

Die Energie der Welt ist konstant. Die Entropie der Welt strebt einem Maximum zu.
(The energy of the world is constant. The entropy of the world tends towards a maximum.)

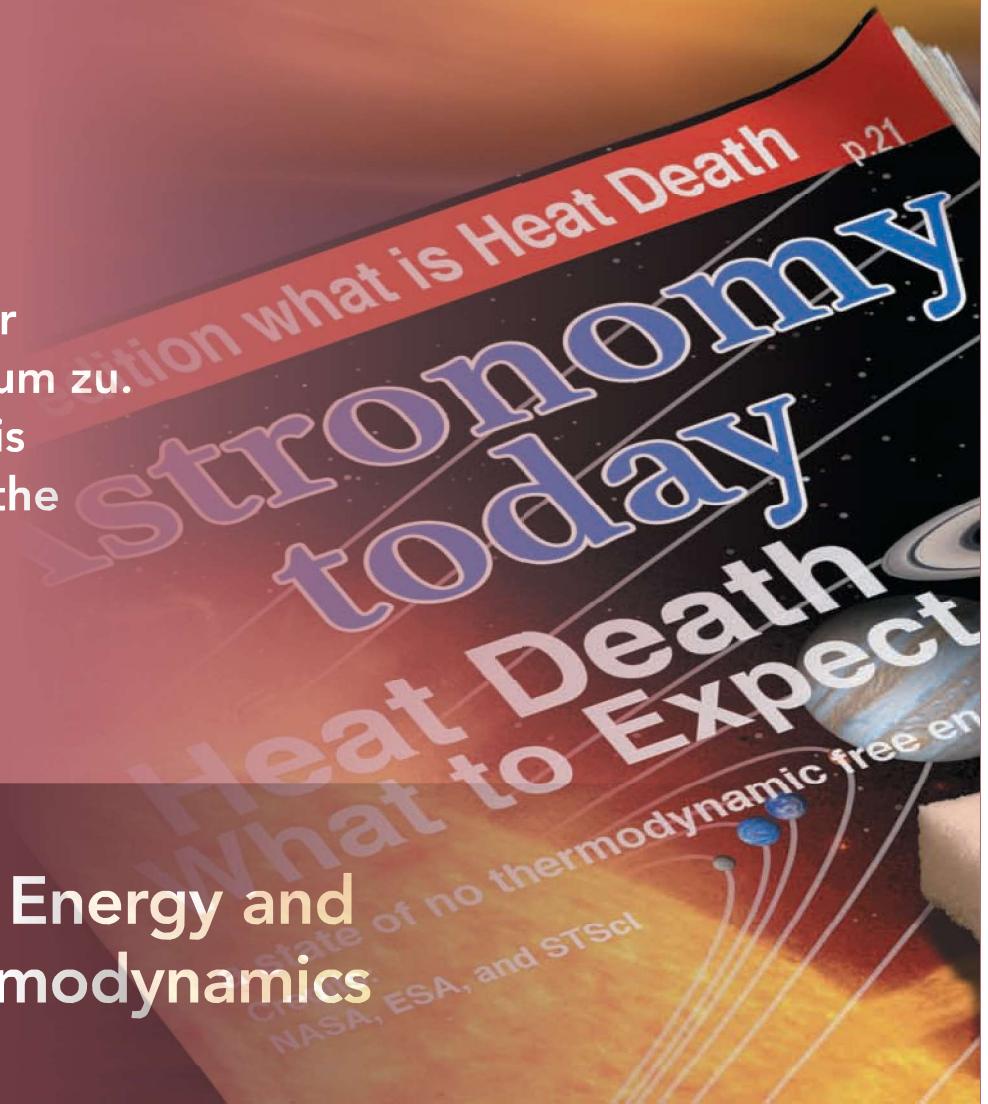
—RUDOLF CLAUSIUS (1822–1888)

CHAPTER

19

Free Energy and Thermodynamics

Throughout this book, we have examined chemical and physical changes. We have studied how fast chemical changes occur (kinetics) and how to predict how far they will go (through the use of equilibrium constants). We have learned that acids neutralize bases and that gases expand to fill their containers. We now turn to the following question: why do these changes occur in the first place? What ultimately drives physical and chemical changes in matter? The answer may surprise you. The driving force behind chemical and physical change in the universe is a quantity called *entropy*, which is related to the dispersion (spreading out) of energy. Nature tends toward that state in which energy is spread out to the greatest extent possible. Although it does not seem obvious at first glance, the freezing of water below 0 °C, the dissolving of a solid into a solution, the neutralization of an acid by a base, and even the development of a person from an embryo all increase the entropy in the universe (they all result in greater energy dispersion). In our universe, entropy always increases.





Hot coffee cools down because of the pervasive tendency of energy to dissipate (or disperse) over time.

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19.1 Cold Coffee and Dead Universes

Nature hates concentrated energy. We all know this from experience. The hot coffee you just poured for yourself will be cold in 30 minutes because the concentrated thermal energy in the coffee dissipates into the surrounding room. Similarly, the concentrated energy contained in the gasoline that you just added to your car will soon

dissipate into thermal energy as you drive your car to transport yourself around town. The energy in the hot coffee and the gasoline is not destroyed (recall from Chapter 7 that energy cannot be created nor destroyed). Instead it is dispersed or dissipated, changed from a concentrated form into a more spread out form. The pervasive tendency for energy to spread out or dissipate when not prevented from doing so is known as *the second law of thermodynamics*, the main topic of this chapter.

The second law of thermodynamics has profound implications, not just for the cooling off of coffee or the use of fuels, but for many other processes as well. As we will see, the second law determines the spontaneous direction of *all processes*. In other words, if you want to know if a particular process will occur (such as the cooling of coffee or the burning of fuel), you just have to determine if the process disperses or spreads out energy. If it does, the process occurs. If it does not, the process does not occur. In the cooling of coffee, we can easily tell that energy spreads out. However, for other processes, it is not so obvious. For example, the melting of ice above 0 °C disperses energy and therefore spontaneously occurs; but below 0 °C the melting of ice *does not* disperse energy and therefore does not happen. Later in this chapter, we examine why the temperature of the surroundings makes a difference.

The second law of thermodynamics is so pervasive and powerful that it predicts the fate of the universe itself. Over time, we know that the concentrated energy of the sun will disperse itself into the surroundings so that the sun burns out. Similarly, all concentrated energy in the universe will disperse so that eventually *nothing* can happen anymore. Cosmologists call this fate *heat death*, and it is the most plausible explanation for the future of our universe. However, we need not worry about either of these because the sun has several more billion years left in it, and our universe has something like 10^{100} years left before it winds down. For now, we can concentrate on understanding the second law and how it applies to predicting the spontaneity of chemical processes.

ANSWER NOW!



19.1 Cc Conceptual Connection

THE SECOND LAW Which process is inconsistent with the second law of thermodynamics?

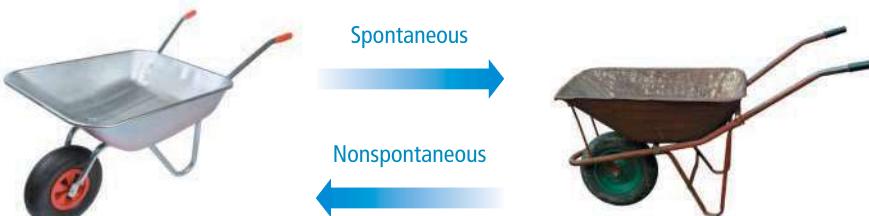
- (a) The spontaneous creation of energy from nothing.
- (b) The spontaneous creation of matter from nothing.
- (c) The spontaneous concentration of energy from dispersed energy.

19.2

Spontaneous and Nonspontaneous Processes

A fundamental goal of thermodynamics is to predict *spontaneity*. For example, will rust spontaneously form when iron comes into contact with oxygen? Will water spontaneously decompose into hydrogen and oxygen? A **spontaneous process** is one that occurs *without ongoing outside intervention* (such as the performance of work by some external force). For example, when you drop a book in a gravitational field, it spontaneously drops to the floor. When you place a ball on a slope, it spontaneously rolls down the slope.

For simple mechanical systems, such as the dropping of a book or the rolling of a ball, predicting spontaneity is fairly intuitive. A mechanical system tends toward lowest potential energy, which is usually easy to see (at least in *simple* mechanical systems).



► Iron spontaneously rusts when it comes in contact with oxygen.

The Concept of Chemical Potential

Mechanical potential energy predicts the direction in which a mechanical system will spontaneously move.

Mechanical potential energy



Direction of spontaneous change

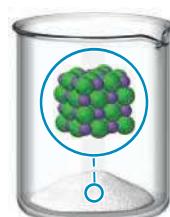


(a)

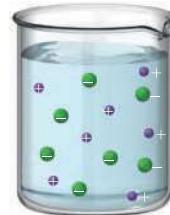
We seek a chemical potential that predicts the direction in which a chemical system will spontaneously move.

Chemical potential

Direction of spontaneous change



Solid NaCl

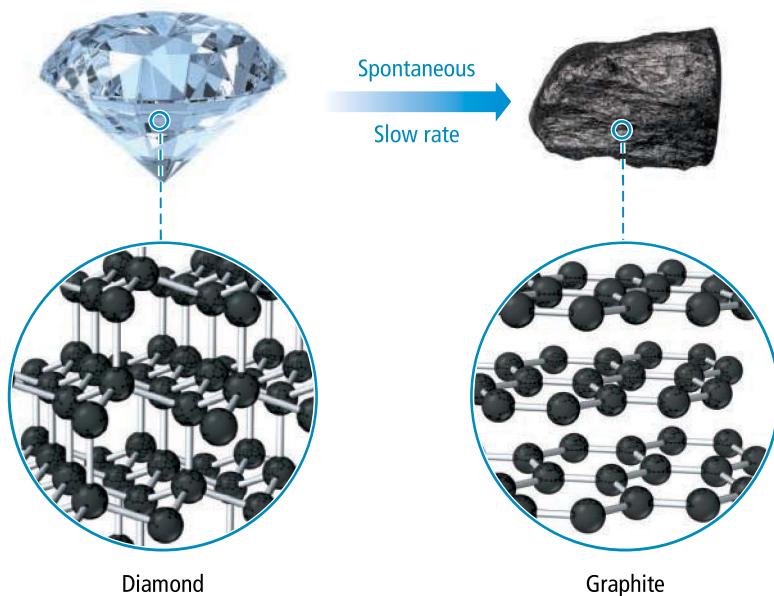


Dissolved ions

(b)

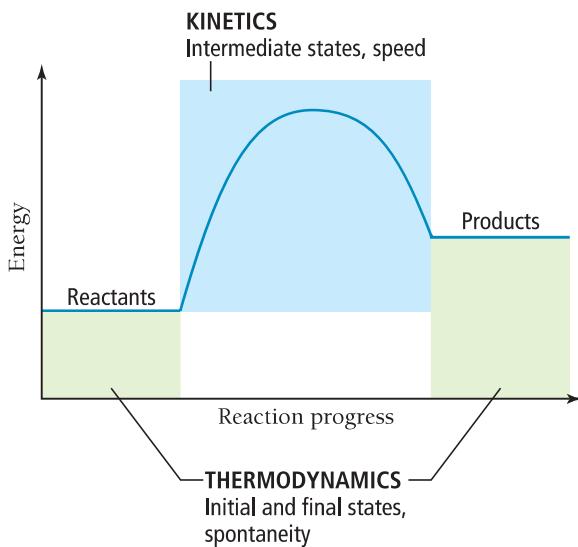
However, the prediction of spontaneity for chemical systems is not so intuitively obvious. To make these predictions, we need to develop a criterion for the spontaneity of chemical systems. In other words, we need to develop a *chemical potential* that predicts the direction of a chemical system, much as mechanical potential energy predicts the direction of a mechanical system (Figure 19.1▲).

We must not confuse the *spontaneity* of a chemical reaction with the *speed* of a chemical reaction. In thermodynamics, we study the *spontaneity* of a reaction—the direction in which, and the extent to which, a chemical reaction proceeds. In kinetics, we study the *speed* of the reaction—how fast a reaction takes place (Figure 19.2►). A reaction may be thermodynamically spontaneous but kinetically slow at a given temperature. For example, the conversion of diamond to graphite is thermodynamically spontaneous. But your diamonds will not become worthless anytime soon because the process is extremely slow kinetically. Although the rate of a spontaneous process can be increased by the use of a catalyst, a nonspontaneous process cannot be made spontaneous by the use of a catalyst. Catalysts affect only the rate of a reaction, not the spontaneity.



◀ FIGURE 19.1 Mechanical Potential Energy and Chemical Potential

Even though graphite is thermodynamically more stable than diamond, the conversion of diamond to graphite is kinetically so slow that it does not occur at any measurable rate.

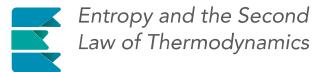


▲ FIGURE 19.2 Thermodynamics and Kinetics Thermodynamics deals with the relative chemical potentials of the reactants and products. It enables us to predict whether a reaction will be spontaneous and to calculate how much work it can do. Kinetics deals with the chemical potential of intermediate states and enables us to determine why a reaction is slow or fast.

One more observation about nonspontaneity—a nonspontaneous process is not *impossible*. For example, the extraction of iron metal from iron ore is a nonspontaneous process; it does not happen if the iron ore is left to itself, but that does not mean it is impossible. As we will see later in this chapter, a nonspontaneous process can be made spontaneous by coupling it to another process that is spontaneous or by supplying energy from an external source. Iron can be separated from its ore if external energy is supplied, usually by means of another reaction (that is itself highly spontaneous).

WATCH NOW!

KEY CONCEPT VIDEO 19.3



See Section 7.6 for the definition of enthalpy.

19.3

Entropy and the Second Law of Thermodynamics

The first candidate in our search for a chemical potential might be enthalpy, which we defined in Chapter 7. Perhaps, just as a mechanical system proceeds in the direction of lowest potential energy, so a chemical system might proceed in the direction of lowest enthalpy. If this were the case, all exothermic reactions would be spontaneous and all endothermic reactions would not. However, although *most* spontaneous processes are exothermic, some spontaneous processes are *endothermic*. For example, above 0 °C, ice spontaneously melts (an endothermic process). So enthalpy must not be the sole criterion for spontaneity.

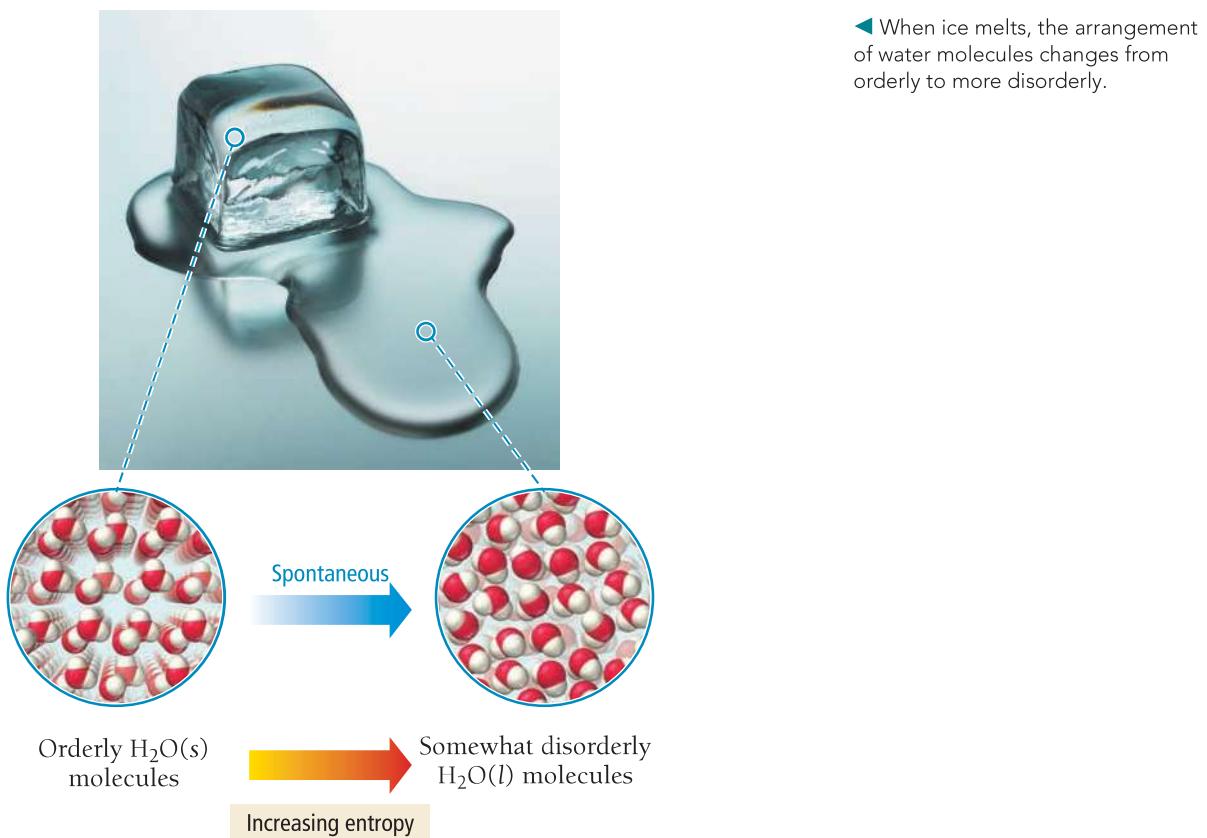
We can learn more about the driving force behind chemical processes by considering several processes (like ice melting) that involve an increase in enthalpy. The processes listed here are energetically uphill (they are endothermic), yet they occur spontaneously. What drives them?

- the melting of ice above 0 °C
- the evaporation of liquid water to gaseous water
- the dissolution of sodium chloride in water

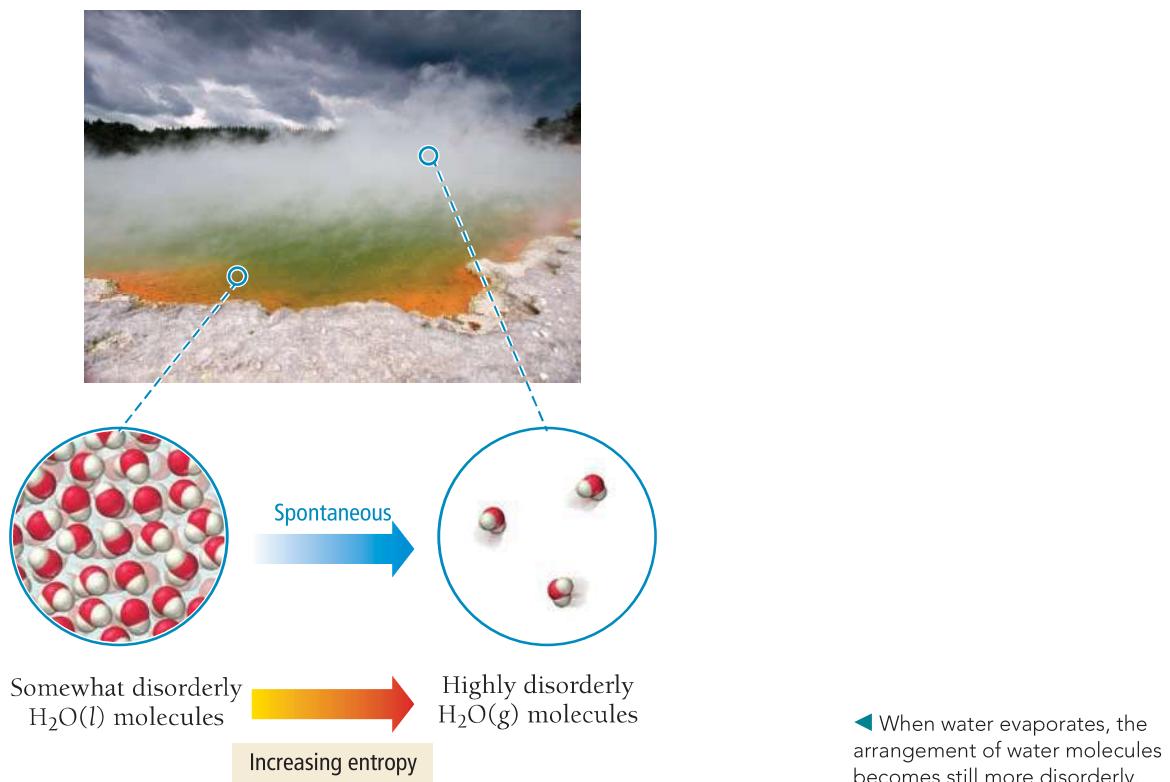
Each of these processes is endothermic *and* spontaneous. Do they have anything in common? Notice that, in each process, disorder or randomness increases.

The use of the word *disorder* here is analogous to our macroscopic notions of disorder. The definition of molecular disorder, which is covered shortly, is very specific.

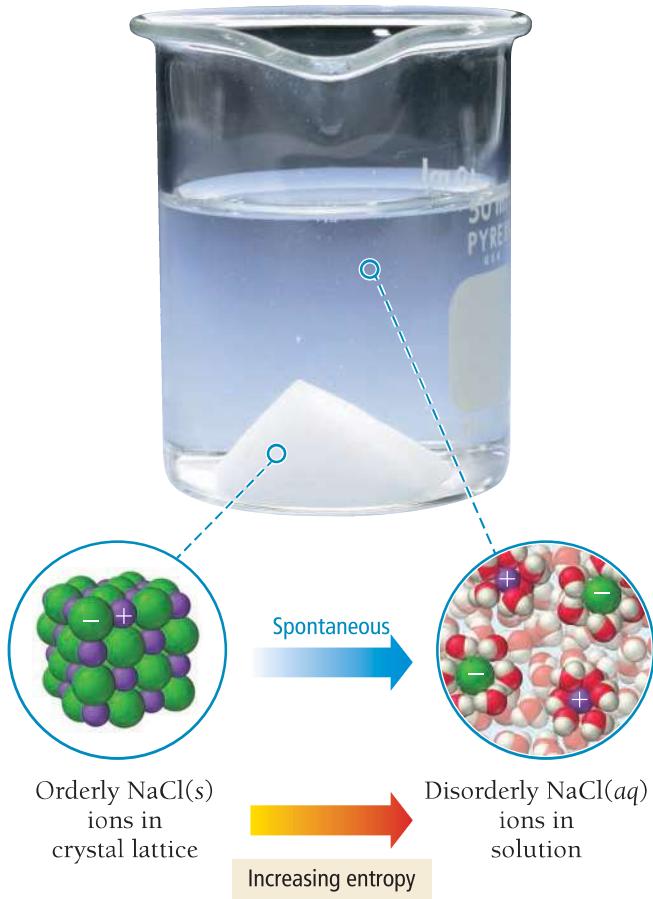
In the melting of ice, the arrangement of the water molecules changes from a highly ordered one (in ice) to a somewhat disorderly one (in liquid water).



During the evaporation of a liquid to a gas, the arrangement changes from a *somewhat* disorderly one (atoms or molecules in the liquid) to a *highly* disorderly one (atoms or molecules in the gas).



In the dissolution of a salt into water, the arrangement again changes from an orderly one (in which the ions in the salt occupy regular positions in the crystal lattice) to a more disorderly one (in which the ions are randomly dispersed throughout the liquid water).



In all three of these processes, a quantity called *entropy*—related to disorder or randomness at the molecular level—increases.

Entropy

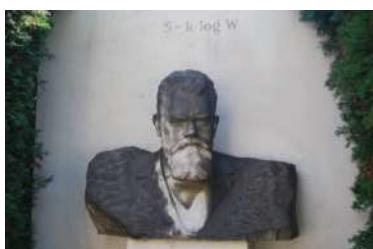
We have hit upon the criterion for spontaneity in chemical systems: entropy. Informally, we can think of entropy as disorder or randomness. But the concept of disorder or randomness on the macroscopic scale—such as the messiness of a drawer—is only *analogous* to the concept of disorder or randomness on the molecular scale. Formally, entropy, abbreviated by the symbol S , has the following definition:

Entropy (S) is a thermodynamic function that increases with the number of energetically equivalent ways to arrange the components of a system to achieve a particular state.

Austrian physicist Ludwig Boltzmann (1844–1906) expressed this definition mathematically as:

$$S = k \ln W$$

where k is the Boltzmann constant (the gas constant divided by Avogadro's number, $R/N_A = 1.38 \times 10^{-23} \text{ J/K}$) and W is the number of energetically equivalent ways to arrange the components of the system. Since W is unitless (it is simply a number), the units of entropy are joules per kelvin (J/K). We talk about the significance of the units shortly. As we can see from the equation, as W increases, entropy increases.



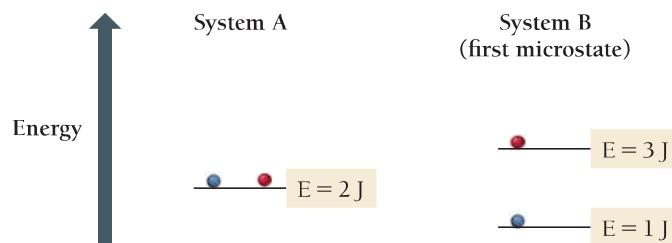
▲ Boltzmann's equation is engraved on his tombstone.

Microstates and Macrostates

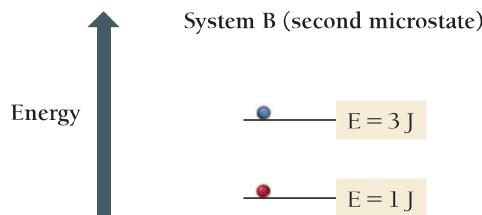
The key to understanding entropy is the quantity W . What does W —the number of energetically equivalent ways to arrange the components of the system—signify? Imagine a system of particles such as a fixed amount of an ideal gas. A given set of conditions (P , V , and T) defines the *state* (or *macrostate*) of the system. As long as these conditions remain constant, the energy of the system also remains constant. However, *exactly where that energy is at any given instant is anything but constant*.

At any one instant, a particular gas particle may have a good deal of kinetic energy. However, after a very short period of time, that particle may have very little kinetic energy (because it lost its energy through collisions with other particles). The exact internal energy distribution among the particles at any one instant is sometimes referred to as a *microstate*. We can think of a microstate as a snapshot of the system at a given instant in time. The next instant, the snapshot (the microstate) changes. However, the *macrostate*—defined by P , V , and T —remains constant. A given macrostate can exist as a result of a large number of different microstates. In other words, the snapshot (or microstate) of a given macrostate is generally different from one moment to the next as the energy of the system is constantly redistributing itself among the particles of the system.

We can think of W in terms of microstates. The quantity, W , is the number of *possible* microstates that can result in a given macrostate. For example, suppose that we have two systems (call them System A and System B) and that each is composed of two particles (one blue and one red). Both systems have a total energy of 4 joules, but System A has only one energy level and System B has two:



Note that each system has the same total energy, 4 J. But System A has one possible microstate because both particles must occupy the same energy level (red particle = 2 J and blue particle = 2 J), while System B has two possible microstates because the red and blue particles can occupy different energy levels (blue particle = 3 J and red particle = 1 J, or, blue particle = 1 J and red particle = 3 J).



This second microstate is not possible for System A because it has only one energy level. For System A, $W = 1$, but for System B, $W = 2$. In other words, System B has more microstates that result in the same 4 J macrostate. Since W is larger for System B than for System A, System B has greater *entropy*; it has more *energetically equivalent ways to arrange the components of the system*.

We can better understand the nature of entropy by turning our attention to energy for a moment. The entropy of a state increases with the number of *energetically equivalent* ways to arrange the components of the system to achieve that particular state. This implies that *the state with the highest entropy also has the greatest dispersal of energy*.

Returning to our previous example, we see that the energy of System B is dispersed over two energy levels instead of being confined to just one. At the heart of entropy is the concept of energy dispersal or energy randomization. *A state in which a given amount of energy is more highly dispersed (or more highly randomized) has more entropy than a state in which the same energy is more highly concentrated.*

We have already alluded to the **second law of thermodynamics**; we now formally define it:

For any spontaneous process, the entropy of the universe increases ($\Delta S_{\text{univ}} > 0$).

The criterion for spontaneity is the entropy of the universe. Processes that increase the entropy of the universe—those that result in greater dispersal or randomization of energy—occur spontaneously. Processes that decrease the entropy of the universe do not occur spontaneously.

See the discussion of state functions in Section 7.3.

Entropy, like enthalpy, is a *state function*—its value depends only on the state of the system, not on how the system arrived at that state. Therefore, for any process, *the change in entropy is the entropy of the final state minus the entropy of the initial state:*

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

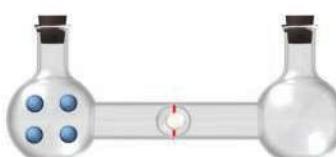
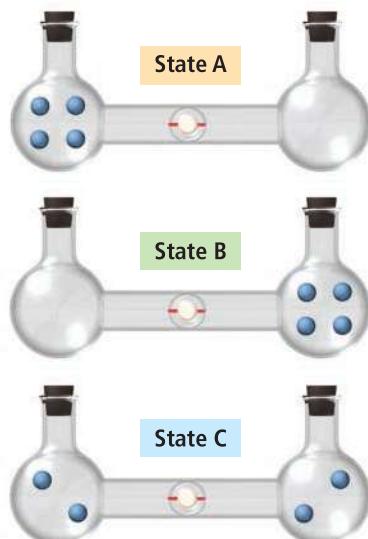
Entropy determines the direction of chemical and physical change. *A chemical system proceeds in a direction that increases the entropy of the universe*—it proceeds in a direction that has the largest number of *energetically equivalent* ways to arrange its components.

The Entropy Change upon the Expansion of an Ideal Gas

See the discussion of work done by an expanding gas in Section 7.4.

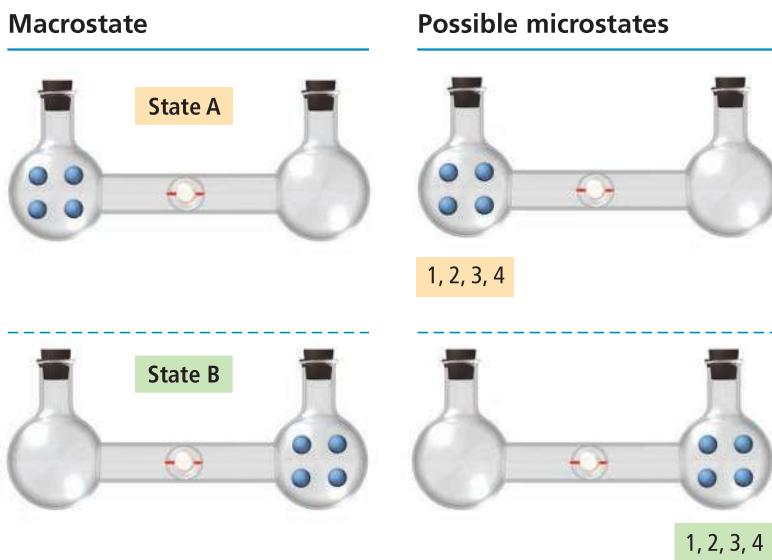
To better understand the tendency toward greater entropy, let us examine the expansion of an ideal gas into a vacuum (a spontaneous process with no associated change in enthalpy). Consider a flask containing an ideal gas that is connected to another, evacuated, flask by a tube equipped with a stopcock. When the stopcock is opened, the gas spontaneously expands into the evacuated flask. Since the gas is expanding into a vacuum, the pressure against which it expands is zero, and therefore the work ($w = -P_{\text{ext}} \Delta V$) is also zero.

However, even though the total energy of the gas does not change during the expansion, the entropy does change. To picture this, consider a simplified system containing only four gas atoms:

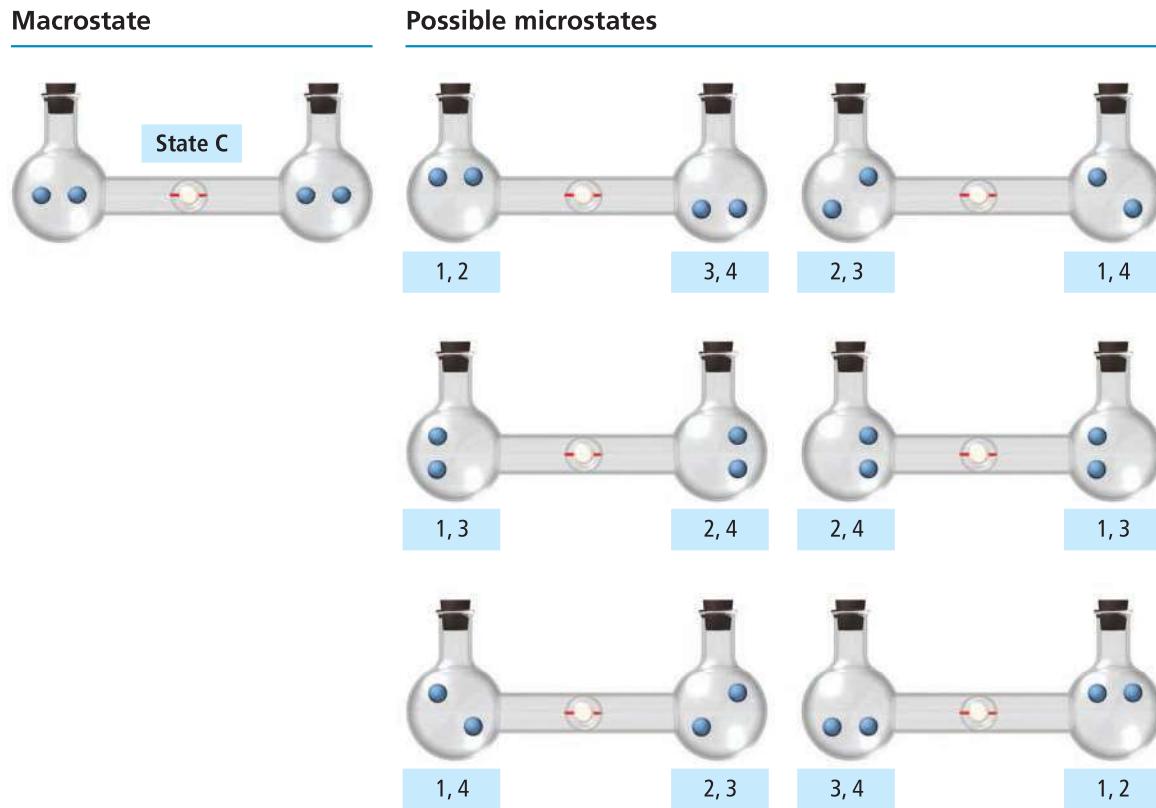


When the stopcock is opened, several possible energetically equivalent final states may result, each with the four atoms distributed in a different way. For example, there could be three atoms in the flask on the left and one in the flask on the right, or vice versa. For simplicity, we consider only the possibilities shown in the figure in the left margin, which are state A, state B, and state C. Since the energy of any one atom is the same in either flask, and since the atoms do not interact, states A, B, and C are energetically equivalent.

Now we ask the following question for each state: how many microstates give rise to the same macrostate? To keep track of the microstates, we label the atoms 1–4. Although they have different numbered labels, since the atoms are all the same, there is externally no difference between them. For states A and B, only one microstate results in the specified macrostate—atoms 1–4 on the left side or the right side, respectively:



For state C, however, six different possible microstates all result in the same macrostate (two atoms on each side):



This means that if the atoms are just randomly moving between the two flasks, the statistical probability of finding the atoms in state C is six times greater than the probability of finding the atoms in state A or state B. Consequently, even for a simple system consisting of only four atoms, the atoms are most likely to be found in state C. State C has the greatest entropy—it has the greatest number of energetically equivalent ways to distribute its components.

As the number of atoms increases, the number of microstates that leads to the atoms being equally distributed between the two flasks increases dramatically. For example, with 10 atoms, the number of microstates leading to an equal distribution of atoms between two flasks is 252, and with 20 atoms the number of microstates is 184,756. Yet, the number of microstates that leads to all of the atoms being only in the left flask (or all only in the right

In these drawings, the exact location of an atom within a flask is insignificant. The significant aspect is whether the atom is in the left flask or the right flask.

For n particles, the number of ways to put r particles in one flask and $n - r$ particles in the other flask is $n! / [(n - r)!r!]$. For 10 atoms, $n = 10$ and $r = 5$.

flask) does not increase—it is always only 1. In other words, the arrangement in which the atoms are equally distributed between the two flasks has a much larger number of possible microstates and therefore much greater entropy. The system thus tends toward that state.

The *change in entropy* in transitioning from a state in which all of the atoms are in the left flask to the state in which the atoms are evenly distributed between both flasks is *positive* because the final state has a greater entropy than the initial state:

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

\uparrow

\uparrow

Since S_{final} is greater than S_{initial} , ΔS is positive and the process is spontaneous according to the second law. Notice that when the atoms are confined to one flask, their energy is also confined to that one flask; however, when the atoms are evenly distributed between both flasks, their energy is spread out over a greater volume. As the gas expands into the empty flask, energy is dispersed.

The second law explains many phenomena not explained by the first law. In Chapter 7, we learned that heat travels from a substance at higher temperature to one at lower temperature. For example, if we drop an ice cube into water, heat travels from the water to the ice cube—the water cools and the ice warms (and eventually melts). Why? The first law would not prohibit some heat from flowing the other way—from the ice to the water. The ice could lose 10 J of heat (cooling even more), and the water could gain 10 J of heat (warming even more). The first law of thermodynamics would not be violated by such a heat transfer. Imagine putting ice into water only to have the water get warmer as it absorbed thermal energy from the ice! It will never happen because heat transfer from cold to hot violates the second law of thermodynamics. According to the second law, energy is dispersed, not concentrated. The transfer of heat from a substance of higher temperature to one of lower temperature results in greater energy randomization—the energy that was concentrated in the hot substance becomes dispersed between the two substances. The second law accounts for this pervasive tendency.

ANSWER NOW!

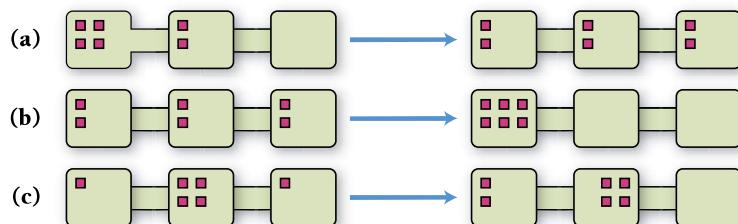


19.2 Cc

Conceptual Connection



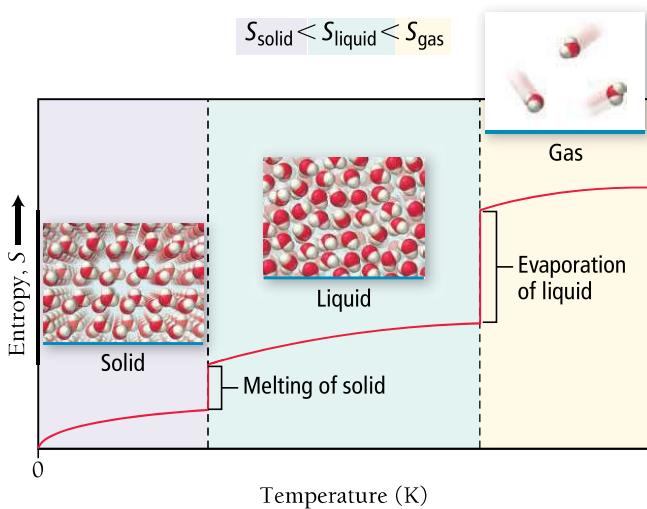
ENTROPY Consider these three changes in the possible distributions of six gaseous particles within three interconnected boxes. Which change has a positive ΔS ?



19.4

Entropy Changes Associated with State Changes

The entropy of a sample of matter *increases* as it changes state from a solid to a liquid or from a liquid to a gas (Figure 19.3►). We first consider this idea conceptually, and then we turn to actually calculating the value of ΔS for this change. Recall that, in Chapter 7, we distinguished between a thermodynamic system and its surroundings. This distinction is useful in our discussion of entropy. For a change of state in a substance, we consider the substance to be the system. The surroundings are then the rest of the universe. Here, we focus on the entropy of the *system* undergoing the change of state (not the surroundings, which we address in Section 19.5).



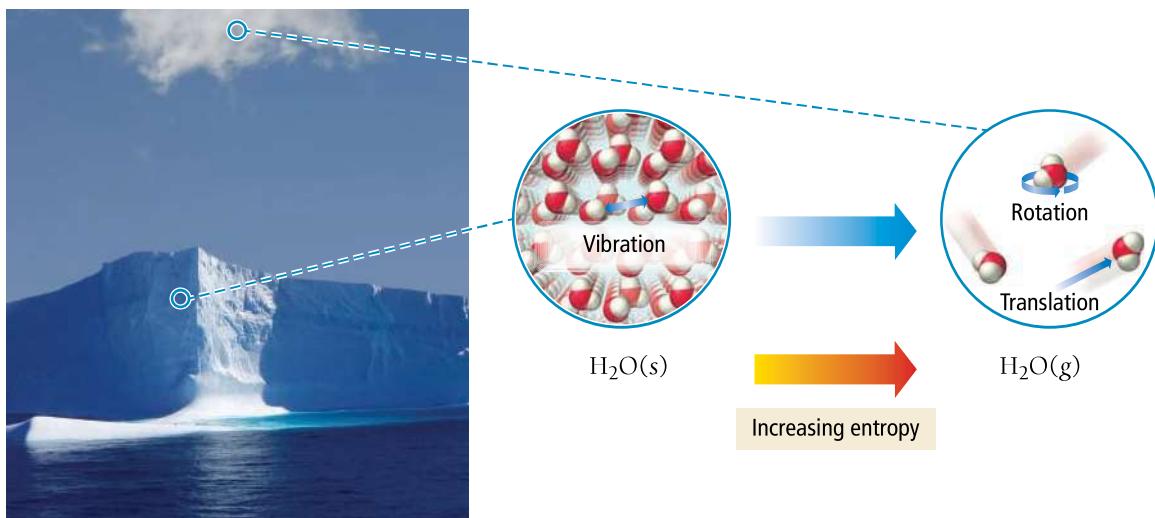
◀ FIGURE 19.3 Entropy and State Change Entropy increases when matter changes from a solid to a liquid and from a liquid to a gas.

Entropy and State Change: The Concept

We can informally think of the increase in entropy in going from a solid to a liquid or from a liquid to a gas by analogy with macroscopic disorder. The gaseous state is more disorderly than the liquid state, which is in turn more disorderly than the solid state. More formally, however, the differences in entropy are related to the number of energetically equivalent ways of arranging the particles in each state—there are more in the gas than in the liquid and more in the liquid than in the solid.

A gas has more energetically equivalent configurations because it has more ways to distribute its energy than a solid. The energy in a molecular solid consists largely of the vibrations between its molecules. If the same substance is in its gaseous state, however, the energy can take the form of straight-line motions of the molecules (called translational energy) and rotations of the molecules (called rotational energy). In other words, when a solid vaporizes into a gas, there are new “places” to put energy (Figure 19.4▼). The gas thus has more possible microstates (more energetically equivalent configurations) than the solid and therefore a greater entropy.

Additional “Places” for Energy



▲ FIGURE 19.4 “Places” for Energy In the solid state, energy is contained largely in the vibrations between molecules. In the gas state, energy can be contained in both the straight-line motion of molecules (translational energy) and the rotation of molecules (rotational energy).

We can now predict the sign of ΔS for processes involving changes of state (or phase). In general, entropy increases ($\Delta S > 0$) for each of the following:

- the phase transition from a solid to a liquid
- the phase transition from a solid to a gas
- the phase transition from a liquid to a gas
- an increase in the number of moles of a gas during a chemical reaction

ANSWER NOW!



19.3 Cc Conceptual Connection

ENTROPY AND STATE CHANGES

Which process undergoes a *decrease* in entropy for water?

- The melting of ice in a glass
- The boiling of water in a saucepan
- The condensation of water on the sides of a cold glass

EXAMPLE 19.1 Predicting the Sign of Entropy Change

Predict the sign of ΔS for each process.

- $\text{H}_2\text{O}(g) \longrightarrow \text{H}_2\text{O}(l)$
- Solid carbon dioxide sublimes.
- $2 \text{N}_2\text{O}(g) \longrightarrow 2 \text{N}_2(g) + \text{O}_2(g)$

SOLUTION

- Since a gas has a greater entropy than a liquid, the entropy decreases and ΔS is negative.
- Since a solid has a lower entropy than a gas, the entropy increases and ΔS is positive.
- Since the number of moles of gas increases, the entropy increases and ΔS is positive.

FOR PRACTICE 19.1

Predict the sign of ΔS for each process.

- Water boils.
- $\text{I}_2(g) \longrightarrow \text{I}_2(s)$
- $\text{CaCO}_3(s) \longrightarrow \text{CaO}(s) + \text{CO}_2(g)$

Entropy and State Changes: The Calculation

We have just seen how the entropy of system increases with the transition from a solid to a liquid to a gas. We can calculate the actual changes in entropy that occur in the system during these state transitions. Recall from Sections 12.5 and 12.6 that a change in state is accompanied by an exchange of heat between the system and surroundings. For example, melting and vaporization are endothermic (they absorb heat from the surroundings), while freezing and condensation are exothermic (they give off heat to the surroundings).

The definition of entropy that we introduced previously ($S = k \ln W$) shows how entropy is related to the distribution of energy among the particles that compose matter. On a macroscopic scale, we can define the change in entropy that occurs when a system exchanges a quantity of heat (q) with its surroundings at a constant temperature (T) with the following equation:

$$\Delta S = \frac{q_{\text{rev}}}{T} \quad (\text{constant temperature}) \quad [19.1]$$

In this equation, ΔS is the entropy change of the system, q_{rev} is the heat exchanged with the surroundings in a *reversible* process (more on this to come), and T is the temperature in K. The temperature must be constant throughout the change—the process must be *isothermal*. Let's address two important concepts related to this equation, the units of entropy and reversible processes.

Units of Entropy

In Section 19.3, we saw that the units of entropy are J/K. We can now better understand these units. Entropy is a measure of energy dispersal per unit temperature and therefore has the units of energy (J) over temperature (K). For example, when a substance melts

(an endothermic process), it absorbs a certain amount of energy from the surroundings. That energy becomes dispersed into the system (as the substance changes state from a solid to a liquid) and the entropy of the substance increases. The change in entropy is related to the amount of energy the substance absorbs (units of J) divided by the temperature of the substance (units of K).

Reversible Processes

A **reversible process** is one that reverses direction upon an infinitesimally small change in some property. The melting of ice when the ice and its surroundings are both at exactly 0 °C is an example of a reversible process. An infinitesimally small *removal* of heat reverses the melting and causes freezing instead. An infinitesimally small *addition* of heat causes the melting to resume. All reversible processes are in a constant state of equilibrium and represent highly idealized conditions. In contrast, the melting of ice that happens when we set an ice cube on a countertop at room temperature is *irreversible*. In this case, the countertop and the surrounding air are at 25.0 °C, and an infinitesimally small removal of heat does not reverse the melting.

We can use Equation 19.1 to calculate the change in the entropy of a system that undergoes a state change. For example, when ice melts at its melting point, the heat exchanged with the surroundings is ΔH_{fus} and the temperature is 273 K:

$$\begin{aligned} q_{\text{rev}} &= \Delta H_{\text{fus}} = 6.02 \text{ kJ/mol} \\ T &= 273 \text{ K} \end{aligned}$$

We substitute these quantities into Equation 19.1 to determine the change in entropy of the system when 1 mol of ice melts at its melting point:

$$\begin{aligned} \Delta S &= \frac{q_{\text{rev}}}{T} \\ &= \frac{(1 \text{ mol}) \frac{6.02 \times 10^3 \text{ J}}{\text{mol}}}{273 \text{ K}} \\ &= 22.1 \text{ J/K} \end{aligned}$$

The value of ΔS is positive, as we would expect for a transition from solid to liquid.

WATCH NOW!

INTERACTIVE WORKED EXAMPLE 19.2



EXAMPLE 19.2 Calculating ΔS for a Change of State

Calculate the change in entropy that occurs in the system when 25.0 g of water condenses from a gas to a liquid at the normal boiling point of water (100.00 °C).

SOLUTION

Because the condensation is occurring at the boiling point of water and the temperature is constant, you can use Equation 19.1 to calculate the change in entropy of the system.	$\Delta S = \frac{q_{\text{rev}}}{T}$
Gather the necessary quantities. Look up the value of the enthalpy of vaporization for water at its boiling point in Table 12.7. The enthalpy of condensation is the same in value but opposite in sign.	$\begin{aligned} \Delta H_{\text{vap}} &= 40.7 \text{ kJ/mol} \\ \Delta H_{\text{condensation}} &= -40.7 \text{ kJ/mol} \\ T(\text{K}) &= T(\text{°C}) + 273.15 \\ &= 100.00 + 273.15 \\ &= 373.15 \text{ K} \end{aligned}$
Calculate the temperature in K.	
Substitute into Equation 19.1 to calculate the change in entropy for the system.	$\begin{aligned} \Delta S &= \frac{q_{\text{rev}}}{T} \\ &= \frac{25.0 \text{ g} \times \frac{1 \text{ mol}}{18.02 \text{ g}} \times \left(\frac{-40.7 \times 10^3 \text{ J}}{\text{mol}} \right)}{373.15 \text{ K}} \\ &= -151 \text{ J/K} \end{aligned}$

—Continued on the next page

Continued—

CHECK The answer has the correct units for entropy (J/K). The answer is negative, as you would expect for the condensation of a gas to a liquid.

FOR PRACTICE 19.2 Calculate the change in entropy that occurs in the system when 10.0 g of acetone ($\text{C}_3\text{H}_6\text{O}$) vaporizes from a liquid to a gas at its normal boiling point (56.1 °C).

19.5

Heat Transfer and Changes in the Entropy of the Surroundings

We have now seen that the criterion for spontaneity is an increase in the entropy of the universe. However, you can probably think of several spontaneous processes in which entropy seems to decrease. For example, when water freezes at temperatures below 0 °C, the entropy of the water decreases, yet the process is spontaneous. Similarly, when water vapor in air condenses into fog on a cold night, the entropy of the water also decreases. Why are these processes spontaneous?

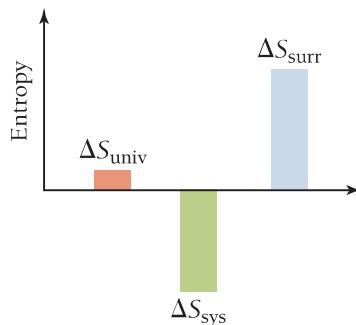
To answer this question, we must return to the second law: for any spontaneous process, the entropy of the *universe* increases ($\Delta S_{\text{univ}} > 0$). Even though the entropy of the *water* decreases during freezing and condensation, the entropy of the *universe* must somehow increase in order for these processes to be spontaneous. If we define the water as the system, then ΔS_{sys} is the entropy change for the water itself, ΔS_{surr} is the entropy change for the surroundings, and ΔS_{univ} is the entropy change for the universe. The entropy change for the universe is the sum of the entropy changes for the system and the surroundings:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

The second law states that the entropy of the universe must increase ($\Delta S_{\text{univ}} > 0$) for a process to be spontaneous. The entropy of the *system* can decrease ($\Delta S_{\text{sys}} < 0$) as long as the entropy of the *surroundings* increases by a greater amount ($\Delta S_{\text{surr}} > -\Delta S_{\text{sys}}$), so that the overall entropy of the *universe* undergoes a net increase.

For liquid water freezing or water vapor condensing, we know that the change in entropy for the system (ΔS_{sys}) is negative, as we discussed in Section 19.4. For ΔS_{univ} to be positive, therefore, ΔS_{surr} must be positive and greater in absolute value (or magnitude) than ΔS_{sys} , as shown graphically here:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$



Even though (as we saw earlier) enthalpy by itself cannot determine spontaneity, the increase in the entropy of the surroundings caused by the release of heat explains why exothermic processes are so often spontaneous.

But why does the freezing of ice or the condensation of water increase the entropy of the surroundings? Because both processes are *exothermic*: they give off heat to the surroundings. Because we think of entropy as the dispersal or randomization of energy, *the release of heat energy by the system disperses that energy into the surroundings, increasing the entropy of the surroundings*. The freezing of water below 0 °C and the condensation of water vapor on a cold night both increase the entropy of the universe because the heat given off to the surroundings increases the entropy of the surroundings to a sufficient degree to overcome the entropy decrease in the water.

Summarizing Entropy Changes in the Surroundings:

- An exothermic process increases the entropy of the surroundings.
- An endothermic process decreases the entropy of the surroundings.

The Temperature Dependence of ΔS_{surr}

We have just seen how the freezing of water increases the entropy of the surroundings by dispersing heat energy into the surroundings. Yet we know that the freezing of water is not spontaneous at all temperatures. The freezing of water becomes *nonspontaneous* above 0 °C. Why? Because the magnitude of the increase in the entropy of the surroundings due to the dispersal of energy into the surroundings is *temperature dependent*.

The greater the temperature, the smaller the increase in entropy for a given amount of energy dispersed into the surroundings. Recall that the units of entropy are joules per kelvin: energy units divided by temperature units. As we have seen, *entropy is a measure of energy dispersal (joules) per unit temperature (kelvins)*. The higher the temperature, the lower the amount of entropy for a given amount of energy dispersed. We can understand the temperature dependence of entropy changes due to heat flow with a simple analogy. Imagine that you have \$1000 to give away. If you gave the \$1000 to a millionaire, the impact on his net worth would be negligible (because he already has so much money). If you gave the same \$1000 to a poor man, however, his net worth would change substantially (because he has so little money). Similarly, if you disperse 1000 J of energy into surroundings that are hot, the entropy increase is small (because the impact of the 1000 J is small on surroundings that already contain a lot of energy). If you disperse the same 1000 J of energy into surroundings that are cold, however, the entropy increase is large (because the impact of the 1000 J is great on surroundings that contain little energy). For this same reason, the impact of the heat released to the surroundings by the freezing of water depends on the temperature of the surroundings—the higher the temperature, the smaller the impact.

We can now understand why water spontaneously freezes at low temperature but not at high temperature. For the freezing of liquid water into ice, the change in entropy of the system is negative at all temperatures:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

Negative

Positive and large at low temperature
Positive and small at high temperature

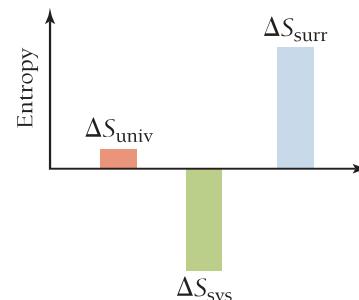
At low temperatures, on one hand, the decrease in entropy of the system is overcome by the large increase in the entropy of the surroundings (a positive quantity), resulting in a positive ΔS_{univ} and a spontaneous process. At high temperatures, on the other hand, the decrease in entropy of the system is not overcome by the increase in entropy of the surroundings (because the magnitude of the positive ΔS_{surr} is smaller at higher temperatures), resulting in a negative ΔS_{univ} ; therefore, the freezing of water is not spontaneous at high temperature as shown graphically in the margin at right.

Quantifying Entropy Changes in the Surroundings

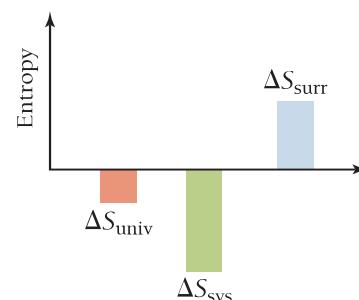
We have seen that when a system exchanges heat with the surroundings, it changes the entropy of the surroundings. In Section 19.4, we saw that, at constant temperature, we can use Equation 19.1 ($\Delta S = q_{\text{rev}}/T$)

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \quad (\text{for water freezing})$$

Low Temperature: Spontaneous



High Temperature: Nonspontaneous



to quantify the entropy change in the system. We can use the same equation to quantify entropy changes in the surroundings. In other words, the change in entropy of the surroundings depends on: (a) the amount of heat transferred into or out of the surroundings; and (b) the temperature of the surroundings.

Since the surroundings are usually an infinitely large bath at constant temperature, the heat transferred into or out of that bath under conditions of constant pressure (where only PV work is allowed) is simply $-\Delta H_{\text{sys}}$. The negative sign reflects that, according to the first law of thermodynamics, any heat leaving the system must go into the surroundings and vice versa ($q_{\text{sys}} = -q_{\text{surr}}$). If we incorporate this idea into Equation 19.1, we get the following equation:

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T} \quad (\text{constant } P, T) \quad [19.2]$$

For any chemical or physical process occurring at constant temperature and pressure, the entropy change of the surroundings is equal to the heat dispersed into or out of the surroundings ($-\Delta H_{\text{sys}}$) divided by the temperature of the surroundings in kelvins. Notice that:

- A process that emits heat into the surroundings (ΔH_{sys} negative) *increases* the entropy of the surroundings (positive ΔS_{surr}).
- A process that absorbs heat from the surroundings (ΔH_{sys} positive) *decreases* the entropy of the surroundings (negative ΔS_{surr}).
- The magnitude of the change in entropy of the surroundings is proportional to the magnitude of ΔH_{sys} .

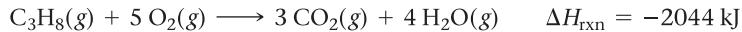
Equation 19.1 gives us insight into why exothermic processes have a tendency to be spontaneous at low temperatures—they increase the entropy of the surroundings. As temperature increases, however, a given negative ΔH_{sys} produces a smaller positive ΔS_{surr} ; for this reason, exothermicity becomes less of a determining factor for spontaneity as temperature increases.

WATCH NOW!

INTERACTIVE WORKED EXAMPLE 19.3

EXAMPLE 19.3 Calculating Entropy Changes in the Surroundings

Consider the combustion of propane gas:



- Calculate the entropy change in the surroundings when this reaction occurs at 25 °C.
- Determine the sign of the entropy change for the system.
- Determine the sign of the entropy change for the universe. Is the reaction spontaneous?

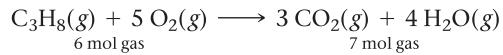
SOLUTION

- (a) The entropy change of the surroundings is given by Equation 19.2. Substitute the value of ΔH_{rxn} and the temperature in kelvins and calculate ΔS_{surr} .

$$T = 273 + 25 = 298 \text{ K}$$

$$\begin{aligned} \Delta S_{\text{surr}} &= \frac{-\Delta H_{\text{rxn}}}{T} \\ &= \frac{-(-2044 \text{ kJ})}{298 \text{ K}} \\ &= +6.86 \text{ kJ/K} \\ &= +6.86 \times 10^3 \text{ J/K} \end{aligned}$$

- (b) Determine the number of moles of gas on each side of the reaction. An increase in the number of moles of gas implies a positive ΔS_{sys} .



ΔS_{sys} is positive.

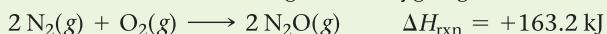
- (c) The change in entropy of the universe is the sum of the entropy changes of the system and the surroundings. If the entropy changes of the system and surroundings are both the same sign, the entropy change for the universe also has the same sign.

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

Positive
Positive

Therefore, ΔS_{univ} is positive and the reaction is spontaneous.

FOR PRACTICE 19.3 Consider the reaction between nitrogen and oxygen gas to form dinitrogen monoxide:



- (a) Calculate the entropy change in the surroundings when this reaction occurs at 25 °C.
 (b) Determine the sign of the entropy change for the system.
 (c) Determine the sign of the entropy change for the universe. Is the reaction spontaneous?

FOR MORE PRACTICE 19.3 For a reaction, $\Delta H_{\text{rxn}} = -107 \text{ kJ}$ and $\Delta S_{\text{rxn}} = 285 \text{ J/K}$. At what temperature is the change in entropy for this reaction equal to the change in entropy for the surroundings?

ENTROPY AND BIOLOGICAL SYSTEMS By absorbing energy from their surroundings and synthesizing large, complex biological molecules, plants and animals tend to concentrate energy, not disperse it. How can this happen?

- (a) Biological systems only appear to concentrate energy. In reality, large, complex biological molecules have more entropy than the substances from which they are composed.
 (b) Biological systems can decrease their own entropy by creating more entropy in their surroundings.
 (c) Biological systems are an exception to the second law of thermodynamics.



ANSWER NOW!



19.6 Gibbs Free Energy

Equation 19.2 establishes a relationship between the enthalpy change in a system and the entropy change in the surroundings. Recall that for any process the entropy change of the universe is the sum of the entropy change of the system and the entropy change of the surroundings:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \quad [19.3]$$

Combining Equation 19.3 with Equation 19.2 gives us the following relationship at constant temperature and pressure:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} \quad [19.4]$$

Using Equation 19.4, we can calculate ΔS_{univ} while focusing only on the *system*. If we multiply Equation 19.4 by $-T$, we arrive at the equation:

$$\begin{aligned} -T\Delta S_{\text{univ}} &= -T\Delta S_{\text{sys}} + T \frac{\Delta H_{\text{sys}}}{T} \\ &= \Delta H_{\text{sys}} - T\Delta S_{\text{sys}} \end{aligned} \quad [19.5]$$

If we drop the subscript *sys* (from now on ΔH and ΔS without subscripts mean ΔH_{sys} and ΔS_{sys}) we get the equation:

$$-T\Delta S_{\text{univ}} = \Delta H - TS \quad [19.6]$$

The right-hand side of Equation 19.6 represents the change in a thermodynamic function called *Gibbs free energy*. The formal definition of **Gibbs free energy (G)** is:

$$G = H - TS \quad [19.7]$$

where H is enthalpy, T is the temperature in kelvins, and S is entropy. The *change* in Gibbs free energy, symbolized by ΔG , is expressed as follows (at constant temperature):

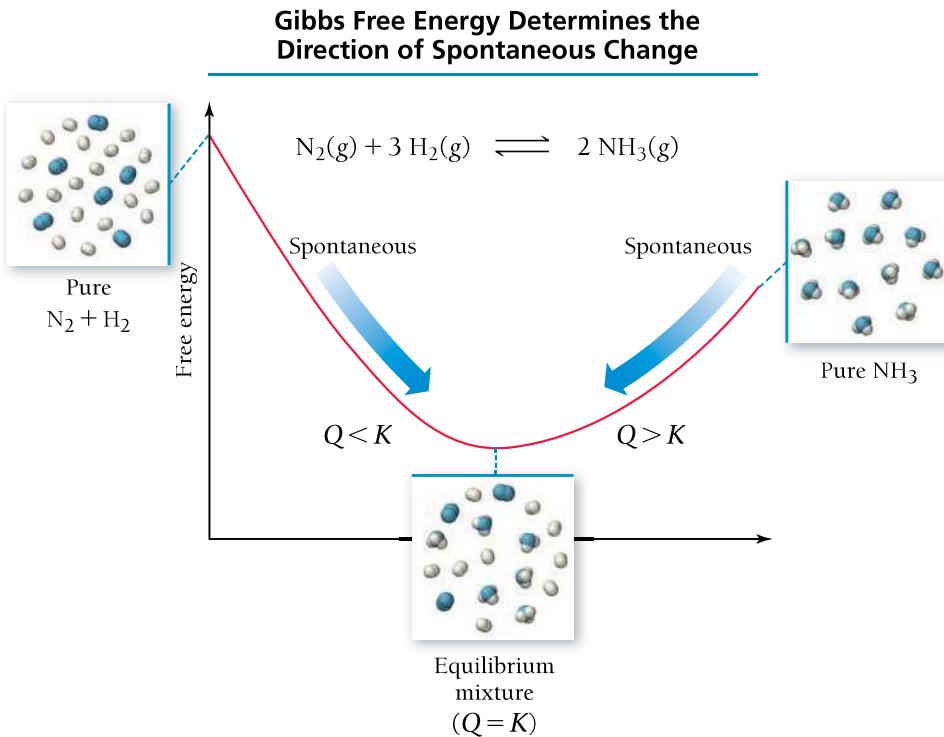
$$\Delta G = \Delta H - T\Delta S \quad [19.8]$$

If we combine Equations 19.6 and 19.8, we have an equation that makes clear the significance of ΔG :

$$\Delta G = -T\Delta S_{\text{univ}} \quad (\text{constant } T, P) \quad [19.9]$$

The change in Gibbs free energy for a process occurring at constant temperature and pressure is proportional to the negative of ΔS_{univ} . Since ΔS_{univ} is a criterion for spontaneity, ΔG is also a criterion for spontaneity (although opposite in sign). In fact, Gibbs free energy is also called *chemical potential* because it is analogous to mechanical potential energy discussed earlier. Just as mechanical systems tend toward lower potential energy, so chemical systems tend toward lower Gibbs free energy (toward lower chemical potential) (Figure 19.5▼).

► FIGURE 19.5 Gibbs Free Energy Gibbs free energy is also called chemical potential because it determines the direction of spontaneous change for chemical systems.



Summarizing Gibbs Free Energy (at Constant Temperature and Pressure):

- ΔG is proportional to the negative of ΔS_{univ} .
- A decrease in Gibbs free energy ($\Delta G < 0$) corresponds to a spontaneous process.
- An increase in Gibbs free energy ($\Delta G > 0$) corresponds to a nonspontaneous process.

Notice that we can calculate changes in Gibbs free energy solely with reference to the system. So, to determine whether a process is spontaneous, we only have to find the change in *entropy* for the system (ΔS) and the change in *enthalpy* for the system (ΔH). We can then predict the spontaneity of the process at any temperature. In Chapter 7, we learned how to calculate changes in enthalpy (ΔH) for chemical reactions. In Section 19.7, we learn how to calculate changes in entropy (ΔS) for chemical reactions. We can then use those two quantities to calculate changes in free energy (ΔG) for chemical reactions and predict their spontaneity (Section 19.8). Before we move on to these topics, let's examine some examples that demonstrate how ΔH , ΔS , and T affect the spontaneity of chemical processes.

WATCH NOW!

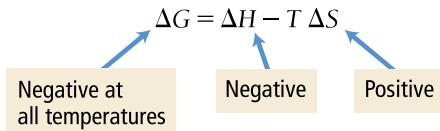
KEY CONCEPT VIDEO 19.6

The Effect of ΔH , ΔS , and T on Reaction Spontaneity

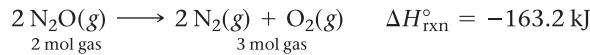
The Effect of ΔH , ΔS , and T on Spontaneity

Case 1: ΔH Negative, ΔS Positive

If a reaction is exothermic ($\Delta H < 0$) and if the change in entropy for the reaction is positive ($\Delta S > 0$), then the change in free energy is negative at all temperatures and the reaction is spontaneous at all temperatures:



As an example, consider the dissociation of N₂O:

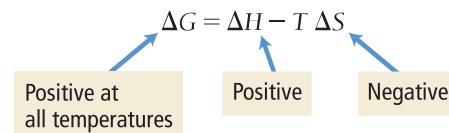


The change in *enthalpy* is negative—heat is emitted, increasing the entropy of the surroundings. The change in *entropy* for the reaction is positive, which means that the entropy of the system increases. (We can see that the change in entropy is positive from the balanced equation—the number of moles of gas increases.) Since the entropy of both the system and the surroundings increases, the entropy of the universe must also increase, making the reaction spontaneous at all temperatures.

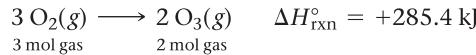
Recall from Chapter 7 that ΔH° represents the standard enthalpy change. The definition of the standard state was first given in Section 7.9 and is summarized in Section 19.7.

Case 2: ΔH Positive, ΔS Negative

If a reaction is endothermic ($\Delta H > 0$), and if the change in entropy for the reaction is negative ($\Delta S < 0$), then the change in free energy is positive at all temperatures and the reaction is nonspontaneous at all temperatures:



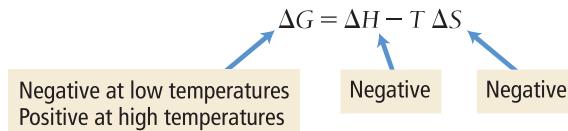
As an example, consider the formation of ozone from oxygen:



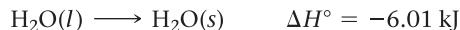
The change in *enthalpy* is positive—heat is therefore absorbed, *decreasing* the entropy of the surroundings. The change in *entropy* is negative, which means that the entropy of the system decreases. (We can see that the change in entropy is negative from the balanced equation—the number of moles of gas decreases.) Since the entropy of both the system and the surroundings decreases, the entropy of the universe must also decrease, making the reaction nonspontaneous at all temperatures.

Case 3: ΔH Negative, ΔS Negative

If a reaction is exothermic ($\Delta H < 0$) and if the change in entropy for the reaction is negative ($\Delta S < 0$), then the sign of the change in free energy depends on temperature. The reaction is spontaneous at low temperature but nonspontaneous at high temperature:



As an example, consider the freezing of liquid water to form ice:



The change in *enthalpy* is negative—heat is emitted, increasing the entropy of the surroundings. The change in *entropy* is negative, which means that the entropy of the system decreases. (We can see that the change in entropy is negative from the balanced equation—a liquid turns into a solid.)

Unlike the two previous cases, where the changes in *entropy* of the system and of the surroundings had the *same* sign, the changes here are *opposite* in sign. Therefore, the sign of the change in free energy depends on the relative magnitudes of the two changes. At a low enough temperature, the heat emitted into the surroundings causes a large entropy change in the surroundings, making the process spontaneous. At high temperature, the same amount of heat is dispersed into warmer surroundings, so the positive entropy change in the surroundings is smaller, resulting in a nonspontaneous process.

Case 4: ΔH Positive, ΔS Positive

If a reaction is endothermic ($\Delta H > 0$), and if the change in entropy for the reaction is positive ($\Delta S > 0$), then the sign of the change in free energy again depends on

temperature. The reaction is nonspontaneous at low temperature but spontaneous at high temperature:

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

As an example, consider the vaporizing of liquid water to gaseous water:



The change in *enthalpy* is positive—heat is absorbed from the surroundings, so the entropy of the surroundings decreases. The change in *entropy* is positive, which means that the entropy of the system increases. (We can see that the change in entropy is positive from the balanced equation—a liquid turns into a gas.) The changes in entropy of the system and the surroundings again have opposite signs, only this time the entropy of the surroundings decreases while the entropy of the system increases. In cases such as this, high temperature favors spontaneity because the absorption of heat from the surroundings has less effect on the entropy of the surroundings as temperature increases.

Table 19.1 summarizes these effects. Notice that when ΔH and ΔS have opposite signs, the spontaneity of the reaction does not depend on temperature. *When ΔH and ΔS have the same sign, however, the spontaneity does depend on temperature.* The temperature at which the reaction changes from being spontaneous to being nonspontaneous (or vice versa) is the temperature at which ΔG changes sign, which we can find by setting $\Delta G = 0$ and solving for T , as shown in part b of Example 19.4.

TABLE 19.1 ■ The Effect of ΔH , ΔS , and T on Spontaneity

ΔH	ΔS	Low Temperature	High Temperature	Example
−	+	Spontaneous ($\Delta G < 0$)	Spontaneous ($\Delta G < 0$)	$2 \text{ N}_2\text{O}(g) \longrightarrow 2 \text{ N}_2(g) + \text{ O}_2(g)$
+	−	Nonspontaneous ($\Delta G > 0$)	Nonspontaneous ($\Delta G > 0$)	$3 \text{ O}_2(g) \longrightarrow 2 \text{ O}_3(g)$
−	−	Spontaneous ($\Delta G < 0$)	Nonspontaneous ($\Delta G > 0$)	$\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(s)$
+	+	Nonspontaneous ($\Delta G > 0$)	Spontaneous ($\Delta G < 0$)	$\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(g)$

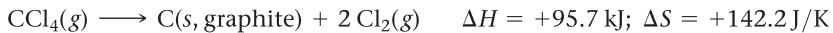
WATCH NOW!

INTERACTIVE WORKED EXAMPLE 19.4

EXAMPLE 19.4

Calculating Gibbs Free Energy Changes and Predicting Spontaneity from ΔH and ΔS

Consider the reaction for the decomposition of carbon tetrachloride gas:



- (a) Calculate ΔG at 25 °C and determine whether the reaction is spontaneous.
- (b) If the reaction is not spontaneous at 25 °C, determine at what temperature (if any) the reaction becomes spontaneous.

SOLUTION

- (a) Use Equation 19.8 to calculate ΔG from the given values of ΔH and ΔS . The temperature must be in kelvins. *Be sure to express both ΔH and ΔS in the same units (usually joules).*

$$\begin{aligned} T &= 273 + 25 = 298 \text{ K} \\ \Delta G &= \Delta H - T \Delta S \\ &= 95.7 \times 10^3 \text{ J} - (298 \text{ K})142.2 \text{ J/K} \\ &= 95.7 \times 10^3 \text{ J} - 42.4 \times 10^3 \text{ J} \\ &= +53.3 \times 10^3 \text{ J} \end{aligned}$$

The reaction is not spontaneous.

- (b) Since ΔS is positive, ΔG becomes more negative with increasing temperature. To determine the temperature at which the reaction becomes spontaneous, use Equation 19.8 to find the temperature at which ΔG changes from positive to negative (set $\Delta G = 0$ and solve for T). The reaction is spontaneous above this temperature.

$$\begin{aligned} \Delta G &= \Delta H - T \Delta S \\ 0 &= 95.7 \times 10^3 \text{ J} - (T)142.2 \text{ J/K} \\ T &= \frac{95.7 \times 10^3 \text{ J}}{142.2 \text{ J/K}} \\ &= 673 \text{ K} \end{aligned}$$

FOR PRACTICE 19.4 Consider the reaction:



Calculate ΔG at 25 °C and determine whether the reaction is spontaneous. Does ΔG become more negative or more positive as the temperature increases?

ΔH, ΔS, AND ΔG Which statement is true regarding the sublimation of dry ice (solid CO₂)?

- (a) ΔH is positive, ΔS is positive, and ΔG is positive at low temperatures and negative at high temperatures.
- (b) ΔH is negative, ΔS is negative, and ΔG is negative at low temperatures and positive at high temperatures.
- (c) ΔH is negative, ΔS is positive, and ΔG is negative at all temperatures.
- (d) ΔH is positive, ΔS is negative, and ΔG is positive at all temperatures.



ANSWER NOW!



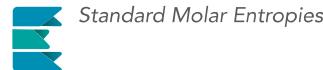
19.7

Entropy Changes in Chemical Reactions: Calculating ΔS_{rxn}°

In Chapter 7, we learned how to calculate standard changes in enthalpy (ΔH_{rxn}°) for chemical reactions. We now turn to calculating standard changes in *entropy* for chemical reactions.

WATCH NOW!

KEY CONCEPT VIDEO 19.7



Defining Standard States and Standard Entropy Changes

Recall from Section 7.9 that the standard enthalpy change for a reaction (ΔH_{rxn}°) is the change in enthalpy for a process in which all reactants and products are in their standard states. Recall also the definition of the standard state:

- **For a Gas:** The standard state for a gas is the pure gas at a pressure of exactly 1 atm.
- **For a Liquid or Solid:** The standard state for a liquid or solid is the pure substance in its most stable form at a pressure of 1 atm and at the temperature of interest (often taken to be 25 °C).
- **For a Substance in Solution:** The standard state for a substance in solution is a concentration of 1 M.

The standard state has recently been changed to a pressure of 1 bar, which is very close to (1 atm = 1.013 bar). Both standards are now in common use.

We define the **standard entropy change for a reaction** (ΔS_{rxn}°) as the change in *entropy* for a process in which all reactants and products are in their standard states. Since entropy is a function of state, the standard change in entropy is therefore the standard entropy of the products minus the standard entropy of the reactants:

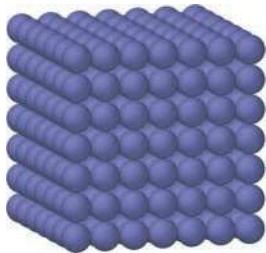
$$\Delta S_{rxn}^\circ = S_{\text{products}}^\circ - S_{\text{reactants}}^\circ$$

But how do we find the standard entropies of the reactants and products? Recall from Chapter 7 that we defined *standard molar enthalpies of formation* (ΔH_f°) to use in calculating ΔH_{rxn}° . We now need to define **standard molar entropies** (S°) to use in calculating ΔS_{rxn}° .

Standard Molar Entropies (S°) and the Third Law of Thermodynamics

In Chapter 7, we defined a *relative zero* for enthalpy. To do this, we assigned a value of zero to the standard enthalpy of formation for an element in its standard state. This was necessary because absolute values of enthalpy cannot be determined. In other words, for

Perfect crystal at 0 K
 $W = 1$ $S = 0$



▲ FIGURE 19.6 Zero Entropy

A perfect crystal at 0 K has only one possible way to arrange its components.

enthalpy, there is no absolute zero against which to measure all other values; therefore, we always have to rely on enthalpy changes from an arbitrarily assigned standard (the elements in their standard states and most stable forms).

For entropy, however, *there is an absolute zero*. The absolute zero of entropy is established by the **third law of thermodynamics**, which states:

The entropy of a perfect crystal at absolute zero (0 K) is zero.

A perfect crystal at a temperature of absolute zero has only one possible way ($W = 1$) to arrange its components (Figure 19.6). Based on Boltzmann's definition of entropy ($S = k \ln W$), its entropy is zero ($S = k \ln 1 = 0$).

We can measure all entropy values against the absolute zero of entropy as defined by the third law. Table 19.2 lists values of standard entropies at 25 °C for selected substances. A more complete list is in Appendix IIB. Standard entropy values are listed in units of joules per mole per kelvin (J/mol · K). The units of mole in the denominator are required because *entropy is an extensive property*—it depends on the amount of the substance.

TABLE 19.2 ■ Standard Molar Entropy Values (S°) for Selected Substances at 298 K

Substance	S° (J/mol · K)	Substance	S° (J/mol · K)	Substance	S° (J/mol · K)
Gases		Liquids		Solids	
$\text{H}_2(g)$	130.7	$\text{H}_2\text{O}(l)$	70.0	$\text{MgO}(s)$	27.0
$\text{Ar}(g)$	154.8	$\text{CH}_3\text{OH}(l)$	126.8	$\text{Fe}(s)$	27.3
$\text{CH}_4(g)$	186.3	$\text{Br}_2(l)$	152.2	$\text{Li}(s)$	29.1
$\text{H}_2\text{O}(g)$	188.8	$\text{C}_6\text{H}_6(l)$	173.4	$\text{Cu}(s)$	33.2
$\text{N}_2(g)$	191.6			$\text{Na}(s)$	51.3
$\text{NH}_3(g)$	192.8			$\text{K}(s)$	64.7
$\text{F}_2(g)$	202.8			$\text{NaCl}(s)$	72.1
$\text{O}_2(g)$	205.2			$\text{CaCO}_3(s)$	91.7
$\text{Cl}_2(g)$	223.1			$\text{FeCl}_3(s)$	142.3
$\text{C}_2\text{H}_4(g)$	219.3				

Some elements exist in two or more forms, called *allotropes*, within the same state.

At 25 °C, the standard molar entropy of any substance is the energy dispersed into one mole of that substance at 25 °C, which depends on the number of “places” to put energy within the substance. The factors that affect the number of “places” to put energy—and therefore the standard entropy—include the state of the substance, the molar mass of the substance, the particular allotrope, its molecular complexity, and its extent of dissolution. Let’s examine each of these separately.

Relative Standard Entropies: Gases, Liquids, and Solids

As we saw in Section 19.3, the entropy of a gas is generally greater than the entropy of a liquid, which is in turn greater than the entropy of a solid. We can see these trends in the tabulated values of standard entropies. For example, consider the relative standard entropies of liquid water and gaseous water at 25 °C:

	S° (J/mol · K)
$\text{H}_2\text{O}(l)$	70.0
$\text{H}_2\text{O}(g)$	188.8

Gaseous water has a much greater standard entropy because, as we discussed in Section 19.3, it has more energetically equivalent ways to arrange its components, which in turn results in greater energy dispersal at 25 °C.

Relative Standard Entropies: Molar Mass

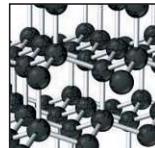
Consider the standard entropies of the noble gases at 25 °C:

S° (J/mol · K)		
He(g)	126.2	
Ne(g)	146.1	
Ar(g)	154.8	
Kr(g)	163.8	
Xe(g)	169.4	

The more massive the noble gas, the greater its entropy at 25 °C. A complete explanation of why entropy increases with increasing molar mass is beyond the scope of this book. Briefly, the energy states associated with the motion of heavy atoms are more closely spaced than those of lighter atoms. The more closely spaced energy states allow for greater dispersal of energy at a given temperature and therefore greater entropy. This trend is true only for elements in the same state. (The effect of a state change—from a liquid to a gas, for example—is far greater than the effect of molar mass.)

Relative Standard Entropies: Allotropes

As mentioned previously, some elements can exist in two or more forms—called *allotropes*—in the same state of matter. For example, the allotropes of carbon include diamond and graphite—both solid forms of carbon. Because the arrangement of atoms within these forms is different, their standard molar entropies are different:

S° (J/mol · K)		
C(s, diamond)	2.4	
C(s, graphite)	5.7	

In diamond, the atoms are constrained by chemical bonds in a highly restricted three-dimensional crystal structure. In graphite, the atoms bond together in sheets, but the sheets have freedom to slide past each other. The less constrained structure of graphite results in more “places” to put energy and therefore greater entropy compared to diamond.

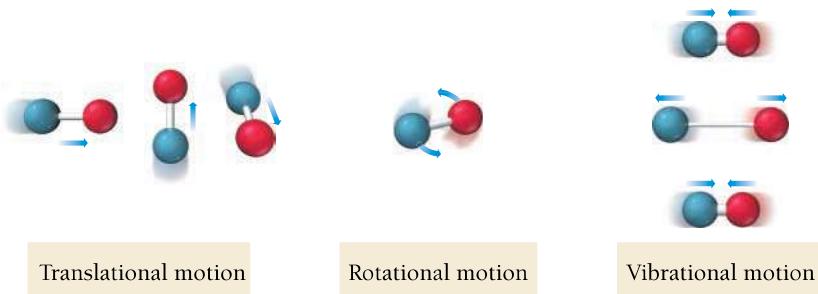
Relative Standard Entropies: Molecular Complexity

For a given state of matter, entropy generally increases with increasing molecular complexity. For example, consider the standard entropies of argon and nitrogen monoxide gas:

	Molar Mass (g/mol)	S° (J/mol · K)
Ar(g)	39.948	154.8
NO(g)	30.006	210.8

Ar has a greater molar mass than NO, yet it has less entropy at 25 °C. Why? Molecules generally have more “places” to put energy than do atoms. In a gaseous sample of argon, on one hand, the only form that energy can take is the translational motion of the atoms. In a gaseous sample of NO, on the other hand, energy can take the form of translational motion, rotational motion, and (at high enough temperatures) vibrational motions of the molecules (Figure 19.7▼). Therefore, for a given state, molecules generally have a greater entropy than free atoms.

► **FIGURE 19.7** “Places” for Energy in Gaseous NO Energy can be contained in translational motion, rotational motion, and (at high enough temperatures) vibrational motion.



Similarly, more complex molecules generally have more entropy than simpler ones. For example, consider the standard entropies of carbon monoxide and ethene gas:

	Molar Mass (g/mol)	S° (J/mol · K)
CO(g)	28.01	197.7
C ₂ H ₄ (g)	28.05	219.3

These two substances have nearly the same molar mass, but the greater complexity of C₂H₄ results in a greater molar entropy. When molecular complexity and molar mass both increase (as is often the case), molar entropy also increases, as demonstrated by the oxides of nitrogen:

S° (J/mol · K)
NO(g) 210.8
NO ₂ (g) 240.1
N ₂ O ₄ (g) 304.4

The increasing molecular complexity as we move down this list, as well as the increasing molar mass, results in more “places” to put energy and therefore greater entropy.

The standard entropies for aqueous solutions are for the solution in its standard state, which is defined as having a concentration of 1 M.

Relative Standard Entropies: Dissolution

The dissolution of a crystalline solid into solution usually results in an increase in entropy. For example, consider the standard entropies of solid and aqueous potassium chlorate:

S° (J/mol · K)
KClO ₃ (s) 143.1
KClO ₃ (aq) 265.7

When solid potassium chlorate dissolves in water, the energy that was concentrated within the crystal becomes dispersed throughout the entire solution. The greater energy dispersal results in greater entropy.

STANDARD ENTROPIES Arrange these gases in order of increasing standard molar entropy: SO₃, Kr, Cl₂.

- (a) Kr < Cl₂ < SO₃
 (c) SO₃ < Cl₂ < Kr
 (b) Kr < SO₃ < Cl₂
 (d) Cl₂ < Kr < SO₃



ANSWER NOW!



Calculating the Standard Entropy Change (ΔS_{rxn}°) for a Reaction

Since entropy is a state function, and since standard entropies for many common substances are tabulated, we can calculate the standard entropy change for a chemical reaction by calculating the difference in entropy between the products and the reactants. More specifically,

To calculate ΔS_{rxn}° , subtract the standard entropies of the reactants multiplied by their stoichiometric coefficients from the standard entropies of the products multiplied by their stoichiometric coefficients. In the form of an equation:

$$\Delta S_{rxn}^\circ = \sum n_p S^\circ(\text{products}) - \sum n_r S^\circ(\text{reactants}) \quad [19.10]$$

In Equation 19.10, n_p represents the stoichiometric coefficients of the products, n_r represents the stoichiometric coefficients of the reactants, and S° represents the standard entropies. Keep in mind when using this equation that, *unlike enthalpies of formation, which are zero for elements in their standard states, standard entropies are always nonzero at 25 °C*. Example 19.5 demonstrates the application of Equation 19.10.

WATCH NOW!

INTERACTIVE WORKED EXAMPLE 19.5

EXAMPLE 19.5 Calculating Standard Entropy Changes (ΔS_{rxn}°)



Calculate ΔS_{rxn}° for the balanced chemical equation:



SOLUTION

Begin by looking up the standard entropy for each reactant and product in Appendix IIB. Always note the correct state—(g), (l), (aq), or (s)—for each reactant and product.

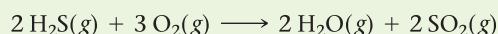
Reactant or product	S° (in J/mol · K)
NH ₃ (g)	192.8
O ₂ (g)	205.2
NO(g)	210.8
H ₂ O(g)	188.8

Calculate ΔS_{rxn}° by substituting the appropriate values into Equation 19.10. Remember to include the stoichiometric coefficients in your calculation.

$$\begin{aligned} \Delta S_{rxn}^\circ &= \sum n_p S^\circ(\text{products}) - \sum n_r S^\circ(\text{reactants}) \\ &= [4(S^\circ_{\text{NO}(g)}) + 6(S^\circ_{\text{H}_2\text{O}(g)})] - [4(S^\circ_{\text{NH}_3(g)}) + 5(S^\circ_{\text{O}_2(g)})] \\ &= [4(210.8 \text{ J/K}) + 6(188.8 \text{ J/K})] - [4(192.8 \text{ J/K}) + 5(205.2 \text{ J/K})] \\ &= 1976.0 \text{ J/K} - 1797.2 \text{ J/K} = 178.8 \text{ J/K} \end{aligned}$$

CHECK Notice that ΔS_{rxn}° is positive, as you would expect for a reaction in which the number of moles of gas increases.

FOR PRACTICE 19.5 Calculate ΔS_{rxn}° for the balanced chemical equation:



19.8

Free Energy Changes in Chemical Reactions: Calculating ΔG_{rxn}°

In the previous section, we learned how to calculate the standard change in entropy for a chemical reaction (ΔS_{rxn}°). However, the criterion for spontaneity at standard conditions is the **standard change in free energy (ΔG_{rxn}°)**. In this section, we examine three methods to calculate the standard change in free energy for a reaction (ΔG_{rxn}°). In the first method, we calculate ΔH_{rxn}° and ΔS_{rxn}° from tabulated values of ΔH_f° and S° , and then

use the relationship $\Delta G_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} - T\Delta S_{\text{rxn}}^{\circ}$ to calculate $\Delta G_{\text{rxn}}^{\circ}$. In the second method, we use tabulated values of free energies of formation to calculate $\Delta G_{\text{rxn}}^{\circ}$ directly. In the third method, we determine the free energy change for a stepwise reaction from the free energy changes of each of the steps. At the end of this section, we discuss what is “free” about free energy. Remember that $\Delta G_{\text{rxn}}^{\circ}$ is extremely useful because it tells us about the spontaneity of a process at standard conditions. The more negative $\Delta G_{\text{rxn}}^{\circ}$ is, the more spontaneous the process (the further it will go toward products to reach equilibrium).

Calculating Standard Free Energy Changes with $\Delta G_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} - T\Delta S_{\text{rxn}}^{\circ}$

In Chapter 7 (Section 7.9), we used tabulated values of standard enthalpies of formation to calculate $\Delta H_{\text{rxn}}^{\circ}$. In the previous section of this chapter, we used tabulated values of standard entropies to calculate $\Delta S_{\text{rxn}}^{\circ}$. We can use these calculated values of $\Delta H_{\text{rxn}}^{\circ}$ and $\Delta S_{\text{rxn}}^{\circ}$ to determine the standard free energy change for a reaction by using the equation:

$$\Delta G_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} - T\Delta S_{\text{rxn}}^{\circ} \quad [19.11]$$

Since tabulated values of standard enthalpies of formation (ΔH_f°) and standard entropies (S°) are usually applicable at 25 °C, the equation should (strictly speaking) be valid only when $T = 298$ K (25 °C). However, the changes in $\Delta H_{\text{rxn}}^{\circ}$ and $\Delta S_{\text{rxn}}^{\circ}$ over a limited temperature range are small when compared to the changes in the value of the temperature itself. Therefore, we can use Equation 19.11 to estimate changes in free energy at temperatures other than 25 °C.

WATCH NOW!

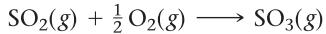
INTERACTIVE WORKED EXAMPLE 19.6

EXAMPLE 19.6

Calculating the Standard Change in Free Energy for a Reaction Using $\Delta G_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} - T\Delta S_{\text{rxn}}^{\circ}$



One of the possible initial steps in the formation of acid rain is the oxidation of the pollutant SO₂ to SO₃ by the reaction:



Calculate $\Delta G_{\text{rxn}}^{\circ}$ at 25 °C and determine whether the reaction is spontaneous.

SOLUTION

Begin by looking up (in Appendix IIB) the standard enthalpy of formation and the standard entropy for each reactant and product.

Reactant or product	ΔH_f° (kJ/mol)	S° (J/mol · K)
SO ₂ (g)	-296.8	248.2
O ₂ (g)	0	205.2
SO ₃ (g)	-395.7	256.8

Calculate $\Delta H_{\text{rxn}}^{\circ}$ using Equation 7.15.

$$\begin{aligned} \Delta H_{\text{rxn}}^{\circ} &= \sum n_p \Delta H_f^{\circ}(\text{products}) - \sum n_r \Delta H_f^{\circ}(\text{reactants}) \\ &= [\Delta H_f^{\circ} \text{ SO}_3(g)] - [\Delta H_f^{\circ} \text{ SO}_2(g) + \frac{1}{2}(\Delta H_f^{\circ} \text{ O}_2(g))] \\ &= -395.7 \text{ kJ} - (-296.8 \text{ kJ} + 0.0 \text{ kJ}) = -98.9 \text{ kJ} \end{aligned}$$

Calculate $\Delta S_{\text{rxn}}^{\circ}$ using Equation 19.10.

$$\begin{aligned} \Delta S_{\text{rxn}}^{\circ} &= \sum n_p S^{\circ}(\text{products}) - \sum n_r S^{\circ}(\text{reactants}) \\ &= [S^{\circ} \text{ SO}_3(g)] - [S^{\circ} \text{ SO}_2(g) + \frac{1}{2}(S^{\circ} \text{ O}_2(g))] \\ &= 256.8 \text{ J/K} - [248.2 \text{ J/K} + \frac{1}{2}(205.2 \text{ J/K})] = -94.0 \text{ J/K} \end{aligned}$$

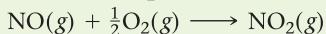
Calculate $\Delta G_{\text{rxn}}^{\circ}$ using the calculated values of $\Delta H_{\text{rxn}}^{\circ}$ and $\Delta S_{\text{rxn}}^{\circ}$ and Equation 19.11. Convert the temperature to kelvins.

$$\begin{aligned} T &= 25 + 273 = 298 \text{ K} \\ \Delta G_{\text{rxn}}^{\circ} &= \Delta H_{\text{rxn}}^{\circ} - T\Delta S_{\text{rxn}}^{\circ} \\ &= -98.9 \times 10^3 \text{ J} - 298 \text{ K}(-94.0 \text{ J/K}) \\ &= -70.9 \times 10^3 \text{ J} = -70.9 \text{ kJ} \end{aligned}$$

The reaction is spontaneous at this temperature because $\Delta G_{\text{rxn}}^{\circ}$ is negative.

FOR PRACTICE 19.6

Consider the oxidation of NO to NO₂:



Calculate $\Delta G_{\text{rxn}}^{\circ}$ at 25 °C and determine whether the reaction is spontaneous at standard conditions.

EXAMPLE 19.7**Estimating the Standard Change in Free Energy for a Reaction at a Temperature Other Than 25 °C Using $\Delta G_{rxn}^\circ = \Delta H_{rxn}^\circ - T\Delta S_{rxn}^\circ$**

For the reaction in Example 19.6, estimate the value of ΔG_{rxn}° at 125 °C. Is the reaction more or less spontaneous at this elevated temperature? That is, is the value of ΔG_{rxn}° more negative (more spontaneous) