

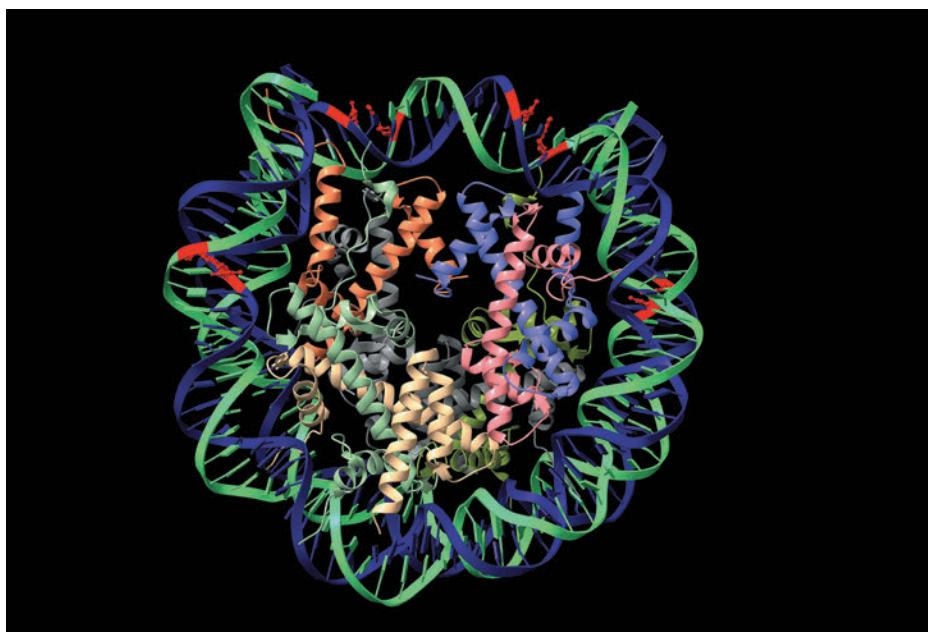
## WHAT'S AHEAD

- 19.1 ► Spontaneous Processes
- 19.2 ► Entropy and the Second Law of Thermodynamics
- 19.3 ► The Molecular Interpretation of Entropy and the Third Law of Thermodynamics
- 19.4 ► Entropy Changes in Chemical Reactions
- 19.5 ► Gibbs Free Energy
- 19.6 ► Free Energy and Temperature
- 19.7 ► Free Energy and the Equilibrium Constant

# 19

# CHEMICAL THERMODYNAMICS

## 19.1 | Spontaneous Processes



The nucleosome is a macromolecule inside the nucleus of a living cell: DNA (the gray outer double-helical portion) surrounds eight protein molecules (the colored molecular models). This overall DNA/protein structure, called the nucleosome, is the basic unit of chromosomes in the nuclei of our cells. These structures are highly ordered, yet also must be unraveled for gene expression to take place. Both packaging and unpackaging of DNA in the nucleosome involve changes in the energy of the system.

The amazing organization of living systems, from complex molecular structures such as those of nucleosomes, to cells, to tissues, and finally to whole plants and animals, is an unending source of wonder and delight to the scientists who study them. Energy must be spent, somehow, to form and maintain these organized systems. But how is that energy channeled to accomplish these tasks? We cannot merely take the requisite atoms, put them in a pot, add energy, and get something like a nucleosome.

Understanding natural processes, whether they be DNA replication, photosynthesis, or merely the rusting of a nail, relies on understanding the general laws that govern chemical reactions.

In this chapter, we explore the connection between energy and the extent of a reaction. Doing so requires a deeper look at *chemical thermodynamics*, the area of chemistry that deals with energy relationships. We first considered thermodynamics in Chapter 5, where we discussed the nature of energy, the first law of thermodynamics, and the concept of enthalpy. In this chapter, we discuss the second law of thermodynamics and the concept of *entropy*, a thermodynamic quantity that we encountered briefly in Chapter 13. We start with a few definitions. By the end of this section, you should be able to

- Explain and apply the terms spontaneous process, reversible process, irreversible process, and isothermal process.

If you release a brick from your hand, it will fall. It never jumps back into your hand no matter how long you wait. Likewise, if you let a nail sit in the rain, it will eventually rust. The rusted nail will never convert to its original condition even when the sun shines and time passes. These are but two examples illustrating that there is directionality to events. We say that events like the falling brick and rusting nail occur spontaneously. A **spontaneous process** is one that occurs on its own without any outside assistance.

A spontaneous process occurs in one direction only, and the reverse of any spontaneous process is always *nonspontaneous*. Drop an egg above a hard surface, for example, and it breaks on impact (Figure 19.1). Now, imagine seeing a video clip in which a broken egg rises from the floor, reassembles itself, and ends up in someone's hand. You would conclude that the video is running in reverse because you know that broken eggs do not rise and reassemble themselves. An egg falling and breaking is a spontaneous process, whereas the egg rising and reassembling itself is a nonspontaneous process.

*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. Ice melts spontaneously at atmospheric pressure when the temperature of the surroundings is above 0 °C. When the surroundings are below 0 °C, however, liquid water freezes spontaneously. The reverse process, melting, is then nonspontaneous as summarized in Figure 19.2.

We must not confuse the *spontaneity* of a process with *speed*. Just because a process is spontaneous does not necessarily mean that it will occur at an observable rate. A spontaneous process can be fast, as in the case of acid-base neutralization, or slow, as in the rusting of iron. Thermodynamics tells us the *direction* and *extent* of reaction but nothing about the rate.

## Go Figure

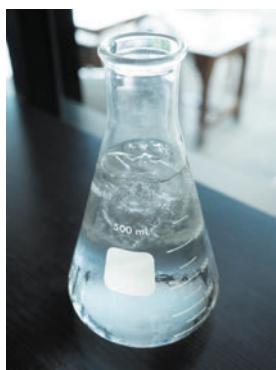
Does the potential energy of the eggs change during this process?



▲ Figure 19.1 A spontaneous process!

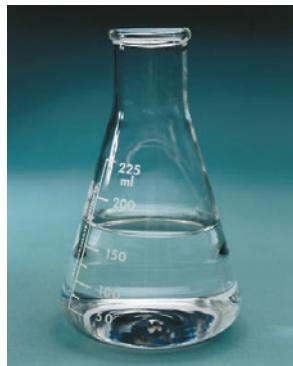
 Go Figure

In which direction is this process exothermic?



Spontaneous for  $T > 0^\circ\text{C}$

Spontaneous for  $T < 0^\circ\text{C}$



▲ **Figure 19.2 Spontaneity can depend on temperature.** At  $T > 0^\circ\text{C}$ , ice melts spontaneously to liquid water. At  $T < 0^\circ\text{C}$ , the reverse process, water freezing to ice, is spontaneous. At  $T = 0^\circ\text{C}$  the two states are in equilibrium.

It is also important to understand that nonspontaneous does not mean impossible. For example, although the decomposition of table salt, NaCl, into sodium and chlorine is nonspontaneous under ordinary conditions, it is possible to decompose molten NaCl by supplying energy from an external source. A spontaneous process occurs without such outside intervention.

 Sample Exercise 19.1

## Identifying Spontaneous Processes



Predict whether each process is spontaneous as described, spontaneous in the reverse direction, or at equilibrium: (a) Water at  $40^\circ\text{C}$  gets hotter when a piece of metal heated to  $150^\circ\text{C}$  is added. (b) Water at room temperature decomposes into  $\text{H}_2(g)$  and  $\text{O}_2(g)$ . (c) Benzene vapor,  $\text{C}_6\text{H}_6(g)$ , at a pressure of 101.3 kPa condenses to liquid benzene at the normal boiling point of benzene,  $80.1^\circ\text{C}$ .

**SOLUTION**

**Analyze** We are asked to judge whether each process is spontaneous 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 reverse process—the reaction of  $\text{H}_2$  and  $\text{O}_2$  to form  $\text{H}_2\text{O}$ —is spontaneous.

- (c) The normal boiling point is the temperature at which a vapor at 101.3 kPa is in equilibrium with its liquid. Thus, this is an equilibrium situation. If the temperature were below  $80.1^\circ\text{C}$ , condensation would be spontaneous.

**► Practice Exercise**

The process of iron being oxidized to make iron(III) oxide (rust) is spontaneous. Which of these statements about this process is/are true? (a) The reduction of iron(III) oxide to iron is also spontaneous. (b) Because the process is spontaneous, the oxidation of iron must be fast. (c) The oxidation of iron is endothermic. (d) Equilibrium is achieved in a closed system when the rate of iron oxidation is equal to the rate of iron(III) oxide reduction. (e) The energy of the universe is decreased when iron is oxidized to rust.

## Seeking a Criterion for Spontaneity

A marble rolling down an incline or a brick falling from your hand loses potential energy. The loss of some form of energy is a common feature of spontaneous change in mechanical systems. In the 1870s, Marcellin Bertholet (1827–1907) suggested that the direction of spontaneous changes in chemical systems is determined by the loss of energy. He proposed that all spontaneous chemical and physical changes are 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 and endothermic. Similarly, many spontaneous dissolution processes, such as the dissolving of  $\text{NH}_4\text{NO}_3$ , are endothermic, as we discovered in Section 13.1. We conclude 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.

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 from Section 5.2 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. The heat transferred between the system and its surroundings,  $q$ , and the work done on or by the system,  $w$ , are *not* state functions—their values depend on the specific way in which the change occurs. That is, their values depend on the *path* taken between states. Understanding two kinds of paths, those that are *reversible* and those that are *irreversible*, is a key to understanding spontaneity.

## Reversible and Irreversible Processes

For any process, we can imagine a hypothetical, ideal path that can be reversed to restore both the system and its surroundings to exactly their original states. This means that after the process is reversed, both the system and surroundings are unchanged. Such an ideal process is said to be reversible.

- A **reversible process** is one for which we can restore the system to its original condition with no change to the surroundings.
- An **irreversible process** is one that leaves the surroundings somehow changed when the system is restored to its original state.

Sometimes these processes are referred to as being *thermodynamically reversible* or *thermodynamically irreversible* to add greater clarity to their meanings.

As an example, let's consider a process involving the transfer of heat. When two objects at different temperatures are in contact, heat flows spontaneously from the hotter object to the colder one. Because it is impossible to make the heat flow in the opposite direction, from colder to hotter, this is an irreversible process. Given this fact, can we imagine any hypothetical conditions under which the heat transfer could be reversible? The answer is yes, but only if we consider temperature changes that are infinitesimally small.

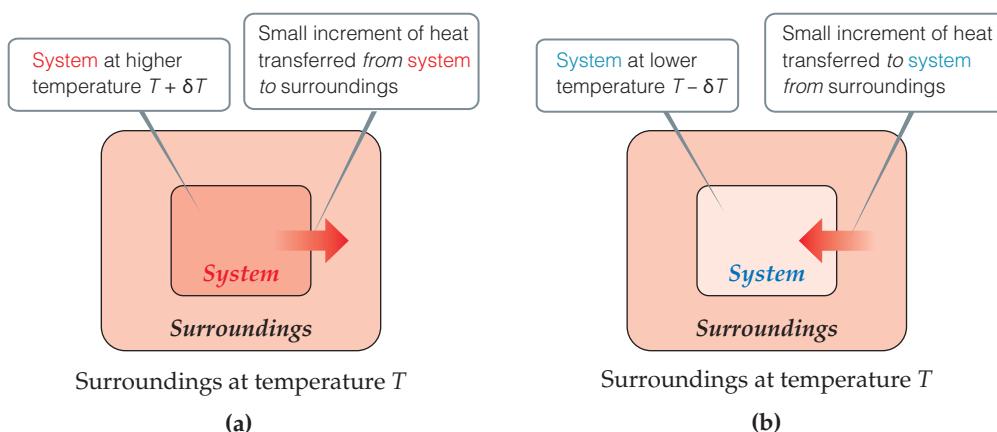
Imagine the system and its surroundings at essentially the same temperature, with just an infinitesimal temperature difference,  $\delta T$ , between them (Figure 19.3). If the surroundings are at temperature  $T$  and the system is at an infinitesimally higher temperature  $T + \delta T$ , then an infinitesimal amount of heat flows from the system to surroundings. We can reverse the direction of heat flow by making an infinitesimal change of temperature in the opposite direction, lowering the system temperature to  $T - \delta T$ . Now the direction of heat flow is from surroundings to system. Thus, for the process to be reversible, the amounts of heat must be infinitesimally small and the transfer of heat must occur infinitely slowly.

*Reversible processes are those that reverse direction whenever an infinitesimal change is made in some property of the system.*

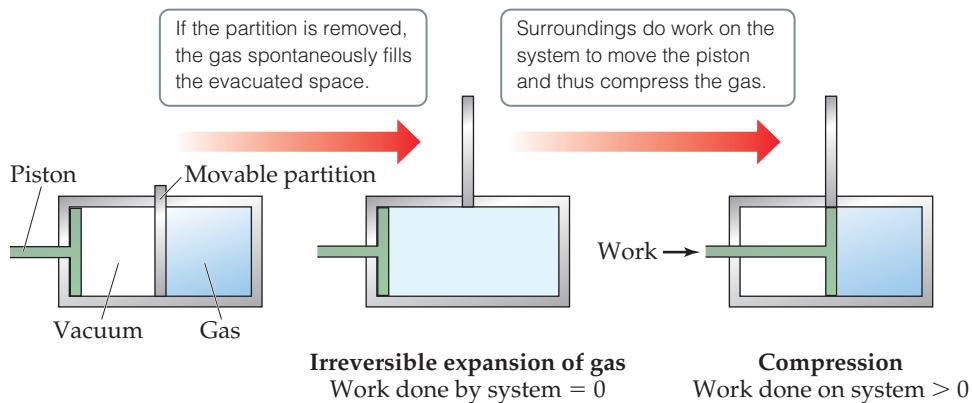
Now let's consider another example, the expansion of an ideal gas at constant temperature (referred to as an **isothermal** process). In the cylinder-piston arrangement of Figure 19.4, when the partition is removed, the gas expands spontaneously to fill the evacuated space. Can we determine whether this particular isothermal expansion is

**Go Figure**

If the flow of heat into or out of the system is to be reversible, what must be true of  $\delta T$ ?



▲ **Figure 19.3** Reversible flow of heat. Heat can flow reversibly between a system and its surroundings only if the two have an infinitesimally small difference in temperature  $\delta T$ . (a) Increasing the temperature of the system by  $\delta T$  causes heat to flow from the hotter system to the colder surroundings. (b) Decreasing the temperature of the system by  $\delta T$  causes heat to flow from the hotter surroundings to the colder system.



▲ **Figure 19.4** An irreversible process. Initially, an ideal gas is confined to the right half of a cylinder. When the partition is removed, the gas spontaneously expands to fill the whole cylinder. No work is done by the system during this expansion. Using the piston to compress the gas back to its original state requires the surroundings to do work on the system.

reversible or irreversible? Because the gas expands into a vacuum with no external pressure, it does no  $P\text{-}V$  work on the surroundings. Thus, for the expansion,  $w = 0$ . 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, meaning that  $w > 0$  for the compression. In other words, the path that restores the system to its original state requires a different value of  $w$  (and, by the first law, a different value of  $q$ ) than the path by which the system was first changed. The fact that the same path cannot be followed to restore the system to its original state indicates that the process is irreversible.

What might a *reversible isothermal expansion* of an ideal gas be? This process will occur only if initially, when the gas is confined to half the cylinder, the external pressure acting on the piston exactly balances the pressure exerted by the gas on the piston. If the external pressure is reduced infinitely slowly, the piston will move outward, allowing the pressure of the confined gas to readjust to maintain the pressure balance. This 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.

From these and other examples we learn two important facts:

- Because real processes can at best only approximate the infinitesimal changes associated with reversible processes, *all real processes are irreversible*.
- Because spontaneous processes are real processes, *all spontaneous processes are irreversible*.

Thus, for any spontaneous change, returning the system to its original condition results in a net change in the surroundings. But what kind of change occurs?

Recall that the first law of thermodynamics states that energy is conserved. In mathematical terms,  $\Delta E = q + w$ ; that is, the change in internal energy of a system is equal to the heat absorbed (or released) by the system plus the work done on (or by) the system. If we return a system to its original condition, no net change in energy takes place, but there is a change in the nature of the energy. Returning the system to its initial condition requires us to do work on the system. Doing work requires a focused, relatively concentrated application of energy. During the process, that focused, concentrated energy gets converted to a more diffuse form. Thus, the net change in the surroundings involves the nature of the energy—it becomes more dispersed and disordered and therefore less able to do work.

What we observe about energy changes is that *energy has a tendency to spread out*. Consider a hot cup of tea. As it cools, energy spreads (or disperses) from the smaller volume of the tea into the greater volume of its surroundings. On a molecular level, the random, chaotic motion of particles (thermal motion) transfers energy through molecular collisions from the higher temperature (greater average kinetic energy) to lower temperature (lesser average kinetic energy) until the tea and its surroundings reach the same temperature. This natural tendency for energy to spread from a more concentrated form to a less concentrated form renders some of the energy unavailable to do work. Interestingly, a reversible process produces the maximum amount of work that can be done by a system on its surroundings.

## Self-Assessment Exercise

**19.1** Suppose you have a system made up of water only, with the container and everything beyond being the surroundings. Consider a process in which the water is first evaporated and then condensed back into its original container. Is this two-step process necessarily reversible?

(a) Yes

(b) No

## Exercises

**19.2** Which of the following processes are spontaneous:  
(a) the evaporation of water at STP to form water vapor of 101.3 kPa pressure; (b) separation of a mixture of water and oil into two separate phases; (c) the souring of milk; (d) the neutralization of hydrochloric acid with sodium hydroxide at STP; (e) the formation of ice from water at 20 °C and 101.3 kPa?

**19.3** (a) Can endothermic chemical reactions be spontaneous? (b) Can a process be spontaneous at one temperature and non-spontaneous at a different temperature? (c) Water can be decomposed to form hydrogen and oxygen, and the hydrogen and oxygen can be recombined to form water. Does this mean that the processes are thermodynamically reversible? (d) Does the amount of work that a system can do on its surroundings depend on the path of the process?

**19.4** The normal boiling point of *n*-octane ( $C_8H_{18}$ ) is 125 °C. (a) Is the condensation of gaseous *n*-octane to liquid *n*-octane an endothermic or exothermic process? (b) In what temperature range is the boiling of *n*-octane a spontaneous process? (c) In what temperature range is it a nonspontaneous process? (d) Is there any temperature at which liquid *n*-octane and gaseous *n*-octane are in equilibrium? Explain.

**19.5** Consider what happens when a sample of the explosive TNT is detonated under atmospheric pressure. (a) Is the detonation a reversible process? (b) What is the sign of  $q$  for this process? (c) Is  $w$  positive, negative, or zero for the process?

19.1 (b)

Answers to Self-Assessment Exercises



## 19.2 | Entropy and the Second Law of Thermodynamics



Refrigeration has had a massive impact on the transportation, storage, and preservation of food. While there are several ways to generate ‘cold,’ the most common one in modern refrigerators uses a vapor-compression cycle. Here a volatile liquid is evaporated by passing it through an expansion valve. This is an endothermic process with the heat drawn from the surroundings, which are cooled as a consequence. This is connected to the food storage compartment of the refrigerator. The gas is then condensed by passing it into a compressor with the heat generated by this condensation being removed via a heat exchanger to be discharged outside the refrigerator. Effectively, heat is removed from a cold area and added to a hot area. This is a nonspontaneous process but may be driven with the input of energy.

By the end of this section, you should be able to

- Define entropy and state the second law of thermodynamics.
- Calculate  $\Delta S$  for a phase change.

In order to apply what we have learned about irreversible processes to predict whether an unfamiliar process is spontaneous, we must examine the thermodynamic quantity called entropy.

**Entropy** is a measure of the tendency for energy to spread or disperse, thereby reducing its ability to accomplish work. In a general sense, it reflects the degree of *randomness* or *disorder* associated with the particles that carry the energy.

In this section, we consider how entropy changes are related to heat transfer and temperature. Our analysis will bring us to a profound statement about entropy changes and spontaneity known as the second law of thermodynamics.

### The Relationship between Entropy and Heat

The entropy,  $S$ , of a system is a state function just like internal energy,  $E$ , and enthalpy,  $H$ . As with these other quantities, the value of  $S$  is a characteristic of the state of a system. Thus, the change in entropy,  $\Delta S$ , 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,  $\Delta S$  is equal to the heat that would be transferred if the process were reversible,  $q_{\text{rev}}$ , divided by the absolute temperature at which the process occurs:

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

Although many possible paths can take the system from one state to another, only one path is associated with a reversible process. Thus, the value of  $q_{\text{rev}}$  is uniquely defined for any two states of the system. Because  $S$  is a state function, we can use Equation 19.2 to calculate  $\Delta S$  for any isothermal process between states, not just the reversible one.

