP.

SAMPLE INTEGRATIVE EXERCISE | Putting Concepts Together

Consider the simple salts NaCl(s) and AgCl(s). We will examine the equilibria in which these salts dissolve in water to form aqueous solutions of ions:



(a) Calculate the value of ΔG° at 298 K for each of the preceding reactions. (b) The two values from part (a) are very different. Is this difference primarily due to the enthalpy term or the entropy term of the standard free-energy change? (c) Use the values of ΔG° to calculate the K_{sp} values for the two salts at 298 K. (d) Sodium chloride is considered a soluble salt, whereas silver chloride is considered insoluble. Are these descriptions consistent with the answers to part (c)? (e) How will ΔG° for the solution process of these salts change with increasing T ? What effect should this change have on the solubility of the salts?

SOLUTION

(a) We will use Equation 19.14 along with ΔG_f° values from Appendix C to calculate the $\Delta G_{\text{soln}}^\circ$ values for each equilibrium. (As we did in Section 13.1, we use the subscript “soln” to indicate that these are thermodynamic quantities for the formation of a solution.) We find

$$\begin{aligned}\Delta G_{\text{soln}}^\circ(\text{NaCl}) &= (-261.9 \text{ kJ/mol}) + (-131.2 \text{ kJ/mol}) - (-384.0 \text{ kJ/mol}) \\ &= -9.1 \text{ kJ/mol}\end{aligned}$$

$$\begin{aligned}\Delta G_{\text{soln}}^\circ(\text{AgCl}) &= (+77.11 \text{ kJ/mol}) + (-131.2 \text{ kJ/mol}) - (-109.70 \text{ kJ/mol}) \\ &= +55.6 \text{ kJ/mol}\end{aligned}$$

(b) We can write $\Delta G_{\text{soln}}^\circ$ as the sum of an enthalpy term, $\Delta H_{\text{soln}}^\circ$, and an entropy term, $-T\Delta S_{\text{soln}}^\circ$: $\Delta G_{\text{soln}}^\circ = \Delta H_{\text{soln}}^\circ + (-T\Delta S_{\text{soln}}^\circ)$. We can calculate the values of $\Delta H_{\text{soln}}^\circ$ and $\Delta S_{\text{soln}}^\circ$ by using Equations 5.31 and 19.8. We can then calculate $-T\Delta S_{\text{soln}}^\circ$ at $T = 298\text{K}$. All these calculations are now familiar to us. The results are summarized in the following table:

Salt	$\Delta H_{\text{soln}}^\circ$	$\Delta S_{\text{soln}}^\circ$	$-T\Delta S_{\text{soln}}^\circ$
NaCl	+3.6 kJ/mol	+43.2 J/mol-K	-12.9 kJ/mol
AgCl	+65.7 kJ/mol	+34.3 J/mol-K	-10.2 kJ/mol

The entropy terms for the solution of the two salts are very similar. That seems sensible because each solution process should lead to a similar increase in randomness as the salt dissolves, forming hydrated ions. [∞∞ \(Section 13.1\)](#) In contrast, we see a very large difference in the enthalpy term for the solution of the two salts. The difference in the values of $\Delta G_{\text{soln}}^\circ$ is dominated by the difference in the values of $\Delta H_{\text{soln}}^\circ$.

(c) The solubility product, K_{sp} , is the equilibrium constant for the solution process. [∞∞ \(Section 17.4\)](#) As such, we can relate K_{sp} directly to $\Delta G_{\text{soln}}^\circ$ by using Equation 19.18:

$$K_{sp} = e^{-\Delta G_{\text{soln}}^\circ/RT}$$

We can calculate the K_{sp} values in the same way we applied Equation 19.18 in Sample Exercise 19.12. We use the $\Delta G_{\text{soln}}^\circ$ values we obtained in part (a), remembering to convert them from kJ/mol to J/mol:

$$\text{NaCl: } K_{sp} = [\text{Na}^+(aq)][\text{Cl}^-(aq)] = e^{-(-9100)/[(8.314)(298)]} = e^{+3.7} = 40$$

$$\text{AgCl: } K_{sp} = [\text{Ag}^+(aq)][\text{Cl}^-(aq)] = e^{-(+55,600)/[(8.314)(298)]} = e^{-22.4} = 1.9 \times 10^{-10}$$

The value calculated for the K_{sp} of AgCl is very close to that listed in Appendix D.

(d) A soluble salt is one that dissolves appreciably in water. [∞∞ \(Section 4.2\)](#) The K_{sp} value for NaCl is greater than 1, indicating that NaCl dissolves to a great extent. The K_{sp} value for AgCl is very small, indicating that very little dissolves in water. Silver chloride should indeed be considered an insoluble salt.

(e) As we expect, the solution process has a positive value of ΔS for both salts (see the table in part b). As such, the entropy term of the free-energy change, $-T\Delta S_{\text{soln}}^\circ$, is negative. If we assume that $\Delta H_{\text{soln}}^\circ$ and $\Delta S_{\text{soln}}^\circ$ do not change much with temperature, then an increase in T will serve to make $\Delta G_{\text{soln}}^\circ$ more negative. Thus, the driving force for dissolution of the salts will increase with increasing T , and we therefore expect the solubility of the salts to increase with increasing T . In Figure 13.17 we see that the solubility of NaCl (and that of nearly any salt) increases with increasing temperature. [∞∞ \(Section 13.3\)](#)

CHAPTER REVIEW

SUMMARY AND KEY TERMS

Section 19.1 Most reactions and chemical processes have an inherent directionality: They are **spontaneous** in one direction and nonspontaneous in the reverse direction. The spontaneity of a process is related to the thermodynamic path the system takes from the initial state to the final state. In a **reversible process**, both the system and its surroundings can be restored to their original state by exactly reversing the change. In an **irreversible process** the system cannot return to its original state without there being a permanent change in the surroundings. Any spontaneous process is irreversible. A process that occurs at a constant temperature is said to be **isothermal**.

Section 19.2 The spontaneous nature of processes is related to a thermodynamic state function called **entropy**, denoted S . For a process that occurs at constant temperature, the entropy change of the system is given by the heat absorbed by the system along a reversible path, divided by the temperature: $\Delta S = q_{\text{rev}}/T$. The way entropy controls the spontaneity of processes is given by the **second law of thermodynamics**, which governs the change in the entropy of the universe, $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$. The second law states that in a reversible process $\Delta S_{\text{univ}} = 0$; in an irreversible (spontaneous) process $\Delta S_{\text{univ}} > 0$. Entropy values are usually expressed in units of joules per kelvin, J/K.

Section 19.3 Molecules can undergo three kinds of motion: In **translational motion** the entire molecule moves in space. Molecules can also undergo **vibrational motion**, in which the atoms of the molecule move toward and away from one another in periodic fashion, and **rotational motion**, in which the entire molecule spins like a top. A particular combination of motions and locations of the atoms and molecules of a system at a particular instant is called a **microstate**. Entropy is a measure of the number of microstates, W , over which the energy of the system is distributed: $S = k \ln W$. The number of available microstates, and therefore the entropy, increases with an increase in volume, temperature, or motion of molecules because any of these changes increases the possible motions and locations of the molecules. As a result, entropy generally increases when liquids or solutions are formed from solids, gases are formed from either solids or liquids, or the number of molecules of gas increases during a chemical reaction. The **third law of**

thermodynamics states that the entropy of a pure crystalline solid at 0 K is zero.

Section 19.4 The third law allows us to assign entropy values for substances at different temperatures. Under standard conditions the entropy of a mole of a substance is called its **standard molar entropy**, denoted S° . From tabulated values of S° , we can calculate the entropy change for any process under standard conditions. For an isothermal process, the entropy change in the surroundings is equal to $-\Delta H/T$.

Section 19.5 The **Gibbs free energy** (or just **free energy**), G , is a thermodynamic state function that combines the two state functions enthalpy and entropy: $G = H - TS$. For processes that occur at constant temperature, $\Delta G = \Delta H - T\Delta S$. For a process occurring at constant temperature and pressure, the sign of ΔG relates to the spontaneity of the process. When ΔG is negative, the process is spontaneous. When ΔG is positive, the process is nonspontaneous but the reverse process is spontaneous. At equilibrium the process is reversible and ΔG is zero. The free energy is also a measure of the maximum useful work that can be performed by a system in a spontaneous process. The standard free-energy change, ΔG° , for any process can be calculated from tabulations of **standard free energies of formation**, ΔG_f° , which are defined in a fashion analogous to standard enthalpies of formation, ΔH_f° . The value of ΔG_f° for a pure element in its standard state is defined to be zero.

Sections 19.6 and 19.7 The values of ΔH and ΔS generally do not vary much with temperature. Therefore, the dependence of ΔG with temperature is governed mainly by the value of T in the expression $\Delta G = \Delta H - T\Delta S$. The entropy term $-T\Delta S$ has the greater effect on the temperature dependence of ΔG and, hence, on the spontaneity of the process. For example, a process for which $\Delta H > 0$ and $\Delta S > 0$, such as the melting of ice, can be nonspontaneous ($\Delta G > 0$) at low temperatures and spontaneous ($\Delta G < 0$) at higher temperatures. Under nonstandard conditions ΔG is related to ΔG° and the value of the reaction quotient, Q : $\Delta G = \Delta G^\circ + RT \ln Q$. At equilibrium ($\Delta G = 0, Q = K$), $\Delta G^\circ = -RT \ln K$. Thus, the standard free-energy change is directly related to the equilibrium constant for the reaction. This relationship expresses the temperature dependence of equilibrium constants.

KEY SKILLS

- Understand the meaning of *spontaneous process*, *reversible process*, *irreversible process*, and *isothermal process*.
- State the second law of thermodynamics.
- Describe the kinds of molecular motion that a molecule can possess.

- Explain how the entropy of a system is related to the number of accessible microstates.
- Predict the sign of ΔS for physical and chemical processes.
- State the third law of thermodynamics.
- Calculate standard entropy changes for a system from standard molar entropies.
- Calculate entropy changes in the surroundings for isothermal processes.
- Calculate the Gibbs free energy from the enthalpy change and entropy change at a given temperature.
- Use free energy changes to predict whether reactions are spontaneous.
- Calculate standard free energy changes using standard free energies of formation.
- Predict the effect of temperature on spontaneity given ΔH and ΔS .
- Calculate ΔG under nonstandard conditions.
- Relate ΔG° and equilibrium constant.

KEY EQUATIONS

- $\Delta S = \frac{q_{\text{rev}}}{T}$ (constant T) [19.2] Relating entropy change to the heat absorbed or released in a reversible process
- $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$ [19.4] The second law of thermodynamics (spontaneous process)
- $S = k \ln W$ [19.5] Relating entropy to the number of microstates
- $\Delta S^\circ = \sum nS^\circ(\text{products}) - \sum mS^\circ(\text{reactants})$ [19.8] Calculating the standard entropy change from standard molar entropies
- $\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T}$ [19.9] The entropy change of the surroundings for a process at constant temperature and pressure
- $\Delta G = \Delta H - T\Delta S$ [19.11] Calculating the Gibbs free-energy change from enthalpy and entropy changes at constant temperature
- $\Delta G^\circ = \sum n\Delta G_f^\circ(\text{products}) - \sum m\Delta G_f^\circ(\text{reactants})$ [19.14] Calculating the standard free-energy change from standard free energies of formation
- $\Delta G = -w_{\text{max}}$ [19.15] Relating the free-energy change to the maximum work a process can perform.
- $\Delta G = \Delta G^\circ + RT \ln Q$ [19.16] Calculating free-energy change under nonstandard conditions.
- $\Delta G^\circ = -RT \ln K$ [19.17] Relating the standard free-energy change and the equilibrium constant.

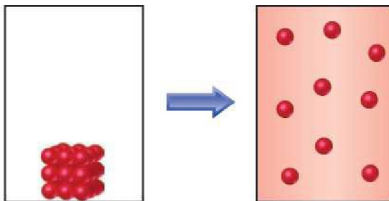
VISUALIZING CONCEPTS

- 19.1** Two different gases occupy two separate bulbs. Consider the process that occurs when the stopcock separating the gases is opened, assuming the gases behave ideally. (a) Draw the final (equilibrium) state. (b) Predict the signs of ΔH and ΔS for the process. (c) Is the process that occurs when the stopcock is opened a reversible one? (d) How does the process affect the entropy of the surroundings? [Sections 19.1 and 19.2]

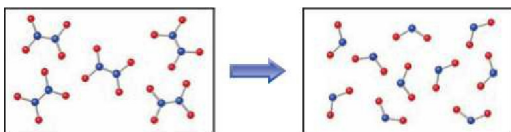


- 19.2** (a) What are the signs of ΔS and ΔH for the process depicted to the right? (b) How might temperature affect

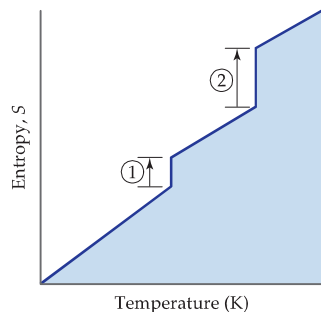
the sign of ΔG ? (c) If energy can flow in and out of the system to maintain a constant temperature during the process, what can you say about the entropy change of the surroundings as a result of this process? [Sections 19.2 and 19.5]



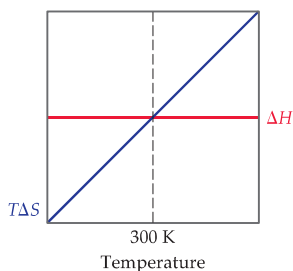
- 19.3 Predict the sign of ΔS accompanying this reaction. Explain your choice. [Section 19.3]



- 19.4 The diagram below shows the variation in entropy with temperature for a substance that is a gas at the highest temperature shown. (a) What processes correspond to the entropy increases along the vertical lines labeled 1 and 2 in this diagram? (b) Why is the entropy change for 2 larger than that for 1? [Section 19.3]

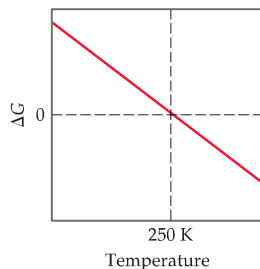


- 19.5 The diagram below shows how ΔH (red line) and $T\Delta S$ (blue line) change with temperature for a hypothetical reaction. (a) What is the significance of the point at 300 K, where ΔH and $T\Delta S$ are equal? (b) In what temperature range is this reaction spontaneous? [Section 19.6]

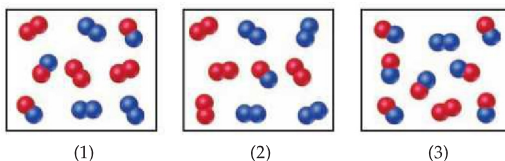


- 19.6 Consider the accompanying diagram, which represents how ΔG for a hypothetical reaction responds to

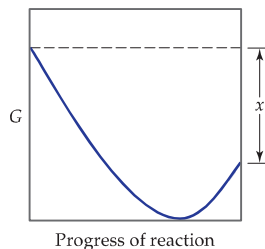
temperature. (a) At what temperature is the system at equilibrium? (b) In what temperature range is the reaction spontaneous? (c) Is ΔH positive or negative? (d) Is ΔS positive or negative? [Sections 19.5 and 19.6]



- 19.7 Consider a reaction $A_2(g) + B_2(g) \rightleftharpoons 2 AB(g)$, with atoms of A shown in red and atoms of B shown in blue. (a) If $K_c = 1$, which system is at equilibrium? (b) What is the sign of ΔG for any process in which the contents of a reaction vessel move to equilibrium? (c) Rank the boxes in order of increasing magnitude of ΔG for the reaction. [Sections 19.5 and 19.7]



- 19.8 The diagram below shows how the free energy, G , changes during a hypothetical reaction $A(g) + B(g) \rightarrow AB(g)$. On the left are pure reactants, each at 1 atm, and on the right is the pure product, also at 1 atm. (a) What is the significance of the minimum in the plot? (b) What does the quantity x , shown on the right side of the diagram, represent? [Section 19.7]



EXERCISES

Spontaneous Processes

- 19.9 Which of the following processes are spontaneous, and which are nonspontaneous: (a) the ripening of a banana, (b) dissolution of sugar in a cup of hot coffee, (c) the reaction of nitrogen atoms to form N_2 molecules at 25 °C

and 1 atm, (d) lightning, (e) formation of CH_4 and O_2 molecules from CO_2 and H_2O at room temperature and 1 atm of pressure?

- 19.10 Which of the following processes are spontaneous: (a) the melting of ice cubes at 10 °C and 1 atm pressure; (b) separating a mixture of N₂ and O₂ into two separate samples, one that is pure N₂ and one that is pure O₂; (c) alignment of iron filings in a magnetic field; (d) the reaction of sodium metal with chlorine gas to form sodium chloride; (e) the dissolution of HCl(g) in water to form concentrated hydrochloric acid?
- 19.11 (a) Give two examples of endothermic processes that are spontaneous. (b) Give an example of a process that is spontaneous at one temperature but nonspontaneous at a different temperature.
- 19.12 The crystalline hydrate Cd(NO₃)₂ · 4H₂O(s) loses water when placed in a large, closed, dry vessel:

$$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}(\text{s}) \longrightarrow \text{Cd}(\text{NO}_3)_2(\text{s}) + 4\text{H}_2\text{O}(\text{g})$$
 This process occurs even though it is endothermic; that is, ΔH is positive. Is this process an exception to Bertholet's generalization? Explain.
- 19.13 Consider the vaporization of liquid water to steam at a pressure of 1 atm. (a) Is this process endothermic or exothermic? (b) In what temperature range is it a spontaneous process? (c) In what temperature range is it a nonspontaneous process? (d) At what temperature are the two phases in equilibrium?
- 19.14 The normal freezing point of 1-propanol (C₃H₈O) is -127 °C. (a) Is the freezing of 1-propanol an endothermic or exothermic process? (b) In what temperature range is the freezing of 1-propanol a spontaneous process? (c) In what temperature range is it a nonspontaneous process? (d) Is there any temperature at which liquid and solid 1-propanol are in equilibrium? Explain.
- 19.15 (a) What is special about a *reversible* process? (b) Suppose a reversible process is reversed, restoring the system to its original state. What can be said about the surroundings after the process is reversed? (c) Under what circumstances will the vaporization of water to steam be a reversible process? (d) Are any of the processes that occur in the world around us reversible in nature? Explain.
- 19.16 (a) What is meant by calling a process *irreversible*? (b) After an irreversible process the system is restored to its original state. What can be said about the condition of the surroundings after the system is restored to its original state? (c) Under what conditions will the condensation of a liquid be an irreversible process?
- 19.17 Consider a process in which an ideal gas changes from state 1 to state 2 in such a way that its temperature changes from 300 K to 200 K. (a) Describe how this change might be carried out while keeping the volume of the gas constant. (b) Describe how it might be carried out while keeping the pressure of the gas constant. (c) Does the change in ΔE depend on the particular pathway taken to carry out this change of state? Explain.
- 19.18 A system goes from state 1 to state 2 and back to state 1. (a) What is the relationship between the value of ΔE for going from state 1 to state 2 to that for going from state 2 back to state 1? (b) Without further information, can you conclude anything about the amount of heat transferred to the system as it goes from state 1 to state 2 as compared to that upon going from state 2 back to state 1? (c) Suppose the changes in state are reversible processes. Can you conclude anything about the work done by the system upon going from state 1 to state 2 as compared to that upon going from state 2 back to state 1?
- 19.19 Consider a system consisting of an ice cube. (a) Under what conditions can the ice cube melt reversibly? (b) If the ice cube melts reversibly, is ΔE zero for the process? Explain.
- 19.20 Consider what happens when a sample of the explosive TNT (Section 8.8: "Chemistry Put to Work: Explosives and Alfred Nobel") is detonated. (a) Is the detonation a spontaneous process? (b) What is the sign of q for this process? (c) Can you determine whether w is positive, negative, or zero for the process? Explain. (d) Can you determine the sign of ΔE for the process? Explain.

Entropy and the Second Law of Thermodynamics

- 19.21 (a) How can we calculate ΔS for an isothermal process? (b) Does ΔS for a process depend on the path taken from the initial to the final state of the system? Explain.
- 19.22 Suppose we vaporize a mole of liquid water at 25 °C and another mole of water at 100 °C. (a) Assuming that the enthalpy of vaporization of water does not change much between 25 °C and 100 °C, which process involves the larger change in entropy? (b) Does the entropy change in either process depend on whether we carry out the process reversibly or not? Explain.
- 19.23 The normal boiling point of methanol (CH₃OH) is 64.7 °C, and its molar enthalpy of vaporization is $\Delta H_{\text{vap}} = 71.8$ kJ/mol. (a) When CH₃OH(l) boils at its normal boiling point, does its entropy increase or decrease? (b) Calculate the value of ΔS when 1.00 mol of CH₃OH(l) is vaporized at 64.7 °C.
- 19.24 The element cesium (Cs) freezes at 28.4 °C, and its molar enthalpy of fusion is $\Delta H_{\text{fus}} = 2.09$ kJ/mol. (a) When molten cesium solidifies to Cs(s) at its normal melting point, is ΔS positive or negative? (b) Calculate the value of ΔS when 15.0 g of Cs(l) solidifies at 28.4 °C.
- 19.25 (a) Express the second law of thermodynamics in words. (b) If the entropy of the system increases during a reversible process, what can you say about the entropy change of the surroundings? (c) In a certain spontaneous process the system undergoes an entropy change, $\Delta S = 42$ J/K. What can you conclude about ΔS_{surr} ?

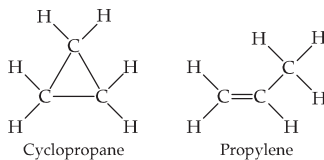
- 19.26 (a) Express the second law of thermodynamics as a mathematical equation. (b) In a particular spontaneous process the entropy of the system decreases. What can you conclude about the sign and magnitude of ΔS_{surr} ? (c) During a certain reversible process, the surroundings undergo an entropy change, $\Delta S_{\text{surr}} = -78 \text{ J/K}$. What is the entropy change of the system for this process?
- 19.27 The volume of 0.100 mol of helium gas at 27 °C is increased isothermally from 2.00 L to 5.00 L. Assuming the gas to be ideal, calculate the entropy change for the process.
- 19.28 The pressure on 0.850 mol of neon gas is increased from 1.25 atm to 2.75 atm at 100 °C. Assuming the gas to be ideal, calculate ΔS for this process.

The Molecular Interpretation of Entropy

- 19.29 How would each of the following changes affect the number of microstates available to a system: (a) increase in temperature, (b) decrease in volume, (c) change of state from liquid to gas?
- 19.30 (a) Using the heat of vaporization in Appendix B, calculate the entropy change for the vaporization of water at 25 °C and at 100 °C. (b) From your knowledge of microstates and the structure of liquid water, explain the difference in these two values.
- 19.31 (a) What do you expect for the sign of ΔS in a chemical reaction in which two moles of gaseous reactants are converted to three moles of gaseous products? (b) For which of the processes in Exercise 19.9 does the entropy of the system increase?
- 19.32 (a) In a chemical reaction two gases combine to form a solid. What do you expect for the sign of ΔS ? (b) How does the entropy of the system change in the processes described in Exercise 19.10?
- 19.33 How does the entropy of the system change when (a) a solid melts, (b) a gas liquefies, (c) a solid sublimates?
- 19.34 How does the entropy of the system change when (a) the temperature of the system increases, (b) the volume of a gas increases, (c) equal volumes of ethanol and water are mixed to form a solution.
- 19.35 (a) State the third law of thermodynamics. (b) Distinguish between translational motion, vibrational motion, and rotational motion of a molecule. (c) Illustrate these three kinds of motion with sketches for the HCl molecule.
- 19.36 (a) The energy of a gas is increased by heating it. Using CO_2 as an example, illustrate the different ways in which additional energy can be distributed among the molecules of the gas. (b) You are told that the number of microstates for a system increases. What does this tell you about the entropy of the system?
- 19.37 (a) Using Figure 19.14 as a model, sketch how the entropy of water changes as it is heated from $-50 \text{ }^\circ\text{C}$ to $110 \text{ }^\circ\text{C}$ at sea level. Show the temperatures at which there are vertical increases in entropy. (b) Which process has the larger entropy change: melting ice or boiling water? Explain.
- 19.38 Propanol ($\text{C}_3\text{H}_7\text{OH}$) melts at $-126.5 \text{ }^\circ\text{C}$ and boils at $97.4 \text{ }^\circ\text{C}$. Draw a qualitative sketch of how the entropy changes as propanol vapor at $150 \text{ }^\circ\text{C}$ and 1 atm is cooled to solid propanol at $-150 \text{ }^\circ\text{C}$ and 1 atm.
- 19.39 For each of the following pairs, choose the substance with the higher entropy per mole at a given temperature: (a) $\text{Ar}(l)$ or $\text{Ar}(g)$, (b) $\text{He}(g)$ at 3 atm pressure or $\text{He}(g)$ at 1.5 atm pressure, (c) 1 mol of $\text{Ne}(g)$ in 15.0 L or 1 mol of $\text{Ne}(g)$ in 1.50 L, (d) $\text{CO}_2(g)$ or $\text{CO}_2(s)$.
- 19.40 For each of the following pairs, indicate which substance possesses the larger standard entropy: (a) 1 mol of $\text{P}_4(g)$ at 300 °C, 0.01 atm, or 1 mol of $\text{As}_4(g)$ at 300 °C, 0.01 atm; (b) 1 mol of $\text{H}_2\text{O}(g)$ at 100 °C, 1 atm, or 1 mol of $\text{H}_2\text{O}(l)$ at 100 °C, 1 atm; (c) 0.5 mol of $\text{N}_2(g)$ at 298 K, 20-L volume, or 0.5 mol $\text{CH}_4(g)$ at 298 K, 20-L volume; (d) 100 g $\text{Na}_2\text{SO}_4(s)$ at 30 °C or 100 g $\text{Na}_2\text{SO}_4(aq)$ at 30 °C.
- 19.41 Predict the sign of the entropy change of the system for each of the following reactions:
 (a) $2 \text{SO}_2(g) + \text{O}_2(g) \longrightarrow 2 \text{SO}_3(g)$
 (b) $\text{Ba}(\text{OH})_2(s) \longrightarrow \text{BaO}(s) + \text{H}_2\text{O}(g)$
 (c) $\text{CO}(g) + 2 \text{H}_2(g) \longrightarrow \text{CH}_3\text{OH}(l)$
 (d) $\text{FeCl}_2(s) + \text{H}_2(g) \longrightarrow \text{Fe}(s) + 2 \text{HCl}(g)$
- 19.42 Predict the sign of ΔS_{sys} for each of the following processes: (a) Gaseous Ar is liquefied at 80 K. (b) Gaseous N_2O_4 dissociates to form gaseous NO_2 . (c) Solid potassium reacts with gaseous O_2 to form solid potassium superoxide, KO_2 . (d) Lead bromide precipitates upon mixing $\text{Pb}(\text{NO}_3)_2(aq)$ and $\text{KBr}(aq)$.

Entropy Changes in Chemical Reactions

- 19.43 In each of the following pairs, which compound would you expect to have the higher standard molar entropy: (a) $\text{C}_2\text{H}_2(g)$ or $\text{C}_2\text{H}_6(g)$; (b) $\text{CO}_2(g)$ or $\text{CO}(g)$? Explain.
- 19.44 Cyclopropane and propylene isomers both have the formula C_3H_6 . Based on the molecular structures shown, which of these isomers would you expect to have the higher standard molar entropy at 25 °C?

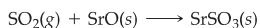


- 19.45** Use Appendix C to compare the standard entropies at 25 °C for the following pairs of substances: **(a)** Sc(s) and Sc(g); **(b)** NH₃(g) and NH₃(aq); **(c)** 1 mol P₄(g) and 2 mol P₂(g); **(d)** C(graphite) and C(diamond). In each case explain the difference in the entropy values.
- 19.46** Using Appendix C, compare the standard entropies at 25 °C for the following pairs of substances: **(a)** CuO(s) and Cu₂O(s); **(b)** 1 mol N₂O₄(g) and 2 mol NO₂(g); **(c)** SiO₂(s) and CO₂(g); **(d)** CO(g) and CO₂(g). For each pair, explain the difference in the entropy values.
- [19.47]** The standard entropies at 298 K for certain of the group 4A elements are as follows: C(s, diamond) = 2.43 J/mol-K; Si(s) = 18.81 J/mol-K; Ge(s) = 31.09 J/mol-K; and Sn(s) = 51.18 J/mol-K. All but Sn have the diamond structure. How do you account for the trend in the S° values?
- [19.48]** Three of the forms of elemental carbon are graphite, diamond, and buckminsterfullerene. The entropies at 298 K for graphite and diamond are listed in Appendix C.
- (a)** Account for the difference in the S° values of graphite and diamond in light of their structures (Figure 11.41). **(b)** What would you expect for the S° value of buckminsterfullerene (Figure 11.43) relative to the values for graphite and diamond? Explain.
- 19.49** Using S° values from Appendix C, calculate ΔS° values for the following reactions. In each case account for the sign of ΔS°.
- (a)** C₂H₄(g) + H₂(g) → C₂H₆(g)
(b) N₂O₄(g) → 2 NO₂(g)
(c) Be(OH)₂(s) → BeO(s) + H₂O(g)
(d) 2 CH₃OH(g) + 3 O₂(g) → 2 CO₂(g) + 4 H₂O(g)
- 19.50** Calculate ΔS° values for the following reactions by using tabulated S° values from Appendix C. In each case explain the sign of ΔS°.
- (a)** N₂H₄(g) + H₂(g) → 2 NH₃(g)
(b) K(s) + O₂(g) → KO₂(s)
(c) Mg(OH)₂(s) + 2 HCl(g) → MgCl₂(s) + 2 H₂O(l)
(d) CO(g) + 2 H₂(g) → CH₃OH(g)

Gibbs Free Energy

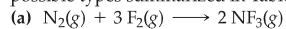
- 19.51** **(a)** For a process that occurs at constant temperature, express the change in Gibbs free energy in terms of changes in the enthalpy and entropy of the system. **(b)** For a certain process that occurs at constant *T* and *P*, the value of Δ*G* is positive. What can you conclude? **(c)** What is the relationship between Δ*G* for a process and the rate at which it occurs?
- 19.52** **(a)** What is the meaning of the standard free-energy change, Δ*G*°, as compared with Δ*G*? **(b)** For any process that occurs at constant temperature and pressure, what is the significance of Δ*G* = 0? **(c)** For a certain process, Δ*G* is large and negative. Does this mean that the process necessarily occurs rapidly?
- 19.53** For a certain chemical reaction, Δ*H*° = -35.4 kJ and Δ*S*° = -85.5 J/K. **(a)** Is the reaction exothermic or endothermic? **(b)** Does the reaction lead to an increase or decrease in the randomness or disorder of the system? **(c)** Calculate Δ*G*° for the reaction at 298 K. **(d)** Is the reaction spontaneous at 298 K under standard conditions?
- 19.54** A certain reaction has Δ*H*° = -19.5 kJ and Δ*S*° = +42.7 J/K. **(a)** Is the reaction exothermic or endothermic? **(b)** Does the reaction lead to an increase or decrease in the randomness or disorder of the system? **(c)** Calculate Δ*G*° for the reaction at 298 K. **(d)** Is the reaction spontaneous at 298 K under standard conditions?
- 19.55** Using data in Appendix C, calculate Δ*H*°, Δ*S*°, and Δ*G*° at 298 K for each of the following reactions. In each case show that Δ*G*° = Δ*H*° - *T*Δ*S*°.
- (a)** H₂(g) + F₂(g) → 2 HF(g)
(b) C(s, graphite) + 2 Cl₂(g) → CCl₄(g)
(c) 2 PCl₃(g) + O₂(g) → 2 POCl₃(g)
(d) 2 CH₃OH(g) + H₂(g) → C₂H₆(g) + 2 H₂O(g)
- 19.56** Use data in Appendix C to calculate Δ*H*°, Δ*S*°, and Δ*G*° at 25 °C for each of the following reactions. In each case show that Δ*G*° = Δ*H*° - *T*Δ*S*°.
- (a)** 2 Cr(s) + 3 Br₂(g) → 2 CrBr₃(s)
(b) BaCO₃(s) → BaO(s) + CO₂(g)
(c) 2 P(s) + 10 HF(g) → 2 PF₅(g) + 5 H₂(g)
(d) K(s) + O₂(g) → KO₂(s)
- 19.57** Using data from Appendix C, calculate Δ*G*° for the following reactions. Indicate whether each reaction is spontaneous under standard conditions.
- (a)** 2 SO₂(g) + O₂(g) → 2 SO₃(g)
(b) NO₂(g) + N₂O(g) → 3 NO(g)
(c) 6 Cl₂(g) + 2 Fe₂O₃(s) → 4 FeCl₃(s) + 3 O₂(g)
(d) SO₂(g) + 2 H₂(g) → S(s) + 2 H₂O(g)
- 19.58** Using data from Appendix C, calculate the change in Gibbs free energy for each of the following reactions. In each case indicate whether the reaction is spontaneous under standard conditions.
- (a)** H₂(g) + Cl₂(g) → 2 HCl(g)
(b) MgCl₂(s) + H₂O(l) → MgO(s) + 2 HCl(g)
(c) 2 NH₃(g) → N₂H₄(g) + H₂(g)
(d) 2 NOCl(g) → 2 NO(g) + Cl₂(g)
- 19.59** Cyclohexane (C₆H₁₂) is a liquid hydrocarbon at room temperature. **(a)** Write a balanced equation for the combustion of C₆H₁₂(l) to form CO₂(g) and H₂O(l). **(b)** Without using thermochemical data, predict whether Δ*G*° for this reaction is more negative or less negative than Δ*H*°.

19.60 Sulfur dioxide reacts with strontium oxide as follows:

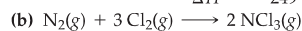


(a) Without using thermochemical data, predict whether ΔG° for this reaction is more negative or less negative than ΔH° . (b) If you had only standard enthalpy data for this reaction, how would you go about making a rough estimate of the value of ΔG° at 298 K, using data from Appendix C on other substances?

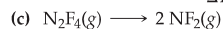
19.61 Classify each of the following reactions as one of the four possible types summarized in Table 19.4:



$$\Delta H^\circ = -249 \text{ kJ}; \Delta S^\circ = -278 \text{ J/K}$$

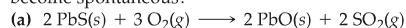


$$\Delta H^\circ = 460 \text{ kJ}; \Delta S^\circ = -275 \text{ J/K}$$

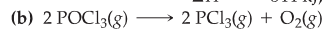


$$\Delta H^\circ = 85 \text{ kJ}; \Delta S^\circ = 198 \text{ J/K}$$

19.62 From the values given for ΔH° and ΔS° , calculate ΔG° for each of the following reactions at 298 K. If the reaction is not spontaneous under standard conditions at 298 K, at what temperature (if any) would the reaction become spontaneous?



$$\Delta H^\circ = -844 \text{ kJ}; \Delta S^\circ = -165 \text{ J/K}$$



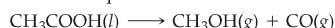
$$\Delta H^\circ = 572 \text{ kJ}; \Delta S^\circ = 179 \text{ J/K}$$

19.63 A particular reaction is spontaneous at 450 K. The enthalpy change for the reaction is +34.5 kJ. What can you conclude about the sign and magnitude of ΔS for the reaction?

19.64 A certain reaction is nonspontaneous at -25°C . The entropy change for the reaction is 95 J/K. What can you conclude about the sign and magnitude of ΔH ?

19.65 For a particular reaction, $\Delta H = -32 \text{ kJ}$ and $\Delta S = -98 \text{ J/K}$. Assume that ΔH and ΔS do not vary with temperature. (a) At what temperature will the reaction have $\Delta G = 0$? (b) If T is increased from that in part (a), will the reaction be spontaneous or nonspontaneous?

19.66 Reactions in which a substance decomposes by losing CO are called *decarbonylation* reactions. The decarbonylation of acetic acid proceeds as follows:



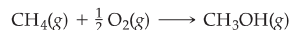
By using data from Appendix C, calculate the minimum temperature at which this process will be spontaneous under standard conditions. Assume that ΔH° and ΔS° do not vary with temperature.

19.67 Consider the following reaction between oxides of nitrogen:



(a) Use data in Appendix C to predict how ΔG° for the reaction varies with increasing temperature. (b) Calculate ΔG° at 800 K, assuming that ΔH° and ΔS° do not change with temperature. Under standard conditions is the reaction spontaneous at 800 K? (c) Calculate ΔG° at 1000 K. Is the reaction spontaneous under standard conditions at this temperature?

19.68 Methanol (CH_3OH) can be made by the controlled oxidation of methane:



(a) Use data in Appendix C to calculate ΔH° and ΔS° for this reaction. (b) How is ΔG° for the reaction expected to vary with increasing temperature? (c) Calculate ΔG° at 298 K. Under standard conditions, is the reaction spontaneous at this temperature? (d) Is there a temperature at which the reaction would be at equilibrium under standard conditions and that is low enough so that the compounds involved are likely to be stable?

[19.69] (a) Use data in Appendix C to estimate the boiling point of benzene, $\text{C}_6\text{H}_6(\text{l})$. (b) Use a reference source, such as the *CRC Handbook of Chemistry and Physics*, to find the experimental boiling point of benzene. How do you explain any deviation between your answer in part (a) and the experimental value?

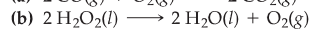
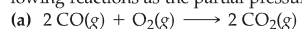
[19.70] (a) Using data in Appendix C, estimate the temperature at which the free-energy change for the transformation from $\text{I}_2(\text{s})$ to $\text{I}_2(\text{g})$ is zero. What assumptions must you make in arriving at this estimate? (b) Use a reference source, such as WebElements (www.webelements.com), to find the experimental melting and boiling points of I_2 . (c) Which of the values in part (b) is closer to the value you obtained in part (a)? Can you explain why this is so?

19.71 Acetylene gas, $\text{C}_2\text{H}_2(\text{g})$, is used in welding. (a) Write a balanced equation for the combustion of acetylene gas to $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$. (b) How much heat is produced in burning 1 mol of C_2H_2 under standard conditions if both reactants and products are brought to 298 K? (c) What is the maximum amount of useful work that can be accomplished under standard conditions by this reaction?

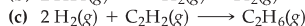
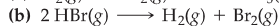
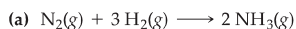
19.72 (a) How much heat is produced in burning 1 mol of ethane (C_2H_6) under standard conditions if reactants and products are brought to 298 K and $\text{H}_2\text{O}(\text{l})$ is formed? (b) What is the maximum amount of useful work that can be accomplished under standard conditions by this system?

Free Energy and Equilibrium

19.73 Explain qualitatively how ΔG changes for each of the following reactions as the partial pressure of O_2 is increased:



19.74 Indicate whether ΔG increases, decreases, or does not change when the partial pressure of H_2 is increased in each of the following reactions:



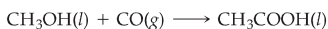
19.75 Consider the reaction $2 \text{NO}_2(\text{g}) \longrightarrow \text{N}_2\text{O}_4(\text{g})$. (a) Using data from Appendix C, calculate ΔG° at 298 K. (b) Calculate ΔG at 298 K if the partial pressures of NO_2 and N_2O_4 are 0.40 atm and 1.60 atm, respectively.

- 19.76 Consider the reaction $6\text{H}_2(\text{g}) + \text{P}_4(\text{g}) \longrightarrow 4\text{PH}_3(\text{g})$.
 (a) Using data from Appendix C, calculate ΔG° at 298 K.
 (b) Calculate ΔG at 298 K if the reaction mixture consists of 8.0 atm of H_2 , 0.050 atm of P_4 , and 0.22 atm of PH_3 .
- 19.77 Use data from Appendix C to calculate the equilibrium constant, K , at 298 K for each of the following reactions:
 (a) $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$
 (b) $\text{C}_2\text{H}_5\text{OH}(\text{g}) \rightleftharpoons \text{C}_2\text{H}_4(\text{g}) + \text{H}_2\text{O}(\text{g})$
 (c) $3\text{C}_2\text{H}_2(\text{g}) \rightleftharpoons \text{C}_6\text{H}_6(\text{g})$
- 19.78 Write the equilibrium-constant expression and calculate the value of the equilibrium constant for each of the following reactions at 298 K, using data from Appendix C:
 (a) $\text{NaHCO}_3(\text{s}) \rightleftharpoons \text{NaOH}(\text{s}) + \text{CO}_2(\text{g})$
 (b) $2\text{HBr}(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{HCl}(\text{g}) + \text{Br}_2(\text{g})$
 (c) $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$
- 19.79 Consider the decomposition of barium carbonate:
 $\text{BaCO}_3(\text{s}) \rightleftharpoons \text{BaO}(\text{s}) + \text{CO}_2(\text{g})$
 Using data from Appendix C, calculate the equilibrium pressure of CO_2 at (a) 298 K and (b) 1100 K.

ADDITIONAL EXERCISES

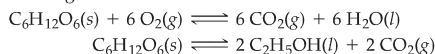
- 19.83 Indicate whether each of the following statements is true or false. If it is false, correct it. (a) The feasibility of manufacturing NH_3 from N_2 and H_2 depends entirely on the value of ΔH for the process $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$. (b) The reaction of $\text{Na}(\text{s})$ with $\text{Cl}_2(\text{g})$ to form $\text{NaCl}(\text{s})$ is a spontaneous process. (c) A spontaneous process can in principle be conducted reversibly. (d) Spontaneous processes in general require that work be done to force them to proceed. (e) Spontaneous processes are those that are exothermic and that lead to a higher degree of order in the system.
- 19.84 For each of the following processes, indicate whether the signs of ΔS and ΔH are expected to be positive, negative, or about zero. (a) A solid sublimates. (b) The temperature of a sample of $\text{Co}(\text{s})$ is lowered from 60 °C to 25 °C. (c) Ethyl alcohol evaporates from a beaker. (d) A diatomic molecule dissociates into atoms. (e) A piece of charcoal is combusted to form $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$.
- 19.85 The reaction $2\text{Mg}(\text{s}) + \text{O}_2(\text{g}) \longrightarrow 2\text{MgO}(\text{s})$ is highly spontaneous and has a negative value for ΔS° . The second law of thermodynamics states that in any spontaneous process there is always an increase in the entropy of the universe. Is there an inconsistency between the above reaction and the second law?
- 19.86 Ammonium nitrate dissolves spontaneously and endothermally in water at room temperature. What can you deduce about the sign of ΔS for this solution process?
- [19.87] *Trouton's rule* states that for many liquids at their normal boiling points, the standard molar entropy of vaporization is about 88 J/mol-K. (a) Estimate the normal boiling point of bromine, Br_2 , by determining $\Delta H_{\text{vap}}^\circ$ for Br_2 using data from Appendix C. Assume that $\Delta H_{\text{vap}}^\circ$ remains constant with temperature and that Trouton's rule holds. (b) Look up the normal boiling point of Br_2 in a chemistry handbook or at the WebElements web site (www.webelements.com).
- 19.80 Consider the following reaction:
 $\text{PbCO}_3(\text{s}) \rightleftharpoons \text{PbO}(\text{s}) + \text{CO}_2(\text{g})$
 Using data in Appendix C, calculate the equilibrium pressure of CO_2 in the system at (a) 400 °C and (b) 180 °C.
- 19.81 The value of K_a for nitrous acid (HNO_2) at 25 °C is given in Appendix D. (a) Write the chemical equation for the equilibrium that corresponds to K_a . (b) By using the value of K_a , calculate ΔG° for the dissociation of nitrous acid in aqueous solution. (c) What is the value of ΔG at equilibrium? (d) What is the value of ΔG when $[\text{H}^+] = 5.0 \times 10^{-2} \text{ M}$, $[\text{NO}_2^-] = 6.0 \times 10^{-4} \text{ M}$, and $[\text{HNO}_2] = 0.20 \text{ M}$?
- 19.82 The K_b for methylamine (CH_3NH_2) at 25 °C is given in Appendix D. (a) Write the chemical equation for the equilibrium that corresponds to K_b . (b) By using the value of K_b , calculate ΔG° for the equilibrium in part (a). (c) What is the value of ΔG at equilibrium? (d) What is the value of ΔG when $[\text{CH}_3\text{NH}_3^+] = [\text{H}^+] = 1.5 \times 10^{-8} \text{ M}$, $[\text{CH}_3\text{NH}_2] = 5.5 \times 10^{-4} \text{ M}$, and $[\text{CH}_3\text{NH}_2] = 0.120 \text{ M}$?
- [19.88] For the majority of the compounds listed in Appendix C, the value of ΔG_f° is more positive (or less negative) than the value of ΔH_f° . (a) Explain this observation, using $\text{NH}_3(\text{g})$, $\text{CCl}_4(\text{l})$, and $\text{KNO}_3(\text{s})$ as examples. (b) An exception to this observation is $\text{CO}(\text{g})$. Explain the trend in the ΔH_f° and ΔG_f° values for this molecule.
- 19.89 Consider the following three reactions:
 (i) $\text{Ti}(\text{s}) + 2\text{Cl}_2(\text{g}) \longrightarrow \text{TiCl}_4(\text{g})$
 (ii) $\text{C}_2\text{H}_6(\text{g}) + 7\text{Cl}_2(\text{g}) \longrightarrow 2\text{CCl}_4(\text{g}) + 6\text{HCl}(\text{g})$
 (iii) $\text{BaO}(\text{s}) + \text{CO}_2(\text{g}) \longrightarrow \text{BaCO}_3(\text{s})$
 (a) For each of the reactions, use data in Appendix C to calculate ΔH° , ΔG° , and ΔS° at 25 °C. (b) Which of these reactions are spontaneous under standard conditions at 25 °C? (c) For each of the reactions, predict the manner in which the change in free energy varies with an increase in temperature.
- 19.90 Using the data in Appendix C and given the pressures listed, calculate ΔG for each of the following reactions:
 (a) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$
 $P_{\text{N}_2} = 2.6 \text{ atm}$, $P_{\text{H}_2} = 5.9 \text{ atm}$, $P_{\text{NH}_3} = 1.2 \text{ atm}$
 (b) $2\text{N}_2\text{H}_4(\text{g}) + 2\text{NO}_2(\text{g}) \longrightarrow 3\text{N}_2(\text{g}) + 4\text{H}_2\text{O}(\text{g})$
 $P_{\text{N}_2\text{H}_4} = P_{\text{NO}_2} = 5.0 \times 10^{-2} \text{ atm}$, $P_{\text{N}_2} = 0.5 \text{ atm}$,
 $P_{\text{H}_2\text{O}} = 0.3 \text{ atm}$
 (c) $\text{N}_2\text{H}_4(\text{g}) \longrightarrow \text{N}_2(\text{g}) + 2\text{H}_2(\text{g})$
 $P_{\text{N}_2\text{H}_4} = 0.5 \text{ atm}$, $P_{\text{N}_2} = 1.5 \text{ atm}$, $P_{\text{H}_2} = 2.5 \text{ atm}$
- 19.91 (a) For each of the following reactions, predict the sign of ΔH° and ΔS° and discuss briefly how these factors determine the magnitude of K . (b) Based on your general chemical knowledge, predict which of these reactions will have $K > 0$. (c) In each case indicate whether K should increase or decrease with increasing temperature.
 (i) $2\text{Mg}(\text{s}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{MgO}(\text{s})$
 (ii) $2\text{KI}(\text{s}) \rightleftharpoons 2\text{K}(\text{g}) + \text{I}_2(\text{g})$
 (iii) $\text{Na}_2(\text{g}) \rightleftharpoons 2\text{Na}(\text{g})$
 (iv) $2\text{V}_2\text{O}_5(\text{s}) \rightleftharpoons 4\text{V}(\text{s}) + 5\text{O}_2(\text{g})$

19.92 Acetic acid can be manufactured by combining methanol with carbon monoxide, an example of a *carbonylation* reaction:



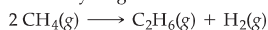
(a) Calculate the equilibrium constant for the reaction at 25 °C. (b) Industrially, this reaction is run at temperatures above 25 °C. Will an increase in temperature produce an increase or decrease in the mole fraction of acetic acid at equilibrium? Why are elevated temperatures used? (c) At what temperature will this reaction have an equilibrium constant equal to 1? (You may assume that ΔH° and ΔS° are temperature independent, and you may ignore any phase changes that might occur.)

19.93 The oxidation of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) in body tissue produces CO_2 and H_2O . In contrast, anaerobic decomposition, which occurs during fermentation, produces ethanol ($\text{C}_2\text{H}_5\text{OH}$) and CO_2 . (a) Using data given in Appendix C, compare the equilibrium constants for the following reactions:

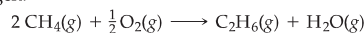


(b) Compare the maximum work that can be obtained from these processes under standard conditions.

[19.94] The conversion of natural gas, which is mostly methane, into products that contain two or more carbon atoms, such as ethane (C_2H_6), is a very important industrial chemical process. In principle, methane can be converted into ethane and hydrogen:

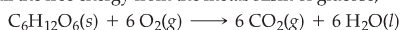


In practice, this reaction is carried out in the presence of oxygen:



(a) Using the data in Appendix C, calculate K for these reactions at 25 °C and 500 °C. (b) Is the difference in ΔG° for the two reactions due primarily to the enthalpy term (ΔH) or the entropy term ($-\Delta S$)? (c) Explain how the preceding reactions are an example of driving a non-spontaneous reaction, as discussed in the “Chemistry and Life” box in Section 19.7. (d) The reaction of CH_4 and O_2 to form C_2H_6 and H_2O must be carried out carefully to avoid a competing reaction. What is the most likely competing reaction?

[19.95] Cells use the hydrolysis of adenosine triphosphate (ATP) as a source of energy (Figure 19.20). The conversion of ATP to ADP has a standard free-energy change of -30.5 kJ/mol . If all the free energy from the metabolism of glucose,



goes into the conversion of ADP to ATP, how many moles of ATP can be produced for each mole of glucose?

[19.96] The potassium-ion concentration in blood plasma is about $5.0 \times 10^{-3} \text{ M}$, whereas the concentration in muscle-cell fluid is much greater (0.15 M). The plasma and intracellular fluid are separated by the cell membrane, which we assume is permeable only to K^+ . (a) What is ΔG for the transfer of 1 mol of K^+ from blood plasma to the cellular fluid at body temperature 37 °C? (b) What is the minimum amount of work that must be used to transfer this K^+ ?

[19.97] The relationship between the temperature of a reaction, its standard enthalpy change, and the equilibrium constant at that temperature can be expressed as the following linear equation:

$$\ln K = \frac{-\Delta H^\circ}{RT} + \text{constant}$$

(a) Explain how this equation can be used to determine ΔH° experimentally from the equilibrium constants at several different temperatures. (b) Derive the preceding equation using relationships given in this chapter. To what is the constant equal?

[19.98] One way to derive Equation 19.3 depends on the observation that at constant T the number of ways, W , of arranging m ideal-gas particles in a volume V is proportional to the volume raised to the m power:

$$W \propto V^m$$

Use this relationship and Boltzmann’s relationship between entropy and number of arrangements (Equation 19.5) to derive the equation for the entropy change for the isothermal expansion or compression of n moles of an ideal gas.

[19.99] About 86% of the world’s electrical energy is produced by using steam turbines, a form of heat engine. In his analysis of an ideal heat engine, Sadi Carnot concluded that the maximum possible efficiency is defined by the total work that could be done by the engine, divided by the quantity of heat available to do the work (for example from hot steam produced by combustion of a fuel such as coal or methane). This efficiency is given by the ratio $(T_{\text{high}} - T_{\text{low}})/T_{\text{high}}$, where T_{high} is the temperature of the heat going into the engine and T_{low} is that of the heat leaving the engine. (a) What is the maximum possible efficiency of a heat engine operating between an input temperature of 700 K and an exit temperature of 288 K? (b) Why is it important that electrical power plants be located near bodies of relatively cool water? (c) Under what conditions could a heat engine operate at or near 100% efficiency? (d) It is often said that if the energy of combustion of a fuel such as methane were captured in an electrical fuel cell instead of by burning the fuel in a heat engine, a greater fraction of the energy could be put to useful work. Make a qualitative drawing like that in Figure 5.10 that illustrates the fact that in principle the fuel cell route will produce more useful work than the heat engine route from combustion of methane.

INTEGRATIVE EXERCISES

19.100 Most liquids follow Trouton’s rule, which states that the molar entropy of vaporization lies in the range of $88 \pm 5 \text{ J/mol}\cdot\text{K}$. The normal boiling points and enthalpies of vaporization of several organic liquids are as follows:

Substance	Normal Boiling Point (°C)	ΔH_{vap} (kJ/mol)
Acetone, $(\text{CH}_3)_2\text{CO}$	56.1	29.1
Dimethyl ether, $(\text{CH}_3)_2\text{O}$	-24.8	21.5
Ethanol, $\text{C}_2\text{H}_5\text{OH}$	78.4	38.6
Octane, C_8H_{18}	125.6	34.4
Pyridine, $\text{C}_5\text{H}_5\text{N}$	115.3	35.1

(a) Calculate ΔS_{vap} for each of the liquids. Do all of the liquids obey Trouton's rule? (b) With reference to intermolecular forces (Section 11.2), can you explain any exceptions to the rule? (c) Would you expect water to obey Trouton's rule? By using data in Appendix B, check the accuracy of your conclusion. (d) Chlorobenzene ($\text{C}_6\text{H}_5\text{Cl}$) boils at 131.8°C . Use Trouton's rule to estimate ΔH_{vap} for this substance.

19.101 Consider the polymerization of ethylene to polyethylene. \rightleftharpoons (Section 12.6) (a) What would you predict for the sign of the entropy change during polymerization (ΔS_{poly})? Explain your reasoning. (b) The polymerization of ethylene is a spontaneous process at room temperature. What can you conclude about the enthalpy change during polymerization (ΔH_{poly})? (c) Use average bond enthalpies (Table 8.4) to estimate the value of ΔH_{poly} per ethylene monomer added. (d) Polyethylene is an *addition polymer*. By comparison, Nylon 66 is a *condensation polymer*. How would you expect ΔS_{poly} for a condensation polymer to compare to that for an addition polymer? Explain.

19.102 In chemical kinetics the *entropy of activation* is the entropy change for the process in which the reactants reach the activated complex. The entropy of activation for bimolecular processes is usually negative. Explain this observation with reference to Figure 14.15.

19.103 The following processes were all discussed in Chapter 18, "Chemistry of the Environment." Estimate whether the entropy of the system increases or decreases during each process: (a) photodissociation of $\text{O}_2(\text{g})$, (b) formation of ozone from oxygen molecules and oxygen atoms, (c) diffusion of CFCs into the stratosphere, (d) desalination of water by reverse osmosis.

19.104 Carbon disulfide (CS_2) is a toxic, highly flammable substance. The following thermodynamic data are available for $\text{CS}_2(\text{l})$ and $\text{CS}_2(\text{g})$ at 298 K:

	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)
$\text{CS}_2(\text{l})$	89.7	65.3
$\text{CS}_2(\text{g})$	117.4	67.2

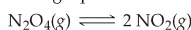
(a) Draw the Lewis structure of the molecule. What do you predict for the bond order of the C—S bonds? (b) Use the VSEPR method to predict the structure of the CS_2 molecule. (c) Liquid CS_2 burns in O_2 with a blue flame, forming $\text{CO}_2(\text{g})$ and $\text{SO}_2(\text{g})$. Write a balanced equation for this reaction. (d) Using the data in the preceding table and in Appendix C, calculate ΔH° and ΔG° for the reaction in part (c). Is the reaction exothermic? Is it spontaneous at 298 K? (e) Use the data in the preceding table to calculate ΔS° at 298 K for the vaporization of $\text{CS}_2(\text{l})$. Is the sign of ΔS° as you would expect for a vaporization? (f) Using data in the preceding table and your answer to part (e), estimate the boiling point of $\text{CS}_2(\text{l})$. Do you predict that the substance will be a liquid or a gas at 298 K and 1 atm?

19.105 The following data compare the standard enthalpies and free energies of formation of some crystalline ionic substances and aqueous solutions of the substances:

Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)
$\text{AgNO}_3(\text{s})$	-124.4	-33.4
$\text{AgNO}_3(\text{aq})$	-101.7	-34.2
$\text{MgSO}_4(\text{s})$	-1283.7	-1169.6
$\text{MgSO}_4(\text{aq})$	-1374.8	-1198.4

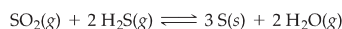
(a) Write the formation reaction for $\text{AgNO}_3(\text{s})$. Based on this reaction, do you expect the entropy of the system to increase or decrease upon the formation of $\text{AgNO}_3(\text{s})$? (b) Use ΔH_f° and ΔG_f° of $\text{AgNO}_3(\text{s})$ to determine the entropy change upon formation of the substance. Is your answer consistent with your reasoning in part (a)? (c) Is dissolving AgNO_3 in water an exothermic or endothermic process? What about dissolving MgSO_4 in water? (d) For both AgNO_3 and MgSO_4 , use the data to calculate the entropy change when the solid is dissolved in water. (e) Discuss the results from part (d) with reference to material presented in this chapter and in the second "Closer Look" box in Section 13.5.

19.106 Consider the following equilibrium:



Thermodynamic data on these gases are given in Appendix C. You may assume that ΔH° and ΔS° do not vary with temperature. (a) At what temperature will an equilibrium mixture contain equal amounts of the two gases? (b) At what temperature will an equilibrium mixture of 1 atm total pressure contain twice as much NO_2 as N_2O_4 ? (c) At what temperature will an equilibrium mixture of 10 atm total pressure contain twice as much NO_2 as N_2O_4 ? (d) Rationalize the results from parts (b) and (c) by using Le Châtelier's principle. \rightleftharpoons (Section 15.7)

19.107 The reaction



is the basis of a suggested method for removal of SO_2 from power-plant stack gases. The standard free energy of each substance is given in Appendix C. (a) What is the equilibrium constant for the reaction at 298 K? (b) In principle, is this reaction a feasible method of removing SO_2 ? (c) If $P_{\text{SO}_2} = P_{\text{H}_2\text{S}}$ and the vapor pressure of water is 25 torr, calculate the equilibrium SO_2 pressure in the system at 298 K. (d) Would you expect the process to be more or less effective at higher temperatures?

19.108 When most elastomeric polymers (e.g., a rubber band) are stretched, the molecules become more ordered, as illustrated here:



Suppose you stretch a rubber band. (a) Do you expect the entropy of the system to increase or decrease? (b) If the rubber band were stretched isothermally, would heat need to be absorbed or emitted to maintain constant temperature?