### $\Delta S$ 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 101.3 kPa, ice and liquid water are in equilibrium at 0 °C. Imagine melting 1 mol of ice at 0 °C, 101.3 kPa to form 1 mol of liquid water at 0 °C, 101.3 kPa. We can achieve this change by adding heat to the system from the surroundings:  $q = \Delta H_{\text{fusion}}$ , where  $\Delta H_{\text{fusion}}$  is the heat of melting. Imagine 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 because we can reverse it by infinitely slowly removing the same amount of heat,  $\Delta H_{\text{fusion}}$ , from the system, using immediate surroundings that are infinitesimally below 0 °C. Thus,  $q_{\text{rev}} = \Delta H_{\text{fusion}}$  for the melting of ice at  $T = 0^\circ\text{C} = 273\text{ K}$ .

The enthalpy of fusion for  $\text{H}_2\text{O}$  is  $\Delta H_{\text{fusion}} = 6.01\text{ kJ/mol}$  (a positive value because melting is an endothermic process). Thus, we can use Equation 19.2 to calculate  $\Delta S_{\text{fusion}}$  for melting 1 mol of ice at 273 K:

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

Notice that (1) we must use the absolute temperature in Equation 19.2, and (2) the units for  $\Delta S, \text{J/K}$ , are energy divided by absolute temperature, as we expect from Equation 19.2.

### Sample Exercise 19.2

#### Calculating $\Delta S$ for a Phase Change

Elemental mercury is a silver liquid at room temperature. Its normal freezing point is  $-38.9^\circ\text{C}$ , 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, which means heat is transferred from the system to the surroundings and  $q < 0$ . Because freezing is the reverse of melting, the enthalpy change that accompanies the freezing of 1 mol of  $\text{Hg}$  is  $-\Delta H_{\text{fusion}} = -2.29\text{ kJ/mol}$ .

**Plan** We can use  $-\Delta H_{\text{fusion}}$  and the atomic weight of  $\text{Hg}$  to calculate  $q$  for freezing 50.0 g of  $\text{Hg}$ . Then we use this value of  $q$  as  $q_{\text{rev}}$  in Equation 19.2 to determine  $\Delta S$  for the system.

#### Solve

For  $q$  we have:

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

Before using Equation 19.2, we must first convert the given Celsius temperature to kelvins:

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

We can now calculate  $\Delta S_{\text{sys}}$ :

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

**Check** The entropy change is negative because our  $q_{\text{rev}}$  value is negative, which it must be because heat flows out of the system in this exothermic process.

**Comment** This procedure can be used to calculate  $\Delta S$  for other isothermal phase changes, such as the vaporization of a liquid at its boiling point.

#### ► Practice Exercise

Do all exothermic phase changes have a negative value for the entropy change of the system? (a) Yes, because the heat transferred from the system has a negative sign. (b) Yes, because the temperature decreases during the phase transition. (c) No, because the entropy change depends on the sign of the heat transferred to or from the system. (d) No, because the heat transferred to the system has a positive sign. (e) More than one of the previous answers is correct.

## A CLOSER LOOK The Entropy Change When a Gas Expands Isothermally

In general, the entropy of any system increases as the system becomes more random or more spread out. Thus, we expect the spontaneous expansion of a gas to result in an increase in entropy. To see how this entropy increase can be calculated, consider the expansion of an ideal gas that is initially constrained by a piston, as in the rightmost part of Figure 19.4. Imagine that we allow the gas to undergo a reversible isothermal expansion by infinitesimally decreasing the external pressure on the piston. The work done on the surroundings by the reversible expansion of the system against the piston can be calculated with the aid of calculus (we do not show the derivation):

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

In this equation,  $n$  is the number of moles of gas,  $R$  is the ideal-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 characteristic of an ideal gas is that its internal energy depends only on temperature, not on pressure. Thus, when an ideal gas expands isothermally,  $\Delta E = 0$ . 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:

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

Let's calculate the entropy change for 1.00 L of an ideal gas at 101.3 kPa, 0 °C temperature, expanding to 2.00 L. From the ideal-gas equation, we can calculate the number of moles in 1.00 L of an ideal gas at 101.3 kPa and 0 °C as we did in Chapter 10:

$$n = \frac{PV}{RT} = \frac{(101.3 \text{ kPa})(1.00 \text{ L})}{(8.314 \text{ L kPa/mol K})(273 \text{ K})} = 4.46 \times 10^{-2} \text{ mol}$$

The gas constant,  $R$ , can also be expressed as 8.314 J/mol K (Table 10.2), and this is the value we must use in Equation 19.3 because we want our answer to be expressed in terms of J rather than in L kPa. 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 due to the expansion.

**Related Exercises: 19.11, 19.66**

## The Second Law of Thermodynamics

The key idea of the first law of thermodynamics is that energy is conserved in any process. Is entropy also conserved in a spontaneous process in the same way that energy is conserved?

Let's try to answer this question by calculating the entropy change of a system and the entropy change of its surroundings when our system is 1 mol of ice (a piece roughly the size of an ice cube) melting in the palm of your hand, which is part of the surroundings. The process is not reversible because the system and surroundings are at different temperatures. Nevertheless, because  $\Delta S$  is a state function, its value is the same regardless of whether the process is reversible or irreversible. Earlier (just before Sample Exercise 19.2) we calculated the entropy change of this system:

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

The portion of the surroundings immediately in contact with the ice is your palm, which we assume is at body temperature, 37 °C = 310 K. We will use this as the temperature of the surroundings. The quantity of heat lost by your palm is  $-6.01 \times 10^3 \text{ J/mol}$ , which is equal in magnitude to the quantity of heat gained by the ice but has the opposite sign. Hence, the entropy change of the surroundings is

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

We can consider that everything in the universe consists of the system of interest and its surroundings. Therefore,  $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$ . Thus, the overall entropy change of the universe is positive in our example:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = (22.0 \text{ J/K}) + (-19.4 \text{ J/K}) = 2.6 \text{ J/K}$$

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  $-22.0 \text{ J/K}$  and  $\Delta S_{\text{univ}}$  would be zero.

In general, any irreversible process results in an increase in the entropy of the universe, whereas any reversible process results in no change in the entropy of the universe:

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

These equations summarize the **second law of thermodynamics**. Because spontaneous processes are irreversible, we can also state the second law this way:

*The entropy of the universe increases for any spontaneous process.*

The second law of thermodynamics tells us the essential character of any spontaneous change—it is always accompanied by an increase in the entropy of the universe. We can use this law as a criterion to predict whether or not a given process is spontaneous. Before seeing how this is done, however, we will find it useful to explore entropy from a molecular perspective.

A word on notation before we proceed: Throughout most of the remainder of this chapter, we will focus on systems rather than surroundings. To simplify the notation, we will usually refer to the entropy change of the system as  $\Delta S$  rather than explicitly indicating  $\Delta S_{\text{sys}}$ .

## Self-Assessment Exercises

- 19.6** Sodium metal reacts with chlorine gas to form sodium chloride. This reaction is spontaneous and is accompanied by a decrease in the entropy of the system (the sodium and chlorine). What can we conclude about the entropy change of the surroundings?  
**(a)** The entropy of the surroundings increases  
**(b)** The entropy of the surroundings remains the same  
**(c)** The entropy of the surroundings decreases
- 19.7**  $\Delta S = 1.09 \text{ J/mol K}$  for the transition of solid rhombic sulfur to solid monoclinic sulfur at  $95.5^\circ\text{C}$ . What is the enthalpy change,  $\Delta H$ , for this transition?  
**(a)**  $11.4 \text{ J/mol}$   
**(b)**  $104 \text{ J/mol}$   
**(c)**  $402 \text{ J/mol}$

## Exercises

- 19.8** Indicate whether each statement is true or false. **(a)** The entropy of the universe increases for any spontaneous process. **(b)** The entropy change of the system is equal and opposite that of the surroundings for any irreversible process. **(c)** The entropy of the system must increase in any spontaneous process. **(d)** The entropy change for an isothermal process depends on both the absolute temperature and the amount of heat reversibly transferred.
- 19.9** The element sodium ( $\text{Na}$ ) melts at  $97.8^\circ\text{C}$ , and its molar enthalpy of fusion is  $\Delta H_{\text{fus}} = 2.60 \text{ kJ/mol}$ . **(a)** When molten sodium solidifies to  $\text{Na}(s)$ , is  $\Delta S$  positive or negative? **(b)** Calculate the value of  $\Delta S$  when 50.0 g of  $\text{Na}(l)$  solidifies at  $97.8^\circ\text{C}$ .
- 19.10** **(a)** Does the entropy of the surroundings increase for spontaneous processes? **(b)** In a particular spontaneous process the entropy of the system decreases. What can you conclude about the sign and magnitude of  $\Delta S_{\text{surr}}$ ? **(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?
- 19.11** **(a)** What sign for  $\Delta S$  do you expect when the pressure on 0.600 mol of an ideal gas at 350 K is increased isothermally from an initial pressure of 76.0 kPa? **(b)** If the final pressure on the gas is 121.6 kPa, calculate the entropy change for the process. **(c)** Do you need to specify the temperature to calculate the entropy change?

19.6 (a) 19.7 (c)

Answers to Self-Assessment Exercises



## 19.3 | The Molecular Interpretation of Entropy and the Third Law of Thermodynamics



Imagine a major sporting event, the final of a football match perhaps, and the roar of the crowd when the winning goal is kicked. Thousands of individual voices, all slightly different, but resulting in a single sound. In our discussion of entropy so far, we have considered the macroscopic interpretation of entropy and its relation to the system, the surroundings and the universe. In this section, we look at the microscopic interpretation of entropy—that is what is going on at a molecular level.

By the end of this section, you should be able to

- Explain how the entropy of a system is related to the number of possible microstates.
- Describe the kinds of molecular motion that a molecule can possess.
- Predict the sign of  $\Delta S$  for physical and chemical processes.
- State the third law of thermodynamics.

As chemists, we are interested in molecules. What does entropy have to do with them and with their transformations? What molecular property does entropy reflect? Ludwig Boltzmann (1844–1906) gave another conceptual meaning to the notion of entropy, and to understand his contribution, we need to examine the ways in which we can interpret entropy at the molecular level.

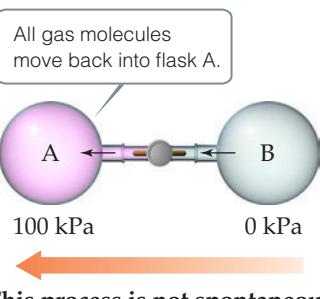
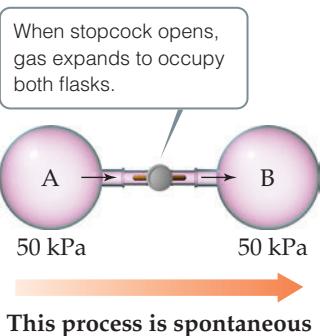
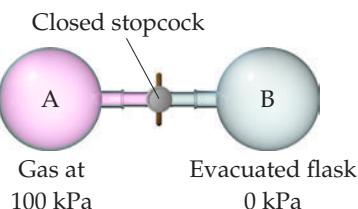
### Expansion of a Gas at the Molecular Level

Consider a simple spontaneous process—the expansion of a gas into a vacuum as shown in [Figure 19.5](#). Though we now understand that the entropy of the universe increases during the expansion, how can we explain the spontaneity of this process at the molecular level? We can get a sense of what makes this expansion spontaneous by envisioning the gas as a collection of particles in constant motion, as we did in discussing the kinetic-molecular theory of gases. When the stopcock in [Figure 19.5](#) is opened, we can view the expansion of the gas as the ultimate result of the gas molecules moving randomly throughout the larger volume.

Let's look at this idea more closely by tracking two of the gas molecules as they move around. Before the stopcock is opened, both molecules are confined to the left flask, as shown in [Figure 19.6\(a\)](#). After the stopcock is opened, the molecules travel randomly throughout the entire apparatus. As [Figure 19.6\(b\)](#) shows, there are four possible arrangements for the two molecules once both flasks are available to them. Because the molecular motion is random, all four arrangements are equally likely.

**Go Figure**

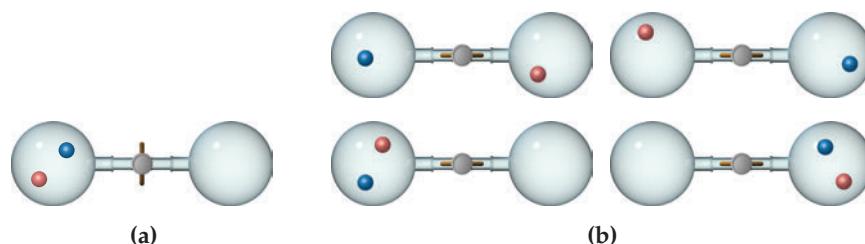
If flask B were smaller than flask A, would the final pressure after the stopcock is opened be greater than, equal to, or less than 50 kPa?



▲ **Figure 19.5 Expansion of a gas into an evacuated space is a spontaneous process.** The reverse process—gas molecules initially distributed evenly in two flasks all moving into one flask—is not spontaneous.

Note that now only one arrangement corresponds to the situation before the stopcock was opened: both molecules in the left flask.

Figure 19.6(b) shows that with both flasks available to the molecules, the probability of the red molecule being in the left flask is two in four (top right and bottom left arrangements), and the probability of the blue molecule being in the left flask is the same (top left and bottom left arrangements). Because the probability is  $\frac{2}{4} = \frac{1}{2}$  that each molecule is in the left flask, the probability that *both* are there is  $(\frac{1}{2})^2 = \frac{1}{4}$ . If we apply the same



The two molecules are colored red and blue to keep track of them.

Four possible arrangements (microstates) once the stopcock is opened.

◀ **Figure 19.6 Possible arrangements of two gas molecules in two flasks.** (a) Before the stopcock is opened, both molecules are in the left flask. (b) After the stopcock is opened, there are four possible arrangements of the two molecules.

analysis to *three* gas molecules, we find that the probability that all three are in the left flask at the same time is  $(1/2)^3 = 1/8$ .

Now let's consider a *mole* of gas. The probability that all the molecules are in the left flask at the same time is  $(1/2)^N$ , where  $N = 6.02 \times 10^{23}$ . This is a vanishingly small number! Thus, there is essentially zero likelihood that all the gas molecules will be in the left flask at the same time. This analysis of the microscopic behavior of the gas molecules leads to the expected macroscopic behavior: The gas spontaneously expands to fill both the left and right flasks, and it does not spontaneously all go back in the left flask.

This molecular view of gas expansion shows the tendency of the molecules to “spread out” among the different arrangements they can take. Before the stopcock is opened, there is only one possible arrangement: all molecules in the left flask. When the stopcock is opened, the arrangement in which all the molecules are in the left flask is but one of an extremely large number of possible arrangements. The most probable arrangements by far are those in which there are essentially equal numbers of molecules in the two flasks. When the gas spreads throughout the apparatus, any given molecule can be in either flask rather than confined to the left flask. We say that with the stopcock opened, the arrangement of gas molecules is more dispersed than when the molecules are all confined in the left flask.

We will see that this notion of increasing dispersion helps us understand entropy at the molecular level.

### 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 microscopic structure. In fact, thermodynamics was a well-developed field before the modern view of atomic and molecular structure was 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<sub>2</sub>O 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 link the microscopic and macroscopic worlds. Here we 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 complex, our discussion will be largely conceptual.

In our discussion of two gas molecules in the two-flask system in Figure 19.6, we saw that the number of possible arrangements helped explain why the gas expands.

Suppose we now consider 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. What is happening to this gas at the microscopic level, and how does what is going on at the microscopic level relate to the entropy of the gas?

Imagine taking a snapshot of the positions and speeds of all the molecules at a given instant. The speed of each molecule relates to its kinetic energy. That particular set of  $6 \times 10^{23}$  positions and kinetic energies of the individual gas molecules is what we call a *microstate* of the system. A **microstate** is a single possible arrangement of the positions and kinetic energies of the molecules when the molecules are in a specific thermodynamic state. We could envision continuing to take snapshots of our system to see other possible microstates.

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 the name *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.

Students sometimes have difficulty distinguishing between the state of a system and the microstates associated with the state.

- A *state* describes the macroscopic view of the system as characterized, for example, by the pressure and temperature of a sample of gas.

- A **microstate** is a particular microscopic arrangement of the atoms or molecules of the system that corresponds to the given state of the system.

Each of the snapshots we described is a microstate—the positions and kinetic energies of individual gas molecules will change from snapshot to snapshot, but each one is a possible arrangement of the collection of molecules corresponding to a single state. For macroscopically sized systems, such as a mole of gas, there is a very large number of microstates for each state—that is,  $W$  is generally an extremely large number.

The connection between the number of microstates of a system,  $W$ , and the entropy of the system,  $S$ , is expressed in a beautifully simple equation developed by Boltzmann and engraved on his tombstone (**Figure 19.7**):

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

In this equation,  $k$  is the Boltzmann constant,  $1.38 \times 10^{-23} \text{ J/K}$ . We see from the equation that:

*Entropy is a measure of how many microstates are associated with a particular macroscopic state.*

From Equation 19.5, we see that the entropy change accompanying any process is

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

Any change in the system that leads to an increase in the number of microstates ( $W_{\text{final}} > W_{\text{initial}}$ ) leads to a positive value of  $\Delta S$ :

*Entropy increases with the number of microstates of the system.*

Let's consider two modifications 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 a greater number of positions available to the gas atoms and therefore a greater number of microstates. 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 does this change affect the entropy of the system? Recall the distribution of molecular speeds presented in Figure 10.12(a). An increase in temperature increases the most probable speed of the molecules and also broadens the distribution of speeds. Hence, the molecules have a greater number of possible kinetic energies, and the number of microstates increases. Thus, the entropy of the system increases with increasing temperature.

## Molecular Motions and Energy

The particles of an ideal gas are idealized points with no volume and no bonds, however—points that we visualize as flitting around through space. Any real molecule can undergo three kinds of more complex motion. The entire molecule can move in one direction, which is the simple motion we visualize for an ideal particle and see in a macroscopic object, such as a thrown ball. We call such movement **translational motion**. The molecules in a gas have more freedom of translational motion than those in a liquid, which have more freedom of translational motion than the molecules of a solid.

A real molecule can also undergo **vibrational motion**, in which the atoms in the molecule move periodically toward and away from one another, and **rotational motion**, in which the molecule spins about an axis. **Figure 19.8** 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.

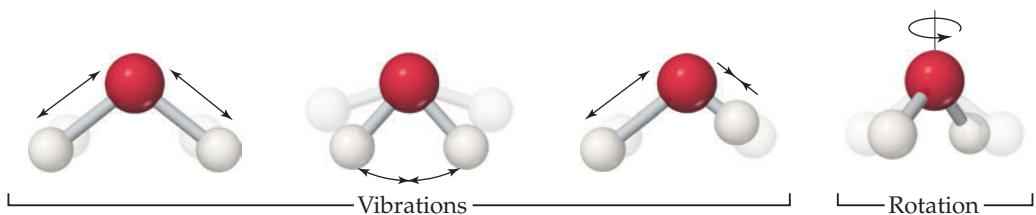


▲ **Figure 19.7** Ludwig Boltzmann's gravestone. Boltzmann's gravestone in Vienna is inscribed with his famous relationship between the entropy of a state,  $S$ , and the number of available microstates,  $W$ . (In Boltzmann's time, "log" was used to represent the natural logarithm.)



### Go Figure

Describe another possible rotational motion for this molecule.



▲ Figure 19.8 Vibrational and rotational motions in a water molecule.

The vibrational and rotational motions possible in real molecules lead to arrangements that a single atom cannot have. A collection of real molecules therefore has a greater number of possible microstates than does the same number of ideal-gas particles. In general, *the number of microstates possible for 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 kinetic energies of the molecules making up the system*. We will also see that the number of microstates increases as the complexity of the molecule increases because there are more vibrational motions available.

Chemists have several ways of describing an increase in the number of microstates possible for a system and therefore an increase in the entropy for the system. Each way seeks to capture a sense of the increased freedom of motion that causes molecules to spread out when not restrained by physical barriers or chemical bonds.

The most common way of describing an increase in entropy is the increase in the *randomness*, or *disorder*, of the system. Another way likens an entropy increase 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 description (randomness or energy dispersal) is conceptually helpful if applied correctly.

### Making Qualitative Predictions about $\Delta S$

It is usually not difficult to estimate qualitatively how the entropy of a system changes during a simple process. As noted earlier, an increase in either the temperature or the volume of a system leads to an increase in the number of microstates, and hence an increase in the entropy. One more factor that correlates with number of microstates is the number of independently moving particles.

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 volume, there is an increase in their freedom of motion, giving rise to a greater number of possible microstates, and hence an increase in entropy.

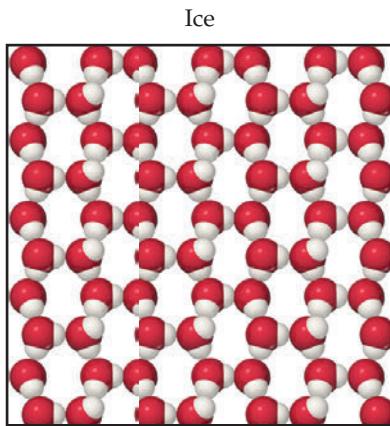
Now consider the phases of water. In ice, hydrogen bonding leads to the rigid structure shown in Figure 19.9. Each molecule in the ice is free to vibrate, but its translational and rotational motions are much more restricted than in liquid water. Although there are hydrogen bonds in liquid water, the molecules can more readily move about relative to one another (translation) and tumble around (rotation). During melting, therefore, the number of possible microstates increases, and so does the entropy. In water vapor, the molecules are essentially independent of one another and have their full range of translational, vibrational, and rotational motions. Thus, water vapor has an even greater number of possible microstates and therefore a higher entropy than liquid water or ice.

When an ionic solid dissolves in water, a mixture of water and ions replaces the pure solid and pure water, as shown for KCl in Figure 19.10. The ions in the solution move in a volume that is larger than the volume in which they were able to move in

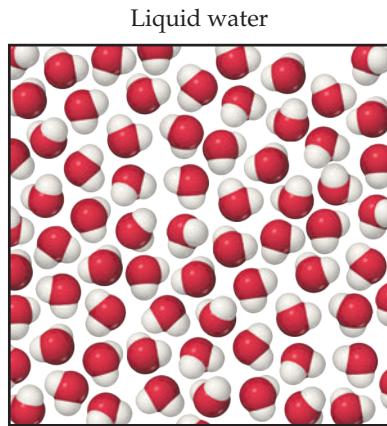

**Go Figure**

In which phase are water molecules least able to have rotational motion?

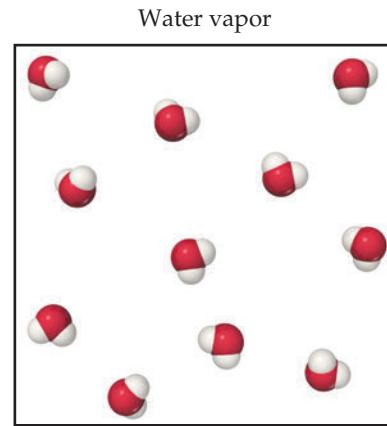
Increasing entropy



Rigid, crystalline structure  
Motion restricted to **vibration** only  
Smallest number of microstates



Increased freedom with respect to **translation**  
Free to **vibrate** and **rotate**  
Larger number of microstates



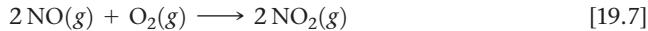
Molecules spread out, essentially independent of one another  
Complete freedom for **translation**, **vibration**, and **rotation**  
Largest number of microstates

▲ **Figure 19.9 Entropy and the phases of water.** The larger the number of possible microstates, the higher the entropy of the system.

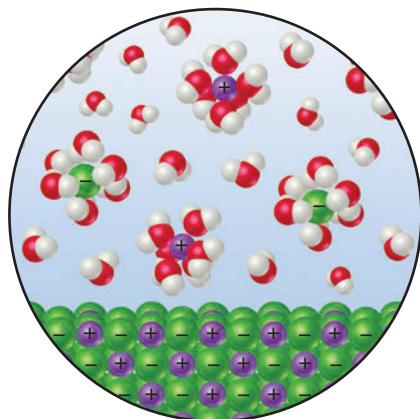
the crystal lattice and so undergo more motion. This increased motion might lead us to conclude that the entropy of the system has increased. We have to be careful, however, because some of the water molecules have lost some freedom of motion because they are now held around the ions as water of hydration. These water molecules are in a *more* ordered state than before because they are now confined to the immediate environment of the ions. Therefore, the dissolving of a salt involves both a disordering process (the ions become less confined) and an ordering process (some water molecules become more confined). The disordering processes are usually dominant, and so the overall effect is an increase in the randomness of the system when most salts dissolve in water.

Now, imagine arranging biomolecules into a highly organized biochemical system, such as the nucleosome in the opening figure of section 19.1. We might expect that the creation of this well-ordered structure would lead to a decrease in the entropy of the system. But this is frequently not the case. Waters of hydration and counterions can be expelled from the interface as two large biomolecules interact, and so the entropy of the system can actually increase—if you consider the water and counterions to be part of the system.

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



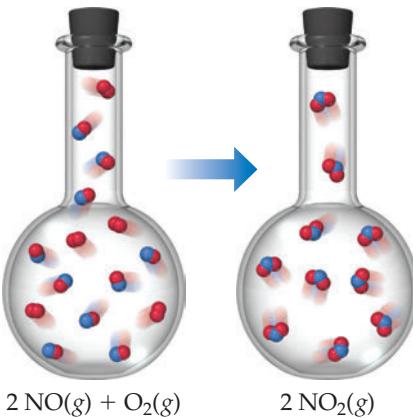
which results in a decrease in the number of molecules—three molecules of gaseous reactants form two molecules of gaseous products (Figure 19.11). The formation of new N—O bonds reduces the motions of the atoms in the system. The formation of new bonds decreases the *number of degrees of freedom*, or 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 possible microstates and therefore a decrease in the entropy of the system.



▲ **Figure 19.10 Entropy changes when an ionic solid dissolves in water.** The ions become more spread out and disordered, but the water molecules that hydrate the ions become less disordered.

 Go Figure

What major factor leads to a decrease in entropy as this reaction takes place?



**▲ Figure 19.11** Entropy decreases when  $\text{NO}(g)$  is oxidized by  $\text{O}_2(g)$  to  $\text{NO}_2(g)$ . A decrease in the number of gaseous molecules leads to a decrease in the entropy of the system.

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

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

### 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 motion decreases. As less energy is stored, the entropy of the system decreases because it has fewer and fewer microstates available. 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**:

*The entropy of a pure, perfect crystalline substance at absolute zero is zero:  $S(0\text{ K}) = 0$ .*

Consider a pure, perfect crystalline solid. At absolute zero, the individual atoms or molecules in the lattice would be perfectly ordered in position. Because none of them would have thermal motion, there is only one possible microstate. As a result, Equation 19.5 becomes  $S = k \ln W = k \ln 1 = 0$ . 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. This means that the degrees of freedom and the entropy both increase. What happens to the entropy, however, as we continue to heat the crystal? We consider this important question in the next section.

### Sample Exercise 19.3

#### Predicting the Sign of $\Delta S$

Predict whether  $\Delta S$  is positive or negative for each process, 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 reactions and asked to predict the sign of  $\Delta S$  for each.

**Plan** We expect  $\Delta S$  to be positive if there is an increase in temperature, increase in volume, or increase in number of gas particles. The question states that the temperature is constant, and so we need to concern ourselves only with volume and number of particles.

#### Solve

- (a) Evaporation involves a large increase in volume as liquid changes to gas. 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, an increase in motional freedom accompanies vaporization and  $\Delta S$  is positive.
- (b) In this process, 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,  $\Delta S$  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  $\text{O}_2$  gas is converted into part of the solid product  $\text{Fe}_2\text{O}_3$ ,  $\Delta S$  is negative.
- (d) The number of moles of reactant gases is the same as the number of moles of product gases, and so the entropy change is expected to be small. The sign of  $\Delta S$  is impossible to predict based on our discussions thus far, but we can predict that  $\Delta S$  will be close to zero.

#### ► Practice Exercise

Indicate whether each process 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)  $2 \text{SO}_2(g) + \text{O}_2(g) \longrightarrow 2 \text{SO}_3(g)$



## Sample Exercise 19.4

### Predicting Relative Entropies

In each pair, choose the system that has greater entropy 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** We examine the state of each system and the complexity of the molecules it contains.

**Solve** (a) HCl(g) has the higher entropy because the particles in gases are more disordered and have more freedom of motion than the particles in solids. (b) When these two systems are at the same pressure, 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. (c) The HCl system has the higher entropy because the number of ways in which an HCl molecule can store energy is greater than the number of ways in which an Ar atom can store energy. (Molecules can rotate and vibrate; atoms cannot.)

### ► Practice Exercise

Choose the system with the greater entropy in each case:

- (a) 1 mol of H<sub>2</sub>(g) at STP or 1 mol of SO<sub>2</sub>(g) at STP, (b) 1 mol of N<sub>2</sub>O<sub>4</sub>(g) at STP or 2 mol of NO<sub>2</sub>(g) at STP.

## CHEMISTRY AND LIFE Entropy and Human Society

Any living organism is a complex, highly organized, well-ordered system, even at the molecular level like the nucleosome we saw at the beginning of section 19.1. Our entropy content is much lower than it would be if we were completely decomposed into carbon dioxide, water, and several other simple chemicals. Does this mean that life is a violation of the second law? No, because the thousands of chemical reactions necessary to produce and maintain life have caused a large increase in the entropy of the rest of the universe. Thus, as the second law requires, the overall entropy change during the lifetime of a human, or any other living system, is positive.

The second law of thermodynamics applies also to the way we humans order our surroundings. In addition to being complex living systems ourselves, we are masters of producing order in the world around us. We manipulate and order matter at the nanoscale level in order to produce the technological breakthroughs that have become

so commonplace in the twenty-first century. We use tremendous quantities of raw materials to produce highly ordered materials. In so doing, we expend a great deal of energy to, in essence, “fight” the second law of thermodynamics.

For every bit of order we produce, however, we produce an even greater amount of disorder. Petroleum, coal, and natural gas are burned to provide the energy necessary for us to achieve highly ordered structures, but their combustion increases the entropy of the universe by releasing CO<sub>2</sub>(g), H<sub>2</sub>O(g), and heat. Thus, even as we strive to create more impressive discoveries and greater order in our society, we drive the entropy of the universe higher, as the second law says we must.

We humans are, in effect, using up our storehouse of energy-rich materials to create order and advance technology. As noted in Chapter 5, we must learn to harness new energy sources, such as solar energy and thereby reduce our dependence on nonrenewable sources.

## Self-Assessment Exercises

- 19.12** What is the entropy of a system that has only a single microstate?
- (a)  $S = 0 \text{ J/K}$
  - (b)  $S = 1 \text{ J/K}$
  - (c)  $S = 6.02 \times 10^{23} \text{ J/K}$
- 19.13** Can an argon atom undergo vibrational motion?
- (a) Yes
  - (b) No
- 19.14** Predict the sign of  $\Delta S$  for the oxidation of glucose at constant temperature: C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>(s) + 6O<sub>2</sub>(g) → 6CO<sub>2</sub>(g) + 6H<sub>2</sub>O(g)
- (a)  $\Delta S > 0$
  - (b)  $\Delta S < 0$

## Exercises

- 19.15** (a) What is the difference between a *state* and a *microstate* of a system? (b) As a system goes from state A to state B, its entropy decreases. What can you say about the number of microstates corresponding to each state? (c) In a particular

spontaneous process, the number of microstates available to the system decreases. What can you conclude about the sign of  $\Delta S_{\text{surr}}$ ?

- 19.16** (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.
- 19.17** (a) In a chemical reaction, two gases combine to form a solid. What do you expect for the sign of  $\Delta S$ ? (b) How does the entropy of the system change in the processes described in Exercise 19.2?
- 19.18** Does the entropy of the system increase, decrease, or stay the same 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?
- 19.19** Indicate whether each statement is true or false. (a) Unlike enthalpy, where we can only ever know changes in  $H$ , we can know absolute values of  $S$ . (b) If you heat a gas such as CO<sub>2</sub>, you will increase its degrees of translational, rotational and vibrational motions. (c) CO<sub>2</sub>(g) and Ar(g) have

nearly the same molar mass. At a given temperature, they will have the same number of microstates.

- 19.20** For each of the following pairs, predict which substance possesses the larger entropy per mole: (a) 1 mol of O<sub>2</sub>(g) at 300 °C, 1.013 kPa, or 1 mol of O<sub>3</sub>(g) at 300 °C, 1.013 kPa; (b) 1 mol of H<sub>2</sub>O(g) at 100 °C, 101.3 kPa, or 1 mol of H<sub>2</sub>O(l) at 100 °C, 101.3 kPa; (c) 0.5 mol of N<sub>2</sub>(g) at 298 K, 20-L volume, or 0.5 mol CH<sub>4</sub>(g) at 298 K, 20-L volume; (d) 100 g Na<sub>2</sub>SO<sub>4</sub>(s) at 30 °C or 100 g Na<sub>2</sub>SO<sub>4</sub>(aq) at 30 °C.
- 19.21** Predict the sign of  $\Delta S_{\text{sys}}$  for each of the following processes: (a) Gaseous H<sub>2</sub> reacts with liquid palmitoleic acid (C<sub>16</sub>H<sub>30</sub>O<sub>2</sub>, unsaturated fatty acid) to form liquid palmitic acid (C<sub>16</sub>H<sub>32</sub>O<sub>2</sub> saturated fatty acid). (b) Liquid palmitic acid solidifies at 1 °C to solid palmitic acid. (c) Silver chloride precipitates upon mixing AgNO<sub>3</sub>(aq) and NaCl(aq). (d) Gaseous H<sub>2</sub> dissociates in an electric arc to form gaseous H atoms (used in atomic hydrogen welding).

19.12 (a)    19.13 (b)    19.14 (a)

### Answers to Self-Assessment Exercises



## 19.4 | Entropy Changes in Chemical Reactions



Some reactions, such as the burning of jet fuel to give gaseous products, have an obvious entropy change associated with them, but can we measure entropy changes in all chemical reactions?

By the end of this section, you should be able to

- Use standard molar entropy values to calculate the entropy change of a chemical reaction.

In Section 5.5, we discussed how calorimetry can be used to measure  $\Delta H$  for chemical reactions. No comparable method exists for measuring  $\Delta S$  for a reaction. However, because the third law establishes a zero point for entropy, we can use experimental measurements to determine the *absolute value of the entropy*,  $S$ . To see schematically how this is done, let's review in greater detail the variation in the entropy of a substance with temperature.

## Temperature Variation of Entropy

We know that the entropy of a pure, perfect crystalline solid at 0 K is zero and that the entropy increases as the temperature of the crystal is increased. **Figure 19.12** shows that the entropy of the solid increases steadily with increasing temperature up to the melting point of the solid. When the solid melts, the atoms or molecules are free to move about the entire volume of the sample. The added degrees of freedom increase the randomness of the substance, thereby increasing its entropy. We therefore see a sharp increase in the entropy at the melting point. After all the solid has melted, the temperature again increases and with it, the entropy.

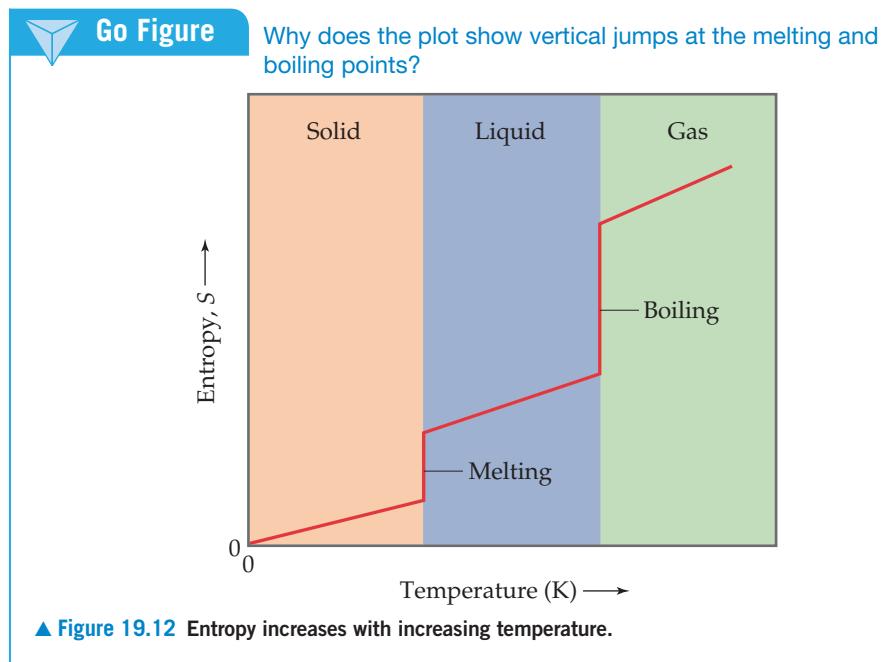
At the boiling point of the liquid, another abrupt increase in entropy occurs. We can understand this increase as resulting from the increased volume available to the atoms or molecules as they enter the gaseous state. When the gas is heated further, the entropy increases steadily as more energy is stored in the translational motion of the gas atoms or molecules.

Another change occurring at higher temperatures is the skewing of molecular speeds toward higher values (Figure 10.12(a)). The expansion of the range of speeds leads to increased kinetic energy and increased disorder and, hence, increased entropy. The conclusions we reach in examining Figure 10.12 are consistent with what we noted earlier: Entropy generally increases with increasing temperature because the increased motional energy leads to a greater number of possible microstates.

Entropy versus temperature graphs such as Figure 19.12 can be obtained by carefully measuring how the heat capacity of a substance varies with temperature, and we can use the data to obtain the absolute entropies at different temperatures. (The theory and methods used for these measurements and calculations are beyond the scope of this text.) Entropies are usually tabulated as molar quantities, in units of joules per mole kelvin (J/mol K).

## Standard Molar Entropies

Molar entropies for substances in their standard states are known as **standard molar entropies** and denoted  $S^\circ$ . The standard state for any substance is defined as the pure



**TABLE 19.1 Standard Molar Entropies of Selected Substances at 298 K**

Substance	$S^\circ$ (J/mol K)
$\text{H}_2(g)$	130.6
$\text{N}_2(g)$	191.5
$\text{O}_2(g)$	205.0
$\text{H}_2\text{O}(g)$	188.8
$\text{NH}_3(g)$	192.5
$\text{CH}_3\text{OH}(g)$	237.6
$\text{C}_6\text{H}_6(g)$	269.2
$\text{H}_2\text{O}(l)$	69.9
$\text{CH}_3\text{OH}(l)$	126.8
$\text{C}_6\text{H}_6(l)$	172.8
$\text{Li}(s)$	29.1
$\text{Na}(s)$	51.4
$\text{K}(s)$	64.7
$\text{Fe}(s)$	27.23
$\text{FeCl}_3(s)$	142.3
$\text{NaCl}(s)$	72.3

substance at 1 atm pressure. **Table 19.1** lists the values of  $S^\circ$  for a number of substances at 298 K; Appendix C gives a more extensive list.

We can make several observations about the  $S^\circ$  values in Table 19.1:

1. Unlike enthalpies of formation, 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 19.12.
3. Standard molar entropies generally increase with increasing molar mass.
4. Standard molar entropies generally increase with an increasing number of atoms in the formula of a substance.

Point 4 is related to the molecular motion discussed in Section 19.3. In general, as the number of atoms increases, the number of possible microstates also increases. **Figure 19.13** compares the standard molar entropies of three hydrocarbons in the gas phase. Notice how the entropy increases as the number of atoms in the molecule increases.

### Calculating the Standard Entropy Change for a Reaction

The entropy change in a chemical reaction equals the sum of the entropies of the products minus 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 balanced chemical equation for the reaction.

### 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 for any system 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 depends 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

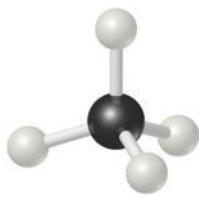
$$\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T} = \frac{-q_{\text{sys}}}{T}$$

Because in a constant-pressure process,  $q_{\text{sys}}$  is simply the enthalpy change for the reaction,  $\Delta H$ , we can write

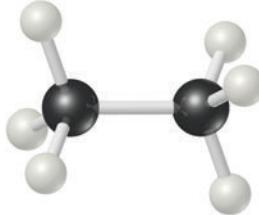
$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T} \quad [\text{at constant P}] \quad [19.9]$$

### Go Figure

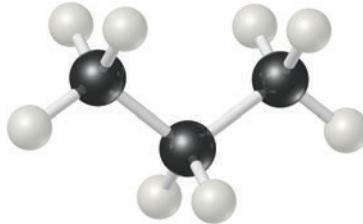
What might you expect for the value of  $S^\circ$  for butane,  $\text{C}_4\text{H}_{10}$ ?



Methane,  $\text{CH}_4$   
 $S^\circ = 186.3 \text{ J/mol K}$



Ethane,  $\text{C}_2\text{H}_6$   
 $S^\circ = 229.6 \text{ J/mol K}$



Propane,  $\text{C}_3\text{H}_8$   
 $S^\circ = 270.3 \text{ J/mol K}$

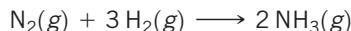
▲ **Figure 19.13** Entropy increases with increasing molecular complexity.



## Sample Exercise 19.5

### Calculating $\Delta S^\circ$ from Tabulated Entropies

Calculate the change in the standard entropy of the system,  $\Delta S^\circ$ , for the synthesis of ammonia from  $\text{N}_2(g)$  and  $\text{H}_2(g)$  at 298 K:



#### SOLUTION

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

**Plan** We can make this calculation using Equation 19.8 and the standard molar entropy values in Table 19.1 and Appendix C.

#### Solve

Using Equation 19.8, we have:

$$\Delta S^\circ = 2 S^\circ(\text{NH}_3) - [S^\circ(\text{N}_2) + 3 S^\circ(\text{H}_2)]$$

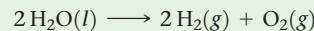
Substituting the appropriate  $S^\circ$  values from Table 19.1 yields:

$$\begin{aligned} \Delta S^\circ &= (2 \text{ mol})(192.5 \text{ J/mol K}) - [(1 \text{ mol})(191.5 \text{ J/mol K}) \\ &\quad + (3 \text{ mol})(130.6 \text{ J/mol K})] \\ &= -198.3 \text{ J/K} \end{aligned}$$

**Check:** The value for  $\Delta S^\circ$  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 molar entropies in Appendix C, calculate the standard entropy change,  $\Delta S^\circ$ , for the “water-splitting” reaction at 298 K:



- (a) 326.3 J/K (b) 265.7 J/K (c) 163.2 J/K (d) 88.5 J/K  
(e) -326.3 J/K

For the ammonia synthesis reaction in Sample Exercise 19.5,  $q_{\text{sys}}$  is the enthalpy change for the reaction under standard conditions,  $\Delta H^\circ$ , so the changes in entropy will be standard entropy changes,  $\Delta S^\circ$ . Therefore, using the procedures described in Section 5.7, we have

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

The negative value tells us that at 298 K the formation of ammonia from  $\text{H}_2(g)$  and  $\text{N}_2(g)$  is exothermic. The surroundings absorb the heat given off by the system, which means 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, calculated as -198.3 J/K in Sample Exercise 19.5.

The overall entropy change for the reaction is

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

Because  $\Delta S_{\text{univ}}^\circ$  is positive for any spontaneous reaction, this calculation indicates that when  $\text{NH}_3(g)$ ,  $\text{H}_2(g)$ , and  $\text{N}_2(g)$  are together at 298 K in their standard states (each at 101.3 kPa pressure), the reaction moves spontaneously toward formation of  $\text{NH}_3(g)$ .

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 15.5.

## Self-Assessment Exercise

- 19.22** If a process (the system) is exothermic, what happens to the entropy of the surroundings?
- It always increases

- It always decreases
- It sometimes increases and sometimes decreases, depending on the process

## Exercises

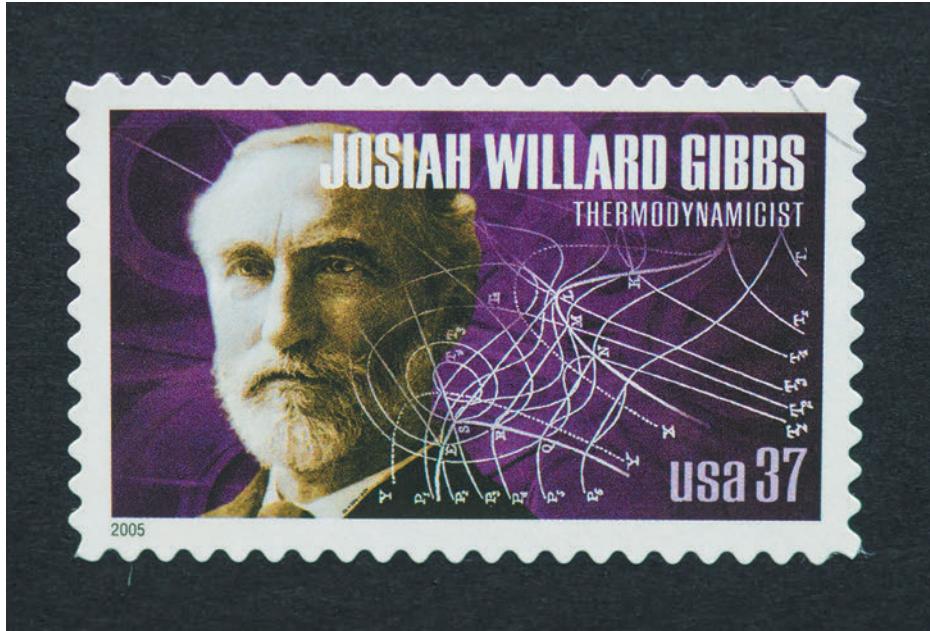
- 19.23** Propanol ( $C_3H_7OH$ ) melts at  $-126.5\text{ }^\circ C$  and boils at  $97.4\text{ }^\circ C$ . Sketch how the entropy changes as propanol is heated from  $-150\text{ }^\circ C$  to  $150\text{ }^\circ C$  at  $101.3\text{ kPa}$ . (Use Figure 19.12 as a model.)
- 19.24** In each of the following pairs, which compound would you expect to have the higher standard molar entropy: (a)  $C_3H_8(g)$  or  $C_4H_{10}(g)$ , (b)  $C_4H_{10}(l)$  or  $C_4H_{10}(g)$ .
- 19.25** Predict which member of each of the following pairs has the greater standard entropy at  $25^\circ C$ : (a)  $C_6H_6(l)$  or  $C_6H_6(g)$ , (b)  $CO(g)$  or  $CO_2(g)$ , (c) 1 mol  $N_2O_4(g)$  or 2 mol  $NO_2(g)$ , (d)  $HCl(g)$  or  $HCl(aq)$ . Use Appendix C to find the standard entropy of each substance.

- 19.26** Three of the forms of elemental carbon are graphite, diamond, and buckminsterfullerene. The entropies at  $298\text{ K}$  for graphite and diamond are listed in Appendix C. (a) Account for the difference in the  $S^\circ$  values of graphite and diamond in light of their structures (Figure 12.29, p. 586). (b) What would you expect for the  $S^\circ$  value of buckminsterfullerene (Figure 12.48, p. 601) relative to the values for graphite and diamond? Explain.
- 19.27** Calculate  $\Delta S^\circ$  values for the following reactions by using tabulated  $S^\circ$  values from Appendix C. In each case, explain the sign of  $\Delta S^\circ$ .
- $2 C_2H_4(g) \longrightarrow C_2H_6(g) + C_2H_2(g)$
  - $Si(s) + 2 Cl_2(g) \longrightarrow SiCl_4(l)$
  - $PbCO_3(s) \longrightarrow PbO(s) + CO_2(g)$
  - $2 H_2S(g) + 3 O_2(g) \longrightarrow 2 SO_2(g) + 2 H_2O(g)$

19.22 (a)

Answers to Self-Assessment Exercise

## 19.5 | Gibbs Free Energy



Josiah Willard Gibbs (1839–1902) was the first person to be awarded a PhD 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.

By the end of this section, you should be able to

- Perform calculations involving Gibbs free energy
- Use the Gibbs free energy to predict if a reaction is spontaneous

We have seen examples of endothermic processes that are spontaneous, such as the dissolution of ammonium nitrate in water. We learned in our discussion of the solution process that a spontaneous process that is endothermic 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. 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.

How can we use  $\Delta H$  and  $\Delta S$  to predict whether a given reaction occurring at constant temperature and pressure will be spontaneous? The means for doing so was first developed by J. Willard Gibbs who proposed a new state function, the **Gibbs free energy** (or just **free energy**)\*,  $G$ , and defined as

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

where  $T$  is the absolute temperature. For an isothermal process, the change in the free energy of the system,  $\Delta G$ , is

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

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

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

where Equation 19.9 substitutes for  $\Delta S_{\text{surr}}$ . Multiplying both sides by  $-T$  gives

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

Comparing Equations 19.11 and 19.13, we see that in a process occurring at constant temperature and pressure, the free-energy change,  $\Delta G$ , is equal to  $-T\Delta S_{\text{univ}}$ . We know that for spontaneous processes,  $\Delta S_{\text{univ}}$  is always positive and, therefore,  $-T\Delta S_{\text{univ}}$  is always negative. Thus, the sign of  $\Delta G$  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  $\Delta G$  and the spontaneity of a reaction is:

- If  $\Delta G < 0$ , the reaction is spontaneous in the forward direction.
- If  $\Delta G = 0$ , the reaction is at equilibrium.
- If  $\Delta G > 0$ , the reaction is nonspontaneous in the forward direction (work must be done to make it occur) but the reverse reaction is spontaneous.

It is more convenient to use  $\Delta G$  as a criterion for spontaneity than to use  $\Delta S_{\text{univ}}$  because  $\Delta G$  relates to the system alone and avoids the complication of having to examine the surroundings.

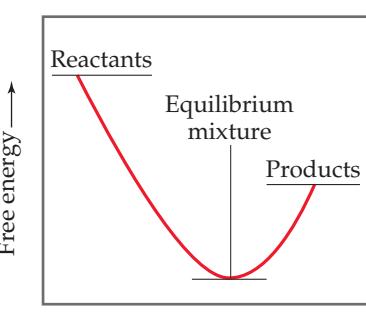
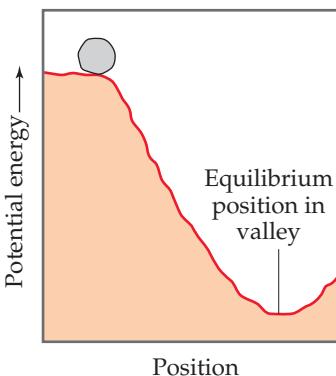
An analogy is often drawn between the free-energy change during a spontaneous reaction and the potential-energy change when a boulder rolls down a hill (**Figure 19.14**).

\*Although IUPAC convention now assigns Gibbs energy as the preferred name for Gibbs free energy or free energy, all three terms are in common usage.

In some countries *Gibbs free energy*  $G$  is also called “free enthalpy” (Germany: “*freie Enthalpie G*”; France “*enthalpie libre G*”)

### Go Figure

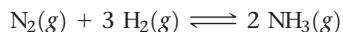
Are the processes that move a system toward equilibrium spontaneous or nonspontaneous?



**▲ Figure 19.14 Potential energy and free energy.** An analogy is shown between the gravitational potential-energy change of a boulder rolling down a hill and the free-energy change in a spontaneous reaction. Free energy always decreases in a spontaneous process when pressure and temperature are held constant.

Potential energy in a gravitational field “drives” the boulder until it reaches a state of minimum potential energy in the valley. Similarly, the free energy of a chemical system decreases until it reaches a minimum value. When this minimum is reached, a state of equilibrium exists. *In any spontaneous process carried out at constant temperature and pressure, the free energy always decreases.*

To illustrate 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:

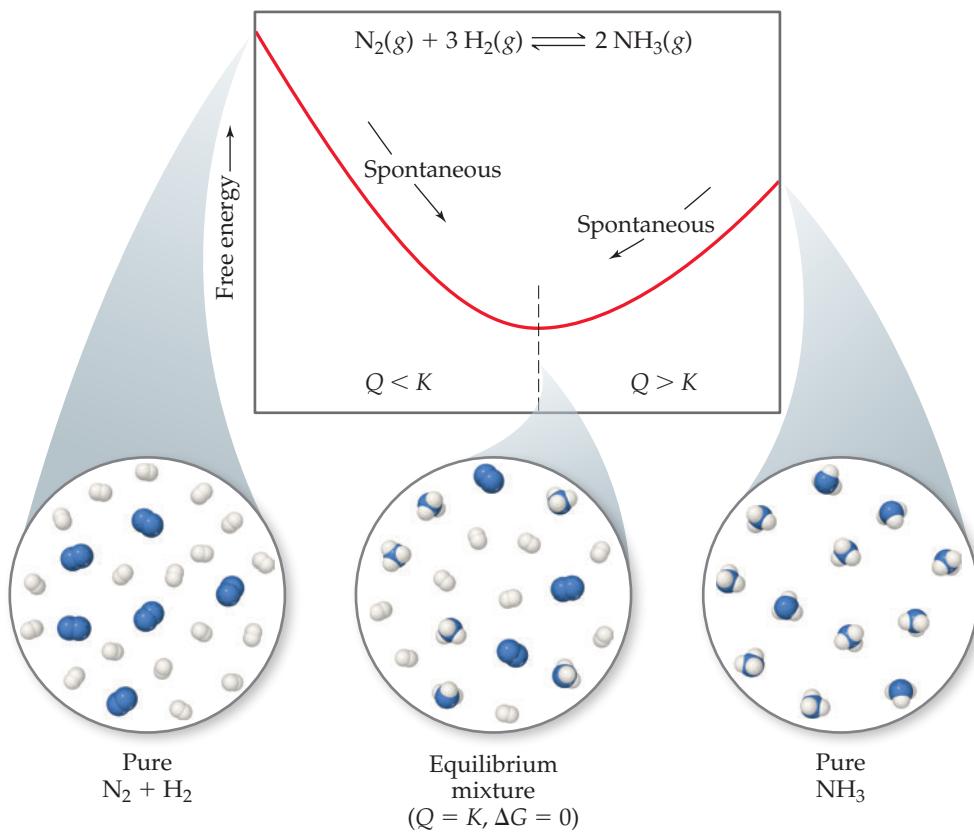


Imagine that we have a reaction vessel that allows us to maintain a constant temperature and pressure and that we have a catalyst that allows the reaction to proceed at a reasonable rate. What happens when we load the vessel with a certain number of moles of  $\text{N}_2$  and three times that number of moles of  $\text{H}_2$ ? As we saw in Figure 15.3, the  $\text{N}_2$  and  $\text{H}_2$  react spontaneously to form  $\text{NH}_3$  until equilibrium is achieved. Similarly, Figure 15.3 shows that if we load the vessel with pure  $\text{NH}_3$ , it decomposes spontaneously to  $\text{N}_2$  and  $\text{H}_2$  until equilibrium is reached. In each case, the free energy of the system gets progressively lower and lower as the reaction moves toward equilibrium, which represents a minimum in the free energy. We illustrate these cases in **Figure 19.15**.

This is a good time to remind ourselves of the significance of the reaction quotient,  $Q$ , for a system that is not at equilibrium. Recall that when  $Q < K$ , there is an excess of

### Go Figure

Why are the spontaneous processes shown sometimes said to be “downhill” in free energy?



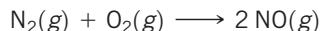
**▲ Figure 19.15** Free energy and approaching equilibrium. In the reaction  $\text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g)$ , if the reaction mixture has too much  $\text{N}_2$  and  $\text{H}_2$  relative to  $\text{NH}_3$  (left),  $Q < K$  and  $\text{NH}_3$  forms spontaneously. If there is more  $\text{NH}_3$  in the mixture relative to the reactants  $\text{N}_2$  and  $\text{H}_2$  (right),  $Q > K$  and the  $\text{NH}_3$  decomposes spontaneously into  $\text{N}_2$  and  $\text{H}_2$ .



## Sample Exercise 19.6

### Calculating Free-Energy Change from $\Delta H^\circ$ , $T$ , and $\Delta S^\circ$

Calculate the standard free-energy change for the formation of  $\text{NO}(g)$  from  $\text{N}_2(g)$  and  $\text{O}_2(g)$  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 conditions?

#### SOLUTION

**Analyze** We are asked to calculate  $\Delta G^\circ$  for the indicated reaction (given  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $T$ ) and to predict whether the reaction is spontaneous under standard conditions at 298 K.

**Plan** To calculate  $\Delta G^\circ$ , 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  $\Delta G^\circ$ .

#### 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  $\Delta G^\circ$  is positive, the reaction is not spontaneous under standard conditions at 298 K.

**Comment** Notice that we converted the units of the  $T\Delta S^\circ$  term to kJ so that they could be added to the  $\Delta H^\circ$  term, whose units are kJ.

#### ► Practice Exercise

Which of these statements is true? (a) All spontaneous reactions have a negative enthalpy change (b) All spontaneous reactions have a positive entropy change (c) All spontaneous reactions have a positive free-energy change (d) All spontaneous reactions have a negative free-energy change (e) All spontaneous reactions have a negative entropy change

reactants relative to products, and the reaction proceeds spontaneously in the forward direction to reach equilibrium, as noted in Figure 19.15. When  $Q > K$ , the reaction proceeds spontaneously in the reverse direction. At equilibrium  $Q = K$ .

## Standard Free Energy of Formation

Recall that we defined *standard enthalpies of formation*,  $\Delta H_f^\circ$ , as the enthalpy change when a substance is formed from its elements under defined standard conditions. We can define **standard free energies of formation**,  $\Delta G_f^\circ$ , in a similar way:  $\Delta G_f^\circ$  for a substance is the free-energy change for its formation from its elements under standard conditions. As is summarized in **Table 19.2**, standard state means 100.0 kPa for gases, the pure solid for solids, and the pure liquid for liquids. 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  $\Delta G$  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, which is the *difference* in free energy between reactants and products.

A listing of standard free energies of formation is given in Appendix C.

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  $\Delta H^\circ$  (Equation 5.31) and  $\Delta S^\circ$  (Equation 19.8):

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

- Perform calculations involving Gibbs free energy
- Use the Gibbs free energy to predict if a reaction is spontaneous

**TABLE 19.2 Conventions Used in Establishing Standard Free Energies**

State of Matter	Standard State
Solid	Pure solid
Liquid	Pure liquid
Gas	100.0 kPa pressure
Solution	1 M concentration
Element	$\Delta G_f^\circ = 0$ for element in standard state



## 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 reaction  $P_4(g) + 6 Cl_2(g) \longrightarrow 4 PCl_3(g)$  at 298 K. (b) What is  $\Delta G^\circ$  for the reverse of this reaction?

#### SOLUTION

**Analyze** We are asked to calculate the free-energy change for a reaction and then to determine the free-energy change for the reverse reaction.

**Plan** 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)  $Cl_2(g)$  is in its standard state, so  $\Delta G_f^\circ$  is zero for this reactant.  $P_4(g)$ , however, is not in its standard state, so  $\Delta G_f^\circ$  is not zero for this reactant. From the balanced equation and values from Appendix C, we have

$$\begin{aligned}\Delta G_{rxn}^\circ &= 4 \Delta G_f^\circ[PCl_3(g)] - \Delta G_f^\circ[P_4(g)] - 6 \Delta G_f^\circ[Cl_2(g)] \\ &= (4 \text{ mol})(-269.6 \text{ kJ/mol}) - (1 \text{ mol})(24.4 \text{ kJ/mol}) - 0 \\ &= -1102.8 \text{ kJ}\end{aligned}$$

That  $\Delta G^\circ$  is negative tells us that a mixture of  $P_4(g)$ ,  $Cl_2(g)$ , and  $PCl_3(g)$  at 25 °C, each present at a partial pressure of

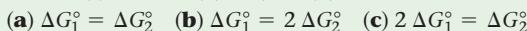
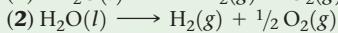
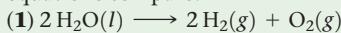
101.3 kPa, would react spontaneously in the forward direction to form more  $PCl_3$ . Remember, however, that the value of  $\Delta G^\circ$  tells us nothing about the rate at which the reaction occurs.

(b) When we reverse the reaction, we reverse the roles of the reactants and products. Thus, reversing the reaction changes the sign of  $\Delta G$  in Equation 19.14, just as reversing the reaction changes the sign of  $\Delta H$ . Hence, using the result from part (a), we have



#### ► Practice Exercise

The following chemical equations describe the same chemical reaction. How do the free energies of these two chemical equations compare?



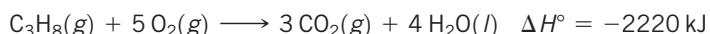
(d) None of these



## Sample Exercise 19.8

### Predicting and Calculating $\Delta G^\circ$

In Section 5.7 we used Hess's law to calculate  $\Delta H^\circ$  for the combustion of propane gas at 298 K:



- (a) Without using data from Appendix C, predict whether  $\Delta G^\circ$  for this reaction is more negative or less negative than  $\Delta H^\circ$ .  
(b) Use data from Appendix C to calculate  $\Delta G^\circ$  for the reaction at 298 K. Is your prediction from part (a) correct?

#### SOLUTION

**Analyze** In part (a) we must predict the value for  $\Delta G^\circ$  relative to that for  $\Delta H^\circ$  on the basis of the balanced equation for the reaction. In part (b) we must calculate the value for  $\Delta G^\circ$  and compare this value 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  $\Delta G^\circ$  is more negative or less negative than  $\Delta H^\circ$ , we need to determine the sign of the term  $T\Delta S^\circ$ . Because  $T$  is the absolute temperature, 298 K, it is always a positive number. We can predict the sign of  $\Delta S^\circ$  by looking at the reaction.

#### Solve

- (a) The reactants are six molecules of gas, and the products are 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 discussed in Section 19.3, we expect a decrease in the number of gas molecules to lead to a decrease in the entropy of the system—the products have fewer possible microstates than the reactants. We therefore expect  $\Delta S^\circ$  and  $T\Delta S^\circ$  to be negative. Because we are subtracting  $T\Delta S^\circ$ , which is a negative number, we predict that  $\Delta G^\circ$  is less negative than  $\Delta H^\circ$ .

(b) Using Equation 19.14 and values from Appendix C, we have

$$\begin{aligned}\Delta G^\circ &= 3 \Delta G_f^\circ[CO_2(g)] + 4 \Delta G_f^\circ[H_2O(l)] \\ &\quad - \Delta G_f^\circ[C_3H_8(g)] - 5 \Delta G_f^\circ[O_2(g)] \\ &= 3 \text{ mol}(-394.4 \text{ kJ/mol}) + 4 \text{ mol}(-237.13 \text{ kJ/mol}) - \\ &\quad 1 \text{ mol}(-23.47 \text{ kJ/mol}) - 5 \text{ mol}(0 \text{ kJ/mol}) = -2108 \text{ kJ}\end{aligned}$$

Notice that we have been careful to use the value of  $\Delta G_f^\circ$  for  $H_2O(l)$ . As in calculating  $\Delta H$  values, the phases of the reactants and products are important. As we predicted,  $\Delta G^\circ$  is less negative than  $\Delta H^\circ$  because of the decrease in entropy during the reaction.

► **Practice Exercise**

If a reaction is exothermic and its entropy change is positive, which statement is true? (a) The reaction is spontaneous at all temperatures (b) The reaction

is nonspontaneous at all temperatures (c) The reaction is spontaneous only at higher temperatures (d) The reaction is spontaneous only at lower temperatures

## 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 consider the sign and magnitude of  $\Delta G$  as exceptionally useful tools in the design of chemical and biochemical reactions. We will see examples of the usefulness of  $\Delta G$  throughout the remainder of this chapter and this text.

When first learning about  $\Delta G$ , two common questions often arise: Why is the sign of  $\Delta G$  an indicator of the spontaneity of reactions? And what is "free" about free energy?

In Section 19.2, we saw that the second law of thermodynamics governs the spontaneity of processes. In order to apply the second law (Equation 19.4), however, we must determine  $\Delta S_{\text{univ}}$ , which is often difficult to evaluate. When  $T$  and  $P$  are constant, however, we can relate  $\Delta S_{\text{univ}}$  to the changes in entropy and enthalpy of just the system by substituting the Equation 19.9 expression for  $\Delta S_{\text{surr}}$  in Equation 19.4:

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

[19.15]

Thus, at constant temperature and pressure, the second law becomes

$$\begin{aligned} \text{Reversible process: } \Delta S_{\text{univ}} &= \Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} = 0 \\ \text{Irreversible process: } \Delta S_{\text{univ}} &= \Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} > 0 \quad [19.16] \\ &\quad (\text{constant } T, P) \end{aligned}$$

Now we can see the relationship between  $\Delta G_{\text{sys}}$  (which we call simply  $\Delta G$ ) and the second law. From Equation 19.11 we know that  $\Delta G = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$ . If we multiply Equations 19.16 by  $-T$  and rearrange, we reach the following conclusion:

$$\begin{aligned} \text{Reversible process: } \Delta G &= \Delta H_{\text{sys}} - T\Delta S_{\text{sys}} = 0 \\ \text{Irreversible process: } \Delta G &= \Delta H_{\text{sys}} - T\Delta S_{\text{sys}} < 0 \quad [19.17] \\ &\quad (\text{constant } T, P) \end{aligned}$$

Equations 19.17 allow us to use the sign of  $\Delta G$  to conclude whether a reaction is spontaneous, nonspontaneous, or at equilibrium. When  $\Delta G < 0$ , a process is irreversible and, therefore, spontaneous. When  $\Delta G = 0$ , the process is reversible and, therefore, at equilibrium. If a process has  $\Delta G > 0$ , then the reverse process will have  $\Delta G < 0$ ; thus, the process as written is nonspontaneous, but its reverse reaction will be irreversible and spontaneous.

The magnitude of  $\Delta G$  is also significant. A reaction for which  $\Delta G$  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  $\Delta G$  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,  $\Delta G$ , 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*:

$$\Delta G = -w_{\text{max}} \quad [19.18]$$

(Remember our sign convention from Table 5.1: Work done by a system is negative.) In other words,  $\Delta G$  gives the theoretical limit to how much work can be done by a process.

The relationship in Equation 19.18 explains why  $\Delta G$  is called the *free* energy change—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, the theoretical maximum work obtained for the combustion of petrol is given by the value of  $\Delta G$  for the combustion reaction. On average, standard internal combustion engines are inefficient in utilizing this potential work—more than 60% of the potential work is lost (primarily as heat) in converting the chemical energy of the petrol to mechanical energy to move the vehicle. When other losses are considered—idling time, braking, aerodynamic drag, and so forth—only about 15% of the potential work from the petrol is used to move the car. Advances in automobile design—such as hybrid technology, and new lightweight materials—have the potential to increase the percentage of useful work obtained from the petrol.

## Self-Assessment Exercises

**19.28** For the reaction  $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$ ,  $\Delta G_f^\circ(\text{NH}_3(g)) = -16.7 \text{ kJ/mol}$ . Calculate the standard free energy change for the reaction.

- (a)  $\Delta G^\circ = -16.7 \text{ kJ}$
- (b)  $\Delta G^\circ = -33.4 \text{ kJ}$
- (c)  $\Delta G^\circ = 16.7 \text{ kJ}$
- (d)  $\Delta G^\circ = 33.4 \text{ kJ}$

**19.29** Is the reaction shown in Exercise 19.28 spontaneous or nonspontaneous in the forward direction?

- (a) Spontaneous
- (b) Nonspontaneous

## Exercises

**19.30** (a) For a process that occurs at constant temperature, does the change in Gibbs free energy depend on changes in the enthalpy and entropy of the system? (b) For a certain process that occurs at constant  $T$  and  $P$ , the value of  $\Delta G$  is positive. Is the process spontaneous? (c) If  $\Delta G$  for a process is large, is the rate at which it occurs fast?

**19.31** A certain reaction has  $\Delta H^\circ = +20.0 \text{ kJ}$  and  $\Delta S^\circ = +100.0 \text{ J/K}$ . (a) Does the reaction lead to an increase or decrease in the randomness or disorder of the system? (b) Does the reaction lead to an increase or decrease in the randomness or disorder of the surroundings? (c) Calculate  $\Delta G^\circ$  for the reaction at 298 K. (d) Is the reaction spontaneous at 298 K under standard conditions?

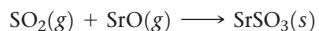
**19.32** Use data in Appendix C to calculate  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$  at 25 °C for each of the following reactions.

- (a)  $4 \text{Cr}(s) + 3 \text{O}_2(g) \longrightarrow 2 \text{Cr}_2\text{O}_3(s)$
- (b)  $\text{BaCO}_3(s) \longrightarrow \text{BaO}(s) + \text{CO}_2(g)$
- (c)  $2 \text{P}(s) + 10 \text{HF}(g) \longrightarrow 2 \text{PF}_5(g) + 5 \text{H}_2(g)$
- (d)  $\text{K}(s) + \text{O}_2(g) \longrightarrow \text{KO}_2(s)$

**19.33** 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 at 298 K under standard conditions.

- (a)  $2 \text{Ag}(s) + \text{Cl}_2(g) \longrightarrow 2 \text{AgCl}(s)$
- (b)  $\text{P}_4\text{O}_{10}(s) + 16 \text{H}_2(g) \longrightarrow 4 \text{PH}_3(g) + 10 \text{H}_2\text{O}(g)$
- (c)  $\text{CH}_4(g) + 4 \text{F}_2(g) \longrightarrow \text{CF}_4(g) + 4 \text{HF}(g)$
- (d)  $2 \text{H}_2\text{O}_2(l) \longrightarrow 2 \text{H}_2\text{O}(l) + \text{O}_2(g)$

**19.34** Sulfur dioxide reacts with strontium oxide as follows:



(a) Without using thermochemical data, predict whether  $\Delta G^\circ$  for this reaction is more negative or less negative than  $\Delta H^\circ$ . (b) If you had only standard enthalpy data for this reaction, how would you estimate the value of  $\Delta G^\circ$  at 298 K, using data from Appendix C on other substances?

19.28 (b)    19.29 (a)

Answers to Self-Assessment Exercises



## 19.6 | Free Energy and Temperature



An ice cube melts in the hand, while water in a glass crystallizes when left in a freezer. The transition between solid and liquid phases has a spontaneous direction that depends on temperature. In this section, we discuss the linkage between free energy and temperature.

By the end of this section, you should be able to

- Predict the effect of temperature on spontaneity given  $\Delta H$  and  $\Delta S$ .

Tabulations of  $\Delta G_f^\circ$ , such as those in Appendix C, make it possible to calculate  $\Delta G^\circ$  for reactions at the standard temperature of 25 °C, but we are often interested in examining reactions at other temperatures. To see how  $\Delta G$  is affected by temperature, let's look again at Equation 19.11:

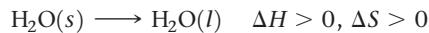
$$\Delta G = \Delta H - T\Delta S = \underset{\text{Enthalpy term}}{\Delta H} + \underset{\text{Entropy term}}{(-T\Delta S)}$$

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

The sign of  $\Delta G$ , which tells us whether a process is spontaneous, depends on the signs and magnitudes of  $\Delta H$  and  $-T\Delta S$ . The various combinations of  $\Delta H$  and  $-T\Delta S$  signs are given in **Table 19.3**.

Note in Table 19.3 that when  $\Delta H$  and  $-T\Delta S$  have opposite signs, the sign of  $\Delta G$  depends on the magnitudes of these two terms. In these instances, temperature is an important consideration. Generally,  $\Delta H$  and  $\Delta S$  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  $-T\Delta S$  increases, and this term becomes relatively more important in determining the sign and magnitude of  $\Delta G$ .

As an example, let's consider once more the melting of ice to liquid water at 101.3 kPa:



This process is endothermic, which means that  $\Delta H$  is positive. Because the entropy increases during the process,  $\Delta S$  is positive, which makes  $-T\Delta S$  negative. At temperatures below 0 °C (273 K), the magnitude of  $\Delta H$  is greater than that of  $-T\Delta S$ . Hence, the positive enthalpy term dominates, and  $\Delta G$  is positive. This positive value of  $\Delta G$  means that ice melting is not spontaneous at  $T < 0$  °C, just as our everyday experience tells us; 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  $T$  increases, so does the magnitude of  $-T\Delta S$ . When  $T > 0$  °C, the magnitude of  $-T\Delta S$  is greater than the magnitude of  $\Delta H$ , which means that the  $-T\Delta S$  term dominates and  $\Delta G$  is negative. The negative value of  $\Delta G$  tells us that ice melting is spontaneous at  $T > 0$  °C.

At the normal melting point of water,  $T = 0$  °C, the two phases are in equilibrium. Recall that  $\Delta G = 0$  at equilibrium; at  $T = 0$  °C,  $\Delta H$  and  $-T\Delta S$  are equal in magnitude and opposite in sign, so they cancel and give  $\Delta G = 0$ .

Our discussion of the temperature dependence of  $\Delta G$  is also relevant to standard free-energy changes. We can calculate the values of  $\Delta H^\circ$  and  $\Delta S^\circ$  at 298 K from the data in Appendix C. If we assume that these values do not change with temperature, we can then use Equation 19.12 to estimate  $\Delta G$  at temperatures other than 298 K.

**TABLE 19.3 How Signs of  $\Delta H$  and  $\Delta S$  Affect Reaction Spontaneity**

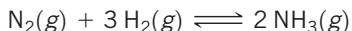
$\Delta H$	$\Delta S$	$-T\Delta S$	$\Delta G = \Delta H - T\Delta S$	Reaction Characteristics	Example
−	+	−	−	Spontaneous at all temperatures	$2 \text{ O}_3(g) \longrightarrow 3 \text{ O}_2(g)$
+	−	+	+	Nonspontaneous at all temperatures	$3 \text{ O}_2(g) \longrightarrow 2 \text{ O}_3(g)$
−	−	+	+ or −	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



For this reaction,  $\Delta H^\circ = -92.38 \text{ kJ}$  and  $\Delta S^\circ = -198.3 \text{ J/K}$ . Assume that  $\Delta H^\circ$  and  $\Delta S^\circ$  for this reaction do not change with temperature. (a) Predict the direction in which  $\Delta G$  for the reaction changes with increasing temperature. (b) Calculate  $\Delta G$  at 25 °C and at 500 °C.

### SOLUTION

**Analyze** In part (a) we are asked to predict the direction in which  $\Delta G$  changes as temperature increases. In part (b) we need to determine  $\Delta G$  for the reaction at two temperatures.

**Plan** We can answer part (a) by determining the sign of  $\Delta S$  for the reaction and then using that information to analyze Equation 19.12. In part (b) we use the given  $\Delta H^\circ$  and  $\Delta S^\circ$  values for the reaction together with Equation 19.12 to calculate  $\Delta G$ .

### Solve

- (a) The temperature dependence of  $\Delta G$  comes from the entropy term in Equation 19.12,  $\Delta G = \Delta H - T\Delta S$ . We expect  $\Delta S$  for this reaction to be negative because the number of molecules of gas is smaller in the products. Because  $\Delta S$  is negative,  $-T\Delta S$  is positive and increases with increasing temperature. As a result,  $\Delta G$  becomes less negative (or more positive) with increasing temperature. Thus, the driving force for the production of  $\text{NH}_3$  becomes smaller with increasing temperature.
- (b) If we assume that the values for  $\Delta H^\circ$  and  $\Delta S^\circ$  do not change with temperature, we can calculate  $\Delta G$  at any temperature by using Equation 19.12. At  $T = 25 \text{ }^\circ\text{C} = 298 \text{ K}$ , 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  $T = 500 \text{ }^\circ\text{C} = 773 \text{ K}$ , we have

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

Notice that we had to convert the units of  $-T\Delta S^\circ$  to kJ in both calculations so that this term can be added to the  $\Delta H^\circ$  term, which has units of kJ.

**Comment** Increasing the temperature from 298 K to 773 K changes  $\Delta G$  from  $-33.3 \text{ kJ}$  to  $+61 \text{ kJ}$ . Of course, the result at 773 K assumes that  $\Delta H^\circ$  and  $\Delta S^\circ$  do not change with temperature. Although these values do change slightly with temperature, the result at 773 K should be a reasonable approximation.

The positive increase in  $\Delta G$  with increasing  $T$  agrees with our prediction in part (a). Our result indicates that in a mixture of  $\text{N}_2(g)$ ,  $\text{H}_2(g)$ , and  $\text{NH}_3(g)$ , each present at a partial pressure of 101.3 kPa, the  $\text{N}_2(g)$  and  $\text{H}_2(g)$  react spontaneously at 298 K to form more  $\text{NH}_3(g)$ . At 773 K, the positive value of  $\Delta G$  tells us that the reverse reaction is spontaneous. Thus, when the mixture of these gases, each at a partial pressure of 101.3 kPa, is heated to 773 K, some of the  $\text{NH}_3(g)$  spontaneously decomposes into  $\text{N}_2(g)$  and  $\text{H}_2(g)$ .

### ► Practice Exercise

What is the temperature above which the Haber ammonia process becomes nonspontaneous?

- (a) 25 °C (b) 47 °C (c) 61 °C (d) 193 °C (e) 500 °C

## Self-Assessment Exercise

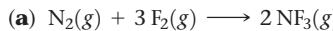
- 19.35** The normal boiling point of toluene is 110 °C. At 100 °C and 101.3 kPa, which term is greater in magnitude for the vaporization of toluene,  $\Delta H_{\text{vap}}$  or  $T\Delta S_{\text{vap}}$ ?

(a)  $\Delta H_{\text{vap}} > T\Delta S_{\text{vap}}$

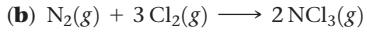
(b)  $T\Delta S_{\text{vap}} > \Delta H_{\text{vap}}$

## Exercises

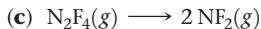
- 19.36** Classify each of the following reactions as one of the four possible types summarized in Table 19.3: (i) spontaneous at all temperatures; (ii) not spontaneous at any temperature; (iii) spontaneous at low  $T$  but not spontaneous at high  $T$ ; (iv) spontaneous at high  $T$  but not spontaneous at low  $T$ .



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



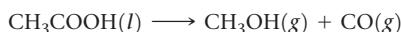
$$\Delta H^\circ = 460 \text{ kJ}; \Delta S^\circ = -275 \text{ J/K}$$



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

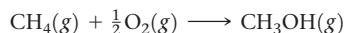
- 19.37** A certain constant-pressure reaction is barely nonspontaneous at 45 °C. The entropy change for the reaction is 72 J/K. Estimate  $\Delta H$ .

- 19.38** Reactions in which a substance decomposes by losing CO are called *decarbonylation* reactions. The decarbonylation of acetic acid proceeds according to:



By using data from Appendix C, calculate the minimum temperature at which this process will be spontaneous under standard conditions. Assume that  $\Delta H^\circ$  and  $\Delta S^\circ$  do not vary with temperature.

- 19.39** Methanol ( $\text{CH}_3\text{OH}$ ) can be made by the controlled oxidation of methane:



(a) Use data in Appendix C to calculate  $\Delta H^\circ$  and  $\Delta S^\circ$  for this reaction. (b) Will  $\Delta G$  for the reaction increase, de-

crease, or stay unchanged with increasing temperature? (c) Calculate  $\Delta G^\circ$  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?

- 19.40** The fuel in high-efficiency natural-gas vehicles consists primarily of methane ( $\text{CH}_4$ ). (a) How much heat is produced in burning 1 mol of  $\text{CH}_4(g)$  under standard conditions if reactants and products are brought to 298 K and  $\text{H}_2\text{O}(l)$  is formed? (b) What is the maximum amount of useful work that can be accomplished under standard conditions by this system?

19.35 (a)

Answers to Self-Assessment Exercise



## 19.7 | Free Energy and the Equilibrium Constant



Standard conditions form an excellent datum from which to work, but often we find ourselves under conditions that are not standard.

In Section 19.5 we saw a special relationship between  $\Delta G$  and equilibrium: For a system at equilibrium,  $\Delta G = 0$ . We have also seen how to use tabulated thermodynamic data to calculate values of the standard free energy change,  $\Delta G^\circ$ . In this final section, we learn two more ways in which we can use free energy to analyze chemical reactions: using  $\Delta G^\circ$  to calculate  $\Delta G$  under *nonstandard* conditions and relating the values of  $\Delta G^\circ$  and  $K$  for a reaction.

By the end of this section, you should be able to:

- Calculate  $\Delta G$  under nonstandard conditions and relate  $\Delta G^\circ$  and equilibrium constant.

### Free Energy under Nonstandard Conditions

The set of standard conditions for which  $\Delta G^\circ$  values pertain is given in Table 19.2. Most chemical reactions occur under nonstandard conditions. For any chemical process, the relationship between the free energy change under standard conditions,  $\Delta G^\circ$ , and the free-energy change under any other conditions,  $\Delta G$ , is given by

$$\Delta G = \Delta G^\circ + RT \ln Q \quad [19.19]$$

In this equation  $R$  is the ideal gas constant,  $8.314 \text{ J/mol K}$ ;  $T$  is the absolute temperature; and  $Q$  is the reaction quotient for the reaction mixture of interest. Recall that the reaction quotient  $Q$  is calculated like an equilibrium constant, except that you use the concentrations at any point of interest in the reaction; if  $Q = K$ , then the reaction is at equilibrium. Under standard conditions, the concentrations of all the reactants and products are equal to  $1 \text{ M}$ . Thus, under standard conditions  $Q = 1$ ,  $\ln Q = 0$ , and Equation 19.19 reduces to  $\Delta G = \Delta G^\circ$  under standard conditions, as it should.

Remember, this does not mean that equilibrium has been established; that occurs when  $\Delta G = 0$ .

When the concentrations of reactants and products are nonstandard, we must calculate  $Q$  in order to determine  $\Delta G$ . We illustrate how this is done in Sample Exercise 19.11. At this stage in our discussion, therefore, it becomes important to note the units used to calculate  $Q$  when using Equation 19.19. The convention used for standard states is used when applying this equation: In determining the value of  $Q$ , the concentrations of gases are always expressed as partial pressures in atmospheres and solutes are expressed as their concentrations in molarities.

## Sample Exercise 19.10

### Relating $\Delta G$ to a Phase Change at Equilibrium

- (a) Write the chemical equation that defines the normal boiling point of liquid tetrachloromethane,  $\text{CCl}_4(l)$ . (b) What is the value of  $\Delta G^\circ$  for the equilibrium in part (a)? (c) Use data from Appendix C and Equation 19.12 to estimate the normal boiling point of  $\text{CCl}_4$ .

### SOLUTION

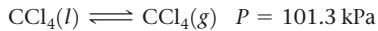
**Analyze** (a) We must write a chemical equation that describes the physical equilibrium between liquid and gaseous  $\text{CCl}_4$  at the normal boiling point. (b) We must determine the value of  $\Delta G^\circ$  for  $\text{CCl}_4$ , in equilibrium with its vapor at the normal boiling point. (c) We must estimate the normal boiling point of  $\text{CCl}_4$ , based on available thermodynamic data.

### Solve

- (a) The normal boiling point is the temperature at which a pure liquid is in equilibrium with its vapor at a pressure of  $101.3 \text{ kPa}$ :

**Plan** (a) The chemical equation is the change of state from liquid to gas. For (b), we need to analyze Equation 19.19 at equilibrium ( $\Delta G = 0$ ), and for (c) we can use Equation 19.12 to calculate  $T$  when  $\Delta G = 0$ .

- (b) At equilibrium,  $\Delta G = 0$ . In any normal boiling point equilibrium, both liquid and vapor are in their standard state of pure liquid and vapor at  $101.3 \text{ kPa}$  (Table 19.2). Consequently,  $Q = 1$ ,  $\ln Q = 0$ , and  $\Delta G = \Delta G^\circ$  for this process. We conclude that  $\Delta G^\circ = 0$  for the equilibrium representing 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.)



$$\Delta G^\circ = 0$$

- (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 need the values of  $\Delta H^\circ$  and  $\Delta S^\circ$  for the  $\text{CCl}_4(l)/\text{CCl}_4(g)$  equilibrium at the normal boiling point to do this calculation. However, we can *estimate* the boiling point by using the values of  $\Delta H^\circ$  and  $\Delta S^\circ$  for the phases of  $\text{CCl}_4$  at  $298 \text{ K}$ , which we obtain from Appendix C and Equations 5.31 and 19.8:

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

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

As expected, the process is endothermic ( $\Delta H > 0$ ) and produces a gas, thus increasing the entropy ( $\Delta S > 0$ ). We 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 that we have used the conversion factor between joules and kilojoules to make the units of  $\Delta H^\circ$  and  $\Delta S^\circ$  match.

**Check** The experimental normal boiling point of  $\text{CCl}_4(l)$  is  $76.5^\circ\text{C}$ . The small deviation of our estimate from the experimental value is due to the assumption that  $\Delta H^\circ$  and  $\Delta S^\circ$  do not change with temperature.

### ► Practice Exercise

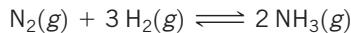
If the normal boiling point of a liquid is  $67^\circ\text{C}$ , and the standard molar entropy change for the boiling process is  $+100 \text{ J/K}$ , estimate the standard molar enthalpy change for the boiling process.

- (a) +6700 J (b) -6700 J (c) +34,000 J (d) -34,000 J

## Sample Exercise 19.11

### Calculating the Free-Energy Change under Nonstandard Conditions

Calculate  $\Delta G$  at  $298 \text{ K}$  for a mixture of  $1.00 \text{ atm}$   $\text{N}_2$ ,  $3.00 \text{ atm}$   $\text{H}_2$ , and  $0.500 \text{ atm}$   $\text{NH}_3$  being used in the Haber process:



### SOLUTION

**Analyze** We are asked to calculate  $\Delta G$  under nonstandard conditions.

**Plan** We can use Equation 19.19 to calculate  $\Delta G$ . Doing so requires that we calculate the value of the reaction quotient  $Q$ .

### Solve

The partial-pressure form of Equation 15.24 gives:

for the specified partial pressures, for which we use the partial pressures form of Equation 15.24 (the equilibrium constant expression). We then use a table of standard free energies of formation to evaluate  $\Delta G^\circ$ .

$$Q = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} P_{\text{H}_2}^3} = \frac{(0.500)^2}{(1.00)(3.00)^3} = 9.26 \times 10^{-3}$$

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 19.19, however. For the units in Equation 19.19 to work out, we will use  $\text{kJ/mol}$  as our units for  $\Delta G^\circ$ , 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  $\text{N}_2$ , per 3 mol of  $\text{H}_2$ , and per 2 mol of  $\text{NH}_3$ .

We now use Equation 19.19 to calculate  $\Delta G$  for these nonstandard conditions:

$$\begin{aligned} \Delta G &= \Delta G^\circ + RT \ln Q \\ &= (-33.3 \text{ kJ/mol}) \\ &\quad + (8.314 \text{ J/mol K})(298 \text{ K})(1 \text{ kJ}/1000 \text{ J}) \ln(9.26 \times 10^{-3}) \\ &= (-33.3 \text{ kJ/mol}) + (-11.6 \text{ kJ/mol}) = -44.9 \text{ kJ/mol} \end{aligned}$$

**Comment** We see that  $\Delta G$  becomes more negative as the pressures of  $\text{N}_2$ ,  $\text{H}_2$ , and  $\text{NH}_3$  are changed from  $1.00 \text{ atm}$  (standard conditions,  $\Delta G^\circ$ ) to  $1.00 \text{ atm}$ ,  $3.00 \text{ atm}$ , and  $0.500 \text{ atm}$ , respectively. The larger negative value for  $\Delta G$  indicates a larger “driving force” to produce  $\text{NH}_3$ .

We would make the same prediction based on Le Châtelier’s principle. Relative to standard conditions, we have increased the pressure of a reactant ( $\text{H}_2$ ) and decreased the pressure of the product ( $\text{NH}_3$ ). Le Châtelier’s principle predicts that both changes shift the reaction to the product side, thereby forming more  $\text{NH}_3$ .

### ► Practice Exercise

Which of the following statements is true? (a) The larger the  $Q$ , the larger the  $\Delta G^\circ$ . (b) If  $Q = 0$ , the system is at equilibrium. (c) If a reaction is spontaneous under standard conditions, it is spontaneous under all conditions. (d) The free-energy change for a reaction is independent of temperature. (e) If  $Q > 1$ ,  $\Delta G > \Delta G^\circ$ .

## Relationship between $\Delta G^\circ$ and K

We can now use Equation 19.19 to derive the relationship between  $\Delta G^\circ$  and the equilibrium constant, K. At equilibrium,  $\Delta G = 0$  and  $Q = K$ . Thus, at equilibrium, Equation 19.19 transforms as follows:

$$\begin{aligned}\Delta G &= \Delta G^\circ + RT \ln Q \\ 0 &= \Delta G^\circ + RT \ln K \\ \Delta G^\circ &= -RT \ln K\end{aligned}\quad [19.20]$$

Equation 19.20 is a very important one, with broad significance in chemistry. By relating K to  $\Delta G^\circ$ , we can also relate K to entropy and enthalpy changes for a reaction.

We can also solve Equation 19.20 for K, to yield an expression that allows us to calculate K if we know the value of  $\Delta G^\circ$ :

$$\begin{aligned}\ln K &= \frac{\Delta G^\circ}{-RT} \\ K &= e^{-\Delta G^\circ/RT}\end{aligned}\quad [19.21]$$

As usual, we must be careful in our choice of units. In Equations 19.20 and 19.21 we again express  $\Delta G^\circ$  in kJ/mol. In the equilibrium expression, we use atmospheres for gas pressures, molarities for solutions; and solids, liquids, and solvents do not appear in the expression. Thus, the equilibrium constant is  $K_p$  for gas-phase reactions and  $K_c$  for reactions in solution.

From Equation 19.20 we see that if  $\Delta G^\circ$  is negative,  $\ln K$  must be positive, which means  $K > 1$ . Therefore, the more negative  $\Delta G^\circ$  is, the larger K is. Conversely, if  $\Delta G^\circ$  is positive,  $\ln K$  is negative, which means  $K < 1$ . Finally, if  $\Delta G^\circ$  is zero,  $K = 1$ .



### Sample Exercise 19.12

#### Calculating an Equilibrium Constant from $\Delta G^\circ$

The standard free-energy change for the Haber process at 25 °C was obtained in Sample Exercise 19.9 for the Haber reaction:



Use this value of  $\Delta G^\circ$  to calculate the equilibrium constant for the process at 25 °C.

#### SOLUTION

**Analyze** We are asked to calculate K for a reaction, given  $\Delta G^\circ$ .

**Plan** We can use Equation 19.21 to calculate K.

**Solve** Remembering to use the absolute temperature for T in Equation 19.21 and the form of R that matches our units, we have

$$K = e^{-\Delta G^\circ/RT} = e^{-(33,300 \text{ J/mol})/(8.314 \text{ J/mol K})(298 \text{ K})} = e^{13.4} = 7 \times 10^5$$

**Comment** This is a large equilibrium constant, which indicates that the product, NH<sub>3</sub>, is greatly favored in the equilibrium mixture at 25 °C. The equilibrium constants for the Haber reaction at temperatures in the range 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<sub>3</sub>.

#### ► Practice Exercise

The  $K_{sp}$  for a very insoluble salt is  $4.2 \times 10^{-47}$  at 298 K.

What is  $\Delta G^\circ$  for the dissolution of the salt in water?

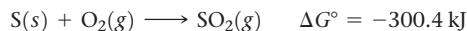
- (a) -265 kJ/mol
- (b) -115 kJ/mol
- (c) -2.61 kJ/mol
- (d) +115 kJ/mol
- (e) +265 kJ/mol

## CHEMISTRY AND LIFE Driving Nonspontaneous Reactions: Coupling 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 *chalocite*, which contains Cu<sub>2</sub>S. The decomposition of Cu<sub>2</sub>S to its elements is nonspontaneous:



Because  $\Delta G^\circ$  is very positive, we cannot obtain 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 S(s) reacting with O<sub>2</sub>(g) to form SO<sub>2</sub>(g):



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



$$\Delta G^\circ = (+86.2 \text{ kJ}) + (-300.4 \text{ kJ}) = -214.2 \text{ kJ}$$

In essence, we have used the spontaneous reaction of S(s) with O<sub>2</sub>(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

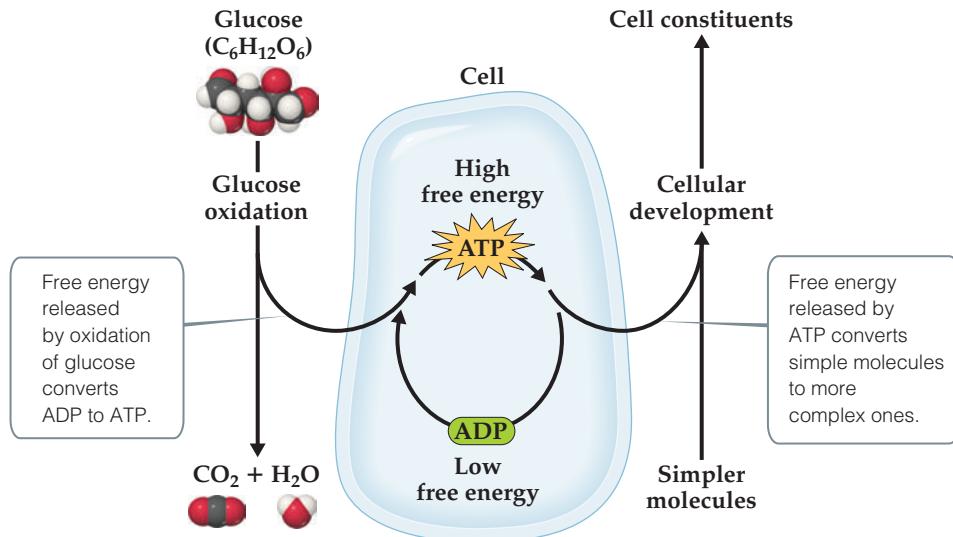
biochemical reactions that are essential for the formation and maintenance of highly ordered biological structures are not spontaneous. These necessary reactions are made to occur by coupling them with spontaneous reactions that release energy. The metabolism of food is the usual source of the free energy needed to do the work of maintaining biological systems. For example, complete oxidation of the sugar glucose, C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>, to CO<sub>2</sub> and H<sub>2</sub>O 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 19.16**, 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.

**Related Exercises: 19.111, 19.112**



▲ **Figure 19.16** Schematic representation of free-energy changes during cell metabolism. The oxidation of glucose to CO<sub>2</sub> and H<sub>2</sub>O 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 drive nonspontaneous reactions, such as the conversion of simple molecules into more complex cell constituents.

## Self-Assessment Exercise

- 19.41** A reaction has a large positive value of  $\Delta G^\circ$ . In what numerical range do you expect the value of  $K$  to be?

- (a)  $K \gg 1$   
 (b)  $0 < K < 1$   
 (c)  $K \ll 0$

## Exercises

**19.42** Indicate whether  $\Delta G$  increases, decreases, or does not change when the partial pressure of  $H_2$  is increased in each of the following reactions:

- (a)  $H_2(g) + NiO(s) \longrightarrow Ni(s) + H_2O(g)$
- (b)  $H_2(g) + S(s) \longrightarrow H_2S(g)$
- (c)  $C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g)$

**19.43** Consider the reaction  $CH_4(g) + 4 Cl_2(g) \longrightarrow CCl_4(g) + 4 HCl(g)$ . (a) Using data from Appendix C, calculate  $\Delta G^\circ$  at 298 K. (b) Calculate  $\Delta G$  at 298 K if the reaction mixture consists of 0.500 atm of  $CH_4(g)$ , 0.250 atm of  $Cl_2(g)$ , 0.100 atm of  $CCl_4(g)$  and 0.150 atm of  $HCl(g)$ .

**19.44** Using data from Appendix C, write the equilibrium-constant expression and calculate the value of the equilibrium constant and the free-energy change for these reactions at 298 K:

- (a)  $NaHCO_3(s) \rightleftharpoons NaOH(s) + CO_2(g)$
- (b)  $2 HBr(g) + Cl_2(g) \rightleftharpoons 2 HCl(g) + Br_2(g)$
- (c)  $2 SO_2(g) + O_2(g) \rightleftharpoons 2 SO_3(g)$

**19.45** Consider the reaction



Using data in Appendix C, calculate the equilibrium pressure of  $CO_2$  in the system at (a) 400 °C and (b) 180 °C.

**19.46** 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  $\Delta G^\circ$  for the equilibrium in part (a). (c) What is the value of  $\Delta G$  at equilibrium? (d) What is the value of  $\Delta G$  when  $[H^+] = 6.7 \times 10^{-9} M$ ,  $[CH_3NH_3^+] = 2.4 \times 10^{-3} M$ , and  $[CH_3NH_2] = 0.098 M$ ?

19.41 (b)

Answers to Self-Assessment Exercise



### 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  $\Delta G^\circ$  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  $\Delta G^\circ$  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  $\Delta G^\circ$  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  $\Delta G^\circ$  values from Appendix C to calculate the  $\Delta G_{soln}^\circ$  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

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

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

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

Salt	$\Delta H_{soln}^\circ$	$\Delta S_{soln}^\circ$	$T\Delta S_{soln}^\circ$
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. 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  $\Delta G_{soln}^\circ$  is dominated by the difference in the values of  $\Delta H_{soln}^\circ$ .

- (c) The solubility product,  $K_{sp}$ , is the equilibrium constant for the solution process. As such, we can relate  $K_{sp}$  directly to  $\Delta G_{\text{soln}}^\circ$  by using Equation 19.21:

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

We can calculate the  $K_{sp}$  values in the same way we applied Equation 19.21 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:

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

$$= e^{+3.7} = 40$$

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

$$= e^{-22.4}$$

$$= 1.9 \times 10^{-10}$$

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.

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  $\Delta S$  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 13.14, we see that the solubility of NaCl (and that of nearly any other salt) increases with increasing temperature.

## Chapter Summary and Key Terms

**SPONTANEOUS PROCESSES (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 a permanent change in the surroundings. Any spontaneous process is irreversible. A process that occurs at a constant temperature is said to be **isothermal**.

**ENTROPY AND THE SECOND LAW OF THERMODYNAMICS (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:  $\Delta S = q_{\text{rev}}/T$ . For any process, the entropy change of the universe equals the entropy change of the system plus the entropy change of the surroundings:  $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$ . The way entropy controls the spontaneity of processes is given by the **second law of thermodynamics**, which states that in an irreversible (spontaneous) process  $\Delta S_{\text{univ}} > 0$ . Entropy values are usually expressed in units of joules per kelvin, J/K.

**THE MOLECULAR INTERPRETATION OF ENTROPY AND THE THIRD LAW OF THERMODYNAMICS (SECTION 19.3)** A particular combination of motions and locations of the atoms and molecules of a system at a particular instant is called a **microstate**. The entropy of a system is a measure of its randomness or disorder. The entropy is related to the number of microstates,  $W$ , corresponding to the state of the system:  $S = k \ln W$ . 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. 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.

### ENTROPY CHANGES IN CHEMICAL REACTIONS (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  $S^\circ$ . From tabulated values of  $S^\circ$ , 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  $-\Delta H/T$ .

**GIBBS FREE ENERGY (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  $\Delta G$  relates to the spontaneity of the process. When  $\Delta G$  is negative, the process is spontaneous. When  $\Delta G$  is positive, the process is nonspontaneous, but the reverse process is spontaneous. At equilibrium the process is reversible and  $\Delta G$  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,  $\Delta G^\circ$ , for any process can be calculated from tabulations of **standard free energies of formation**,  $\Delta G_f^\circ$ , which are defined in a fashion analogous to standard enthalpies of formation,  $\Delta H_f^\circ$ . The value of  $\Delta G_f^\circ$  for a pure element in its standard state is defined to be zero.

**FREE ENERGY, TEMPERATURE, AND THE EQUILIBRIUM CONSTANT (SECTIONS 19.6 AND 19.7)** The values of  $\Delta H$  and  $\Delta S$  for a chemical process generally do not vary much with temperature. Therefore, the dependence of  $\Delta G$  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  $\Delta G$  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,  $\Delta G$  is related to  $\Delta G^\circ$  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.

## Learning Outcomes After studying this chapter, you should be able to:

- Explain and apply the terms spontaneous process, reversible process, irreversible process, and isothermal process. (Section 19.1) *Related Exercises: 19.2, 19.3, 19.57, 19.58*
- Define entropy and state the second law of thermodynamics. (Section 19.2) *Related Exercises: 19.8, 19.63*
- Calculate  $\Delta S$  for a phase change. (Section 19.2) *Related Exercises: 19.9, 19.64*
- Explain how the entropy of a system is related to the number of possible microstates. (Section 19.3) *Related Exercises: 19.15, 19.69*
- Describe the kinds of molecular motion that a molecule can possess. (Section 19.3) *Related Exercise: 19.72*
- Predict the sign of  $\Delta S$  for physical and chemical processes. (Section 19.3) *Related Exercises: 19.18, 19.21, 19.71, 19.74*
- State the third law of thermodynamics. (Section 19.3) *Related Exercise: 19.72*
- Compare the values of standard molar entropies. (Section 19.4) *Related Exercises: 19.24, 19.25, 19.76, 19.77*

- Calculate standard entropy changes for a system from standard molar entropies. (Section 19.4) *Related Exercises: 19.30, 19.80*
- Calculate the Gibbs free energy from the enthalpy change and entropy change at a given temperature. (Section 19.5) *Related Exercises: 19.31, 19.32, 19.81, 19.82*
- Use free-energy changes to predict whether reactions are spontaneous. (Section 19.5) *Related Exercises: 19.31, 19.81*
- Calculate standard free-energy changes using standard free energies of formation. (Section 19.5) *Related Exercises: 19.33, 19.83*
- Predict the effect of temperature on spontaneity given  $\Delta H$  and  $\Delta S$ . (Section 19.6) *Related Exercises: 19.36, 19.39, 19.85, 19.88*
- Calculate  $\Delta G$  under nonstandard conditions. (Section 19.7) *Related Exercises: 19.92, 19.43*
- Relate  $\Delta G^\circ$  and equilibrium constant. (Section 19.7) *Related Exercises: 19.44, 19.45, 19.93, 19.94*

## Key Equations

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

Relating entropy change to the heat absorbed or released in a reversible process

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

The second law of thermodynamics

- $$S = k \ln W$$
 [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

- $$\begin{aligned} \text{Reversible process: } \Delta G &= \Delta H_{\text{sys}} - T\Delta S_{\text{sys}} = 0 \\ \text{Irreversible process: } \Delta G &= \Delta H_{\text{sys}} - T\Delta S_{\text{sys}} < 0 \end{aligned} \quad \left. \right\} \quad [19.17]$$

Relating the free-energy change to the reversibility of a process at constant temperature and pressure

- $$\Delta G = -w_{\text{max}}$$
 [19.18]

Relating the free-energy change to the maximum work a system can perform

- $$\Delta G = \Delta G^\circ + RT \ln Q$$
 [19.19]

Calculating the free-energy change under nonstandard conditions

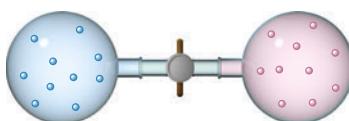
- $$\Delta G^\circ = -RT \ln K$$
 [19.20]

Relating the standard free-energy change and the equilibrium constant

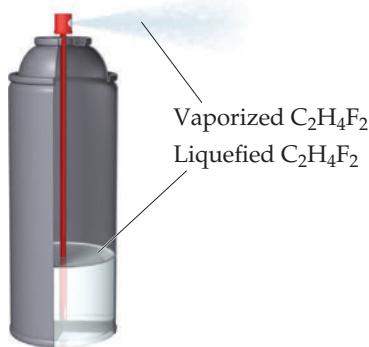
## Exercises

### Visualizing Concepts

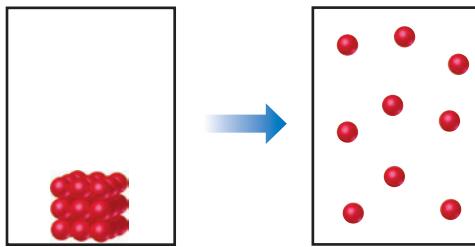
- 19.47** Two different gases occupy the two bulbs shown here. Consider the process that occurs when the stopcock is opened, assuming the gases behave ideally. (a) Draw the final (equilibrium) state. (b) Predict the signs of  $\Delta H$  and  $\Delta S$  for the process. (c) Is the process that occurs 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]



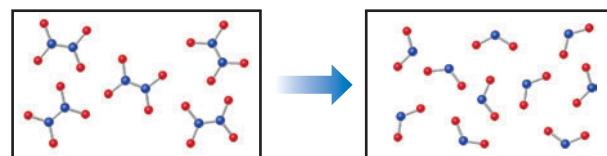
- 19.48** As shown here, one type of computer keyboard cleaner contains liquefied 1,1-difluoroethane ( $C_2H_4F_2$ ), which is a gas at atmospheric pressure. When the nozzle is squeezed, the 1,1-difluoroethane vaporizes out of the nozzle at high pressure, blowing dust out of objects. (a) Based on your experience, is the vaporization a spontaneous process at room temperature? (b) Defining the 1,1-difluoroethane as the system, do you expect  $q_{sys}$  for the process to be positive or negative? (c) Predict whether  $\Delta S$  is positive or negative for this process. (d) Given your answers to (a), (b), and (c), do you think the operation of this product depends more on enthalpy or entropy? [Sections 19.1 and 19.2]



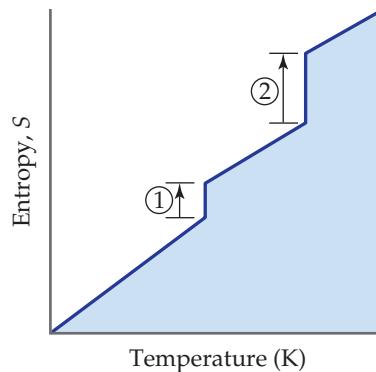
- 19.49** (a) What are the signs of  $\Delta S$  and  $\Delta H$  for the process depicted here? (b) If energy can flow in and out of the system to maintain a constant temperature during the process, what can you say about the entropy change of the surroundings as a result of this process? [Sections 19.2 and 19.5]



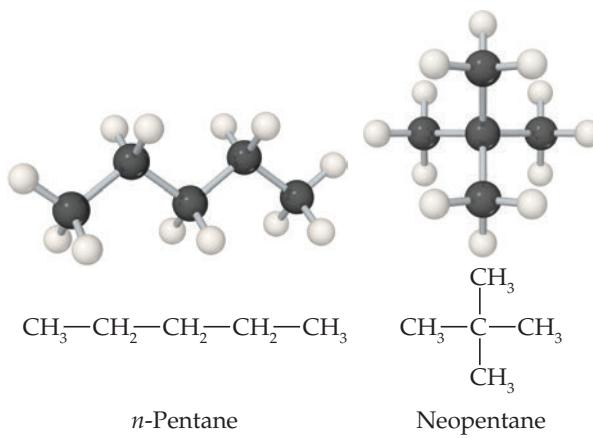
- 19.50** Predict the signs of  $\Delta H$  and  $\Delta S$  for this reaction. Explain your choice. [Section 19.3]



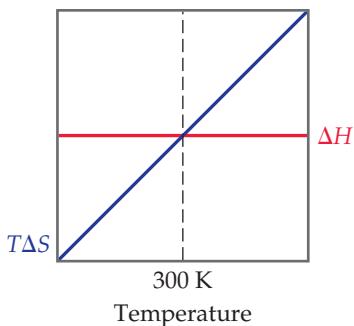
- 19.51** The accompanying diagram shows how entropy varies with temperature for a substance that is a gas at the highest temperature shown. (a) What processes correspond to the entropy increases along the vertical lines labeled 1 and 2? (b) Why is the entropy change for 2 larger than that for 1? (c) If this substance is a perfect crystal at  $T = 0\text{ K}$ , what is the value of  $S$  at this temperature? [Section 19.3]



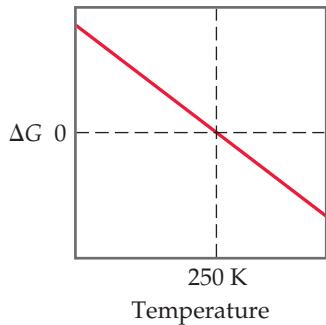
- 19.52** *Isomers* are molecules that have the same chemical formula but different arrangements of atoms, as shown here for two isomers of pentane,  $C_5H_{12}$ . (a) Do you expect a significant difference in the enthalpy of combustion of the two isomers? Explain. (b) Which isomer do you expect to have the higher standard molar entropy? Explain. [Section 19.4]



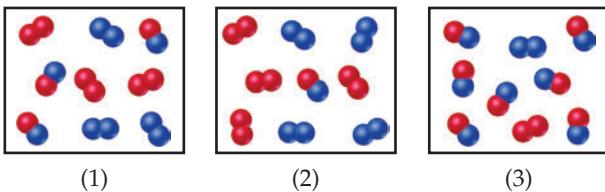
- 19.53** The accompanying diagram shows how  $\Delta H$  (red line) and  $T\Delta S$  (blue line) change with temperature for a hypothetical reaction. (a) What is the significance of the point at 300 K, where  $\Delta H$  and  $T\Delta S$  are equal? (b) In what temperature range is this reaction spontaneous?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



- 19.54** The accompanying diagram shows how  $\Delta G$  for a hypothetical reaction changes as temperature changes. (a) At what temperature is the system at equilibrium? (b) In what temperature range is the reaction spontaneous? (c) Is  $\Delta H$  positive or negative? (d) Is  $\Delta S$  positive or negative? [Sections 19.5 and 19.6]

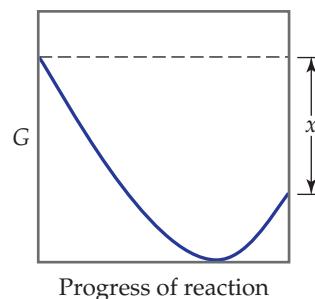


- 19.55** Consider a reaction  $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$ , with atoms of A shown in red in the diagram and atoms of B shown in blue. (a) If  $K_c = 1$ , which box represents the system at equilibrium? (b) If  $K_c = 1$ , which box represents the system at  $Q < K_c$ ? (c) Rank the boxes in order of increasing magnitude of  $\Delta G$  for the reaction. [Sections 19.5 and 19.7]



- 19.56** The accompanying diagram shows how the free energy,  $G$ , changes during a hypothetical reaction  $A(g) + B(g) \rightarrow C(g)$ . On the left are pure reactants A and B, each at 101.3 kPa, and on the right is the pure product, C, also at 101.3 kPa. Indicate whether each of the following statements is true or false. (a) The minimum of the graph

corresponds to the equilibrium mixture of reactants and products for this reaction. (b) At equilibrium, all of A and B have reacted to give pure C. (c) The entropy change for this reaction is positive. (d) The “ $x$ ” on the graph corresponds to  $\Delta G$  for the reaction. (e)  $\Delta G$  for the reaction corresponds to the difference between the top left of the curve and the bottom of the curve. [Section 19.7]



### Spontaneous Processes (Section 19.1)

- 19.57** Which of the following processes are spontaneous and which are nonspontaneous: (a) mixing of water and ethanol, (b) dissolution of sugar in a cup of hot coffee, (c) formation of oxygen atoms from  $O_2$  molecules at STP, (d) rusting of iron, (e) formation of glucose from  $CO_2$  and  $H_2O$  at STP?
- 19.58** Indicate whether each statement is true or false. (a) A reaction that is spontaneous in one direction will be nonspontaneous in the reverse direction under the same reaction conditions. (b) All spontaneous processes are fast. (c) Most spontaneous processes are reversible. (d) An isothermal process is one in which the system loses no heat. (e) The maximum amount of work can be accomplished by an irreversible process rather than a reversible one.

- 19.59** Consider the melting of ice (solid water) to liquid water at a pressure of 101.3 kPa. (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?

- 19.60** Consider the following process: a system changes from state 1 (initial state) to state 2 (final state) in such a way that its temperature changes from 300 K to 400 K. (a) Is this process isothermal? (b) Does the temperature change depend on the particular pathway taken to carry out this change of state? (c) Does the change in the internal energy,  $\Delta E$ , depend on whether the process is reversible or irreversible?

- 19.61** A system goes from state 1 to state 2 and back to state 1. (a) Is  $\Delta E$  the same in magnitude for both the forward and reverse processes? (b) Without further information, can you conclude that the amount of heat transferred to the system as it goes from state 1 to state 2 is the same or different as compared to that upon going from state 2 back to state 1? (c) Suppose the changes in state are reversible processes. Is the work done by the system upon going from state 1 to state 2 the same or different as compared to that upon going from state 2 back to state 1?

- 19.62** 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  $\Delta H$  zero for the process?

## Entropy and the Second Law of Thermodynamics (Section 19.2)

- 19.63** Indicate whether each statement is true or false. (a)  $\Delta S$  depends on whether the process is reversible or irreversible. (b) If a system undergoes an irreversible change, the entropy of the universe increases. (c) Only if the change in entropy of the system is exactly matched by an equal and opposite change in the entropy of the surroundings, the system undergoes a reversible process. (d) If the entropy change of the system is zero, the system undergoes a reversible process.
- 19.64** The normal boiling point of the element mercury ( $Hg$ ) is  $356.7^\circ C$ , and its molar enthalpy of vaporization is  $\Delta H_{vap} = 59.11 \text{ kJ/mol}$ . (a) When  $Hg$  boils at its normal boiling point, does its entropy increase or decrease? (b) Calculate the value of  $\Delta S$  when 2.00 mol of  $Hg$  is vaporized at  $356.7^\circ C$ .
- 19.65** Indicate whether each statement is true or false. (a) The second law of thermodynamics says that entropy can only be produced but cannot not be destroyed. (b) In a certain process the entropy of the system changes by  $1.2 \text{ J/K}$  (increase) and the entropy of the surroundings changes by  $-1.2 \text{ J/K}$  (decrease). Thus, this process must be spontaneous. (c) In a certain process the entropy of the system changes by  $1.3 \text{ J/K}$  (increase) and the entropy of the surroundings changes by  $-1.2 \text{ J/K}$  (decrease). Thus, this process must be reversible.
- 19.66** (a) What sign for  $\Delta S$  do you expect when the volume of 0.200 mol of an ideal gas at  $27^\circ C$  is increased isothermally from an initial volume of 10.0 L? (b) If the final volume is 18.5 L, calculate the entropy change for the process. (c) Do you need to specify the temperature to calculate the entropy change?
- 19.67** (a) Use data in Appendix C to estimate the boiling point of bromine,  $Br_2$ . (b) Use a reference source, such as the CRC Handbook of Chemistry and Physics, to find the experimental boiling point of bromine.

## The Molecular Interpretation of Entropy and the Third Law of Thermodynamics (Section 19.3)

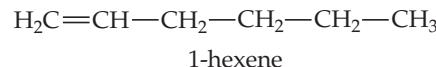
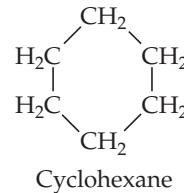
- 19.68** For the isothermal expansion of a gas into a vacuum,  $\Delta E = 0$ ,  $q = 0$ , and  $w = 0$ . (a) Is this a spontaneous process? (b) Explain why no work is done by the system during this process. (c) What is the “driving force” for the expansion of the gas: enthalpy or entropy?
- 19.69** Would each of the following changes increase, decrease, or have no effect on the number of microstates available to a system: (a) increase in temperature, (b) decrease in volume, (c) change of state from liquid to gas?
- 19.70** (a) What do you expect for the sign of  $\Delta S$  in a chemical reaction in which 3 mol of gaseous reactants are converted to 2 mol of gaseous products? (b) For which of the processes in Exercise 19.57 does the entropy of the system increase?
- 19.71** Does the entropy of the system increase, decrease, or stay the same when (a) a solid melts, (b) a gas liquefies, (c) a solid sublimes?
- 19.72** Indicate whether each statement is true or false. (a) The third law of thermodynamics says that the entropy of a perfect, pure crystal at absolute zero increases with the mass of the crystal. (b) “Translational motion” of molecules refers to their change in spatial location as a function of time. (c) “Rotational” and “vibrational” motions contribute to the entropy in atomic gases like He and Xe.

(d) The larger the number of atoms in a molecule, the more degrees of freedom of rotational and vibrational motion it likely has.

- 19.73** For each of the following pairs, predict which substance has the higher entropy per mole at a given temperature: (a)  $I_2(s)$  or  $I_2(g)$  (b)  $O_2(g)$  at 50.7 kPa or  $O_2$  at 101.3 kPa (c) 1 mol of  $N_2$  in 22.4 L or 1 mol of  $N_2$  in 44.8 L. (d)  $CH_3OH(l)$  or  $CH_3OH(s)$ .
- 19.74** Predict the sign of the entropy change of the system for each of the following reactions:
- (a)  $CO(g) + H_2(g) \longrightarrow C(s) + H_2O(g)$   
 (b)  $2 O_2(g) + N_2(g) \longrightarrow 2 NO_2(g)$   
 (c)  $NH_4Cl(s) \longrightarrow HCl(g) + NH_3(g)$   
 (d)  $2 C_2H_4(g) + O_2(g) \longrightarrow 2 C_2H_4O(g)$

## Entropy Changes in Chemical Reactions (Section 19.4)

- 19.75** (a) Using Figure 19.12 as a model, sketch how the entropy of water changes as it is heated from  $-50^\circ C$  to  $110^\circ C$  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.
- 19.76** Cyclohexane and 1-hexene are isomers that both have the formula,  $C_6H_{12}$ . Based on the molecular structures shown, which of these isomers would you expect to have the higher standard molar entropy at  $25^\circ C$ ?



- 19.77** Predict which member of each of the following pairs has the greater standard entropy at  $25^\circ C$ : (a)  $HNO_3(g)$  or  $HNO_3(aq)$ , (b)  $PCl_3(l)$  or  $PCl_3(g)$ , (c)  $Fe_2O_3(s)$  or  $Fe_3O_4(s)$ , (d)  $Li(s)$  or  $Li(g)$ . Use Appendix C to find the standard entropy of each substance.
- 19.78** The standard entropies at 298 K for certain Group 14 elements are:  $C(s, \text{diamond}) = 2.43 \text{ J/mol K}$ ,  $Si(s) = 18.81 \text{ J/mol K}$ ,  $Ge(s) = 31.09 \text{ J/mol K}$ , and  $Sn(s) = 51.818 \text{ J/mol K}$ . All but Sn have the same (diamond) structure. How do you account for the trend in the  $S^\circ$  values?
- 19.79** Using  $S^\circ$  values from Appendix C, calculate  $\Delta S^\circ$  values for the following reactions. In each case, account for the sign of  $\Delta S^\circ$ .
- (a)  $NH_4Cl(s) \longrightarrow NH_4^+(aq) + Cl^-(aq)$   
 (b)  $CH_3OH(g) \longrightarrow CO(g) + 2 H_2(g)$   
 (c)  $CH_4(g) + 2 O_2(g) \longrightarrow CO_2(g) + 2 H_2O(g)$   
 (d)  $CH_4(g) + 2 O_2(g) \longrightarrow CO_2(g) + 2 H_2O(l)$

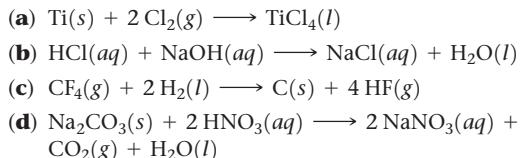
## Gibbs Free Energy (Sections 19.5 and 19.6)

- 19.80** (a) Is the standard free energy change,  $\Delta G^\circ$ , always larger than  $\Delta G$ ? (b) For any process that occurs at constant

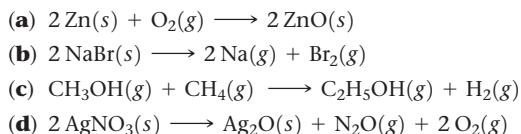
temperature and pressure, what is the significance of  $\Delta G = 0$ ? (c) For a certain process,  $\Delta G$  is large and negative. Does this mean that the process necessarily has a low activation barrier?

- 19.81** For a certain chemical reaction,  $\Delta H^\circ = -40.0 \text{ kJ}$  and  $\Delta S^\circ = -150.0 \text{ J/K}$ . (a) Does the reaction lead to an increase or decrease in the randomness or disorder of the system? (b) Does the reaction lead to an increase or decrease in the randomness or disorder of the surroundings? (c) Calculate  $\Delta G^\circ$  for the reaction at 298 K. (d) Is the reaction spontaneous at 298 K under standard conditions?

- 19.82** Using data in Appendix C, calculate  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$  at 298 K for each of the following reactions.

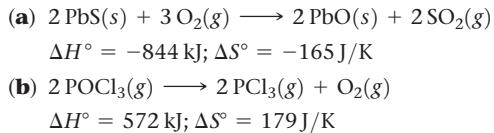


- 19.83** Using data from Appendix C, calculate  $\Delta G^\circ$  for the following reactions. Indicate whether each reaction is spontaneous at 298 K under standard conditions.



- 19.84** Today, most candles are made of paraffin wax. A typical component of paraffin wax is the hydrocarbon  $\text{C}_{31}\text{H}_{64}$  which is solid at room temperature. (a) Write a balanced equation for the combustion of  $\text{C}_{31}\text{H}_{64}(s)$  to form  $\text{CO}_2(g)$  and  $\text{H}_2\text{O}(g)$ . (b) Without using thermochemical data, predict whether  $\Delta G^\circ$  for this reaction is more negative or less negative than  $\Delta H^\circ$ .

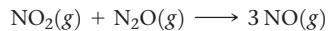
- 19.85** From the values given for  $\Delta H^\circ$  and  $\Delta S^\circ$ , calculate  $\Delta G^\circ$  for each of the following reactions at 298 K. If the reaction is not spontaneous under standard conditions at 298 K, at what temperature (if any) would the reaction become spontaneous?



- 19.86** A particular constant pressure reaction is barely spontaneous at 320 K. The enthalpy change for the reaction is  $+15.2 \text{ kJ}$ . Estimate  $\Delta S$  for the reaction.

- 19.87** For a particular reaction,  $\Delta H = 30.0 \text{ kJ}$  and  $\Delta S = 90.0 \text{ J/K}$ . Assume that  $\Delta H$  and  $\Delta S$  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?

- 19.88** Consider the following reaction between oxides of nitrogen:



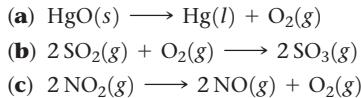
(a) Use data in Appendix C to predict how  $\Delta G$  for the reaction varies with increasing temperature. (b) Calculate  $\Delta G$  at 800 K, assuming that  $\Delta H^\circ$  and  $\Delta S^\circ$  do not change with temperature. Under standard conditions is the reaction spontaneous at 800 K? (c) Calculate  $\Delta G$  at 1000 K. Is the reaction spontaneous under standard conditions at this temperature?

- 19.89** (a) Using data in Appendix C, estimate the temperature at which the free-energy change for the transformation from  $\text{I}_2(s)$  to  $\text{I}_2(g)$  is zero. (b) Use a reference source, such as Web Elements ([www.webelements.com](http://www.webelements.com)), to find the experimental melting and boiling points of  $\text{I}_2$ . (c) Which of the values in part (b) is closer to the value you obtained in part (a)?

- 19.90** Acetylene gas,  $\text{C}_2\text{H}_2(g)$ , is used in welding. (a) Write a balanced equation for the combustion of acetylene gas to  $\text{CO}_2(g)$  and  $\text{H}_2\text{O}(l)$ . (b) How much heat is produced in burning 1 mol of  $\text{C}_2\text{H}_2$  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?

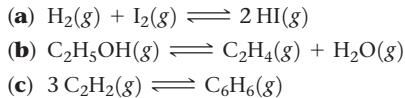
## Free Energy and Equilibrium (Section 19.7)

- 19.91** Indicate whether  $\Delta G$  increases, decreases, or stays the same for each of the following reactions as the partial pressure of  $\text{O}_2$  is increased:

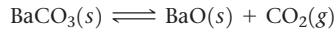


- 19.92** Consider the reaction  $2 \text{NO}(g) + \text{O}_2(g) \longrightarrow 2 \text{NO}_2(g)$ . (a) Using data from Appendix C, calculate  $\Delta G^\circ$  at 298 K. (b) Calculate  $\Delta G$  at 298 K if the partial pressures of all gases are 33.4 kPa.

- 19.93** Use data from Appendix C to calculate the equilibrium constant,  $K$ , and  $\Delta G^\circ$  at 298 K for each of the following reactions:



- 19.94** Consider the decomposition of barium carbonate:



Using data from Appendix C, calculate the equilibrium pressure of  $\text{CO}_2$  at (a) 298 K and (b) 1100 K.

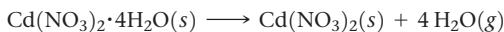
- 19.95** The value of  $K_a$  for nitrous acid ( $\text{HNO}_2$ ) at 25 °C is given in Appendix D. (a) Write the chemical equation for the equilibrium that corresponds to  $K_a$ . (b) By using the value of  $K_a$ , calculate  $\Delta G^\circ$  for the dissociation of nitrous acid in aqueous solution. (c) What is the value of  $\Delta G$  at equilibrium? (d) What is the value of  $\Delta G$  when  $[\text{H}^+] = 5.0 \times 10^{-2} \text{ M}$ ,  $[\text{NO}_2^-] = 6.0 \times 10^{-4} \text{ M}$ , and  $[\text{HNO}_2] = 0.20 \text{ M}$ ?

## Additional Exercises

- 19.96** (a) Which of the thermodynamic quantities  $p$ ,  $H$ ,  $q$ ,  $w$ , and  $G$  are state functions? (b) Consider a system going from state 1 to state 2 in a reversible and an irreversible way. Compare  $q_{\text{rev}}$  and  $q_{\text{irrev}}$ . (c) Consider a system going from

state 1 to state 2 in a reversible and an irreversible way. Compare  $w_{\text{rev}}$  and  $w_{\text{irrev}}$ . (d) For a reversible isothermal process, write an expression for  $\Delta H$  and an expression for  $\Delta G$  in terms of  $q$ ,  $w$  and  $T$ ,  $p$  and  $\Delta V$ .

- 19.97** The crystalline hydrate  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}(s)$  loses water when placed in a large, closed, dry vessel at room temperature:



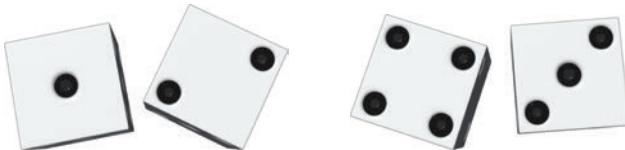
This process is spontaneous and  $\Delta H^\circ$  is positive at room temperature. **(a)** What is the sign of  $\Delta S^\circ$  at room temperature? **(b)** If the hydrated compound is placed in a large, closed vessel that already contains a large amount of water vapor, does  $\Delta S^\circ$  change for this reaction at room temperature?

- 19.98** Indicate whether each of the following statements is true or false. If it is false, correct it. **(a)** The feasibility of manufacturing  $\text{NH}_3$  from  $\text{N}_2$  and  $\text{H}_2$  depends entirely on the value of  $\Delta H$  for the process  $\text{N}_2(g) + 3\text{H}_2(g) \longrightarrow 2\text{NH}_3(g)$ . **(b)** The reaction of  $\text{Na}(s)$  with  $\text{Cl}_2(g)$  to form  $\text{NaCl}(s)$  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.

- 19.99** For each of the following processes, indicate whether the signs of  $\Delta S$  and  $\Delta H$  are expected to be positive, negative, or about zero. **(a)** A solid sublimes. **(b)** The temperature of a sample of  $\text{Co}(s)$  is lowered from  $60^\circ\text{C}$  to  $25^\circ\text{C}$ . **(c)** Ethanol evaporates from a beaker. **(d)** A diatomic molecule dissociates into atoms. **(e)** A piece of charcoal is combusted to form  $\text{CO}_2(g)$  and  $\text{H}_2\text{O}(g)$ .

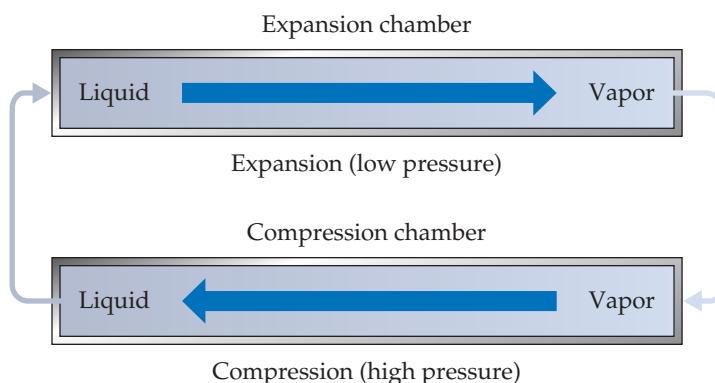
- 19.100** The reaction  $2\text{Mg}(s) + \text{O}_2(g) \longrightarrow 2\text{MgO}(s)$  is highly spontaneous. A classmate calculates the entropy change for this reaction and obtains a large negative value for  $\Delta S^\circ$ . Did your classmate make a mistake in the calculation? Explain.

- 19.101** Consider a system that consists of two standard playing dice, with the state of the system defined by the sum of the values shown on the top faces. **(a)** The two arrangements of top faces shown here can be viewed as two possible microstates of the system. Explain. **(b)** To which state does each microstate correspond? **(c)** How many possible states are there for the system? **(d)** Which state or states have the highest entropy? Explain. **(e)** Which state or states have the lowest entropy? Explain. **(f)** Calculate the absolute entropy of the two-dice system.



- 19.102** Ammonium nitrate dissolves spontaneously and endothermally in water at room temperature. What can you deduce about the sign of  $\Delta S$  for this solution process?

- 19.103** A standard air conditioner involves a *refrigerant* that is typically now a fluorinated hydrocarbon, such as  $\text{CH}_2\text{F}_2$ . An air-conditioner refrigerant has the property that it readily vaporizes at atmospheric pressure and is easily compressed to its liquid phase under increased pressure. The operation of an air conditioner can be thought of as a closed system made up of the refrigerant going through the two stages shown here (the air circulation is not shown in this diagram).



During *expansion*, the liquid refrigerant is released into an expansion chamber at low pressure, where it vaporizes. The vapor then undergoes *compression* at high pressure back to its liquid phase in a compression chamber. **(a)** What is the sign of  $q$  for the expansion? **(b)** What is the sign of  $q$  for the compression? **(c)** In a central air-conditioning system, one chamber is inside the home and the other is outside. Which chamber is where, and why? **(d)** Imagine that a sample of liquid refrigerant undergoes expansion followed by compression, so that it is back to its original state. Would you expect that to be a reversible process? **(e)** Suppose that a house and its exterior are both initially at  $31^\circ\text{C}$ . Some time after the air conditioner is turned on, the house is cooled to  $24^\circ\text{C}$ . Is this process spontaneous or nonspontaneous?

- 19.104** *Trotton's rule* states that for many liquids at their normal boiling points, the standard molar entropy of vaporization is about  $88\text{ J/mol K}$ . **(a)** Estimate the normal boiling point of bromine,  $\text{Br}_2$ , by determining  $\Delta H_{\text{vap}}^\circ$  for  $\text{Br}_2$  using data from Appendix C. Assume that  $\Delta H_{\text{vap}}^\circ$  remains constant with temperature and that Trotton's rule holds. **(b)** Look up the normal boiling point of  $\text{Br}_2$  in a chemistry handbook or at the WebElements website ([www.webelements.com](http://www.webelements.com)) and compare it to your calculation. What are the possible sources of error, or incorrect assumptions, in the calculation?

- 19.105** **(a)** Write the chemical equations that correspond to  $\Delta G_f^\circ$  for  $\text{CH}_4(g)$  and for  $\text{NaCl}(s)$ . **(b)** For these formation reactions, compare  $\Delta G_f^\circ$  and  $\Delta H_f^\circ$ . **(c)** In general, under which condition is  $\Delta G_f^\circ$  more negative (less positive) than  $\Delta H_f^\circ$ ? **(i)** When the temperature is high, **(ii)** when  $\Delta S_f^\circ$  is positive, **(iii)** when the reaction is reversible.

- 19.106** Consider the following three reactions:

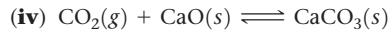
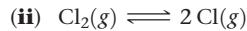
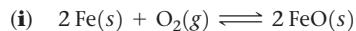
- (i)**  $\text{Ti}(s) + 2\text{Cl}_2(g) \longrightarrow \text{TiCl}_4(g)$   
**(ii)**  $\text{C}_2\text{H}_6(g) + 7\text{Cl}_2(g) \longrightarrow 2\text{CCl}_4(g) + 6\text{HCl}(g)$   
**(iii)**  $\text{BaO}(s) + \text{CO}_2(g) \longrightarrow \text{BaCO}_3(s)$

- (a)** For each of the reactions, use data in Appendix C to calculate  $\Delta H^\circ$ ,  $\Delta G^\circ$ ,  $K$ , and  $\Delta S^\circ$  at  $25^\circ\text{C}$ . **(b)** Which of these reactions are spontaneous under standard conditions at  $25^\circ\text{C}$ ? **(c)** For each of the reactions, predict the manner in which the change in free energy varies with an increase in temperature.

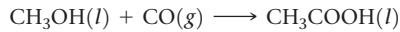
- 19.107** Using the data in Appendix C and given the pressures listed, calculate  $K_p$  and  $\Delta G$  for each of the following reactions:

- (a)**  $\text{N}_2(g) + 3\text{H}_2(g) \longrightarrow 2\text{NH}_3(g)$   
 $P_{\text{N}_2} = 263.4\text{ kPa}, P_{\text{H}_2} = 597.8\text{ kPa}, P_{\text{NH}_3} = 101.3\text{ kPa}$   
**(b)**  $2\text{N}_2\text{H}_4(g) + 2\text{NO}_2(g) \longrightarrow 3\text{N}_2(g) + 4\text{H}_2\text{O}(g)$   
 $P_{\text{N}_2\text{H}_4} = P_{\text{NO}_2} = 5.07\text{ kPa}$ ,  
 $P_{\text{N}_2} = 50.7\text{ kPa}, P_{\text{H}_2\text{O}} = 30.4\text{ kPa}$   
**(c)**  $\text{N}_2\text{H}_4(g) \longrightarrow \text{N}_2(g) + 2\text{H}_2(g)$   
 $P_{\text{N}_2\text{H}_4} = 101.3\text{ kPa}, P_{\text{N}_2} = 152.0\text{ kPa}, P_{\text{H}_2} = 253.3\text{ kPa}$

- 19.108** (a) For each of the following reactions, predict the sign of  $\Delta H^\circ$  and  $\Delta S^\circ$  without doing any calculations. (b) Based on your general chemical knowledge, predict which of these reactions will have  $K > 1$  at 25 °C. (c) In each case, indicate whether  $K$  should increase or decrease with increasing temperature.



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



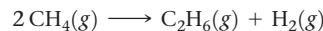
(a) Calculate the equilibrium constant for the reaction at 25 °C. (b) Industrially, this reaction is run at temperatures above 25 °C. Will an increase in temperature produce an increase or decrease in the mole fraction of acetic acid at equilibrium? Why are elevated temperatures used? (c) At what temperature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

- 19.110** The oxidation of glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) in body tissue produces  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . In contrast, anaerobic decomposition, which occurs during fermentation, produces ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) and  $\text{CO}_2$ . (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.

- 19.111** The conversion of natural gas, which is mostly methane, into products that contain two or more carbon atoms, such as ethane ( $\text{C}_2\text{H}_6$ ), 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  $\Delta G^\circ$  for the two reactions due primarily to the enthalpy term ( $\Delta H$ ) or the entropy term ( $-T\Delta S$ )? (c) Explain how the preceding reactions are an example of driving a nonspontaneous reaction, as discussed in the “Chemistry and Life” box in Section 19.7. (d) The reaction of  $\text{CH}_4$  and  $\text{O}_2$  to form  $\text{C}_2\text{H}_6$  and  $\text{H}_2\text{O}$  must be carried out carefully to avoid a competing reaction. What is the most likely competing reaction?

- 19.112** Cells use the hydrolysis of adenosine triphosphate (ATP) as a source of energy (Figure 19.16). The conversion of ATP to ADP has a standard free-energy change of  $-30.5 \text{ kJ/mol}$ . 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?

- 19.113** 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  $\text{K}^+$ . (a) What is  $\Delta G$  for the transfer of 1 mol of  $\text{K}^+$  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  $\text{K}^+$ ?

## Integrative Exercises

- 19.114** Most liquids follow Trouton’s rule (see Exercise 19.104), which states that the molar entropy of vaporization is approximately  $88 \pm 5 \text{ J/mol K}$ . The normal boiling points and enthalpies of vaporization of several organic liquids are as follows:

Substance	Normal Boiling Point (°C)	$\Delta H_{\text{vap}}$ (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, $\text{C}_8\text{H}_{18}$	125.6	34.4
Pyridine, $\text{C}_5\text{H}_5\text{N}$	115.3	35.1

- (a) Calculate  $\Delta S_{\text{vap}}$  for each of the liquids. Do all 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  $\Delta H_{\text{vap}}$  for this substance.

- 19.115** In chemical kinetics, the *entropy of activation* is the entropy change for the process in which the reactants reach the activated complex. Predict whether the entropy of

activation for a bimolecular process is usually positive or negative.

- 19.116** At what temperatures is the following reaction, the reduction of magnetite by graphite to elemental iron, spontaneous?



- 19.117** 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  $\text{O}_2(g)$ , (b) formation of ozone from oxygen molecules and oxygen atoms, (c) diffusion of CFCs into the stratosphere, (d) desalination of water by reverse osmosis.

- 19.118** An ice cube with a mass of 25 g at -18 °C (typical freezer temperature) is dropped into a cup that holds 250 mL of hot water, initially at 85 °C. What is the final temperature in the cup? The density of liquid water is 1.00 g/mL; the specific heat capacity of ice is 2.03 J/g °C; the specific heat capacity of liquid water is 4.184 J/g K; the enthalpy of fusion of water is 6.01 kJ/mol.

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

	$\Delta H_f^\circ$ (kJ/mol)	$\Delta G_f^\circ$ (kJ/mol)
$\text{CS}_2(l)$	89.7	65.3
$\text{CS}_2(g)$	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  $\text{CS}_2$  molecule. (c) Liquid  $\text{CS}_2$  burns in  $\text{O}_2$  with a blue flame, forming  $\text{CO}_2(g)$  and  $\text{SO}_2(g)$ . Write a balanced equation for this reaction. (d) Using the data in the preceding table and in Appendix C, calculate  $\Delta H^\circ$  and  $\Delta G^\circ$  for the reaction in part (c). Is the reaction exothermic? Is it spontaneous at 298 K? (e) Use the data in the table to calculate  $\Delta S^\circ$  at 298 K for the vaporization of  $\text{CS}_2(l)$ . Is the sign of  $\Delta S^\circ$  as you would expect for a vaporization? (f) Using data in the table and your answer to part (e), estimate the boiling point of  $\text{CS}_2(l)$ . Do you predict that the substance will be a liquid or a gas at 298 K and 101.3 kPa?

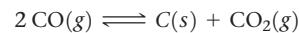
- 19.120** The following data compare the standard enthalpies and free energies of formation of some crystalline ionic substances and aqueous solutions of the substances:

Substance	$\Delta H_f^\circ$ (kJ/mol)	$\Delta G_f^\circ$ (kJ/mol)
$\text{AgNO}_3(s)$	-124.4	-33.4
$\text{AgNO}_3(aq)$	-101.7	-34.2
$\text{MgSO}_4(s)$	-1283.7	-1169.6
$\text{MgSO}_4(aq)$	-1374.8	-1198.4

Write the formation reaction for  $\text{AgNO}_3(s)$ . Based on this reaction, do you expect the entropy of the system to increase or decrease upon the formation of  $\text{AgNO}_3(s)$ ? (b) Use  $\Delta H_f^\circ$  and  $\Delta G_f^\circ$  of  $\text{AgNO}_3(s)$  to determine the entropy change upon formation of the substance. Is your answer consistent with your reasoning in part (a)? (c) Is dissolving  $\text{AgNO}_3$  in water an exothermic or endothermic process? What about dissolving  $\text{MgSO}_4$  in water? (d) For both  $\text{AgNO}_3$  and  $\text{MgSO}_4$ , 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 “A Closer Look” box on page 912.

- 19.121** Consider the Boudouard reaction:



Thermodynamic data on these gases are given in Appendix C. You may assume that  $\Delta H^\circ$  and  $\Delta S^\circ$  do not vary with temperature. (a) At what temperature will an equilibrium mixture of 101.3 kPa total pressure contain 1.00 mol % CO? (b) At what temperature will an equilibrium mixture of 5.07 MPa total pressure contain 1.00 mol % CO?

- 19.122** The reaction



is the basis of a suggested method for removal of  $\text{SO}_2$  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  $\text{SO}_2$ ? (c) If  $P_{\text{SO}_2} = P_{\text{H}_2\text{S}}$  and the vapor pressure of water is 3.33 kPa, calculate the equilibrium  $\text{SO}_2$  pressure in the system at 298 K. (d) Would you expect the process to be more or less effective at higher temperatures?

- 19.123** 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? (c) Try this experiment: Stretch a rubber band and wait a moment. Then place the stretched rubber band on your upper lip, and let it return suddenly to its unstretched state (remember to keep holding on!). What do you observe? Are your observations consistent with your answer to part (b)?

## Design an Experiment

You are measuring the equilibrium constant for a drug candidate binding to its DNA target over a series of different temperatures. You chose your drug candidate based on computer-aided molecular modeling, which indicates that the drug molecule likely would make many hydrogen bonds and favorable dipole–dipole interactions with the DNA site. You perform a set of experiments in buffer solution for the drug–DNA complex and generate a table of  $K$ 's at different  $T$ 's. (a) Derive an equation that relates equilibrium constant to standard enthalpy and entropy changes. (Hint: equilibrium constant, enthalpy and entropy are all related to free energy). (b) Show how you

can graph your  $K$  and  $T$  data to calculate the standard entropy and enthalpy changes for the drug candidate + DNA binding interaction. (c) You are surprised to learn that the enthalpy change for the binding reaction is close to zero, and the entropy change is large and positive. Suggest an explanation and design an experiment to test it. (Hint: Think about water and ions). (d) You try another drug candidate with the DNA target and find that this drug candidate has a large negative enthalpy change upon DNA binding, and the entropy change is small and positive. Suggest an explanation, at the molecular level, and design an experiment to test your hypothesis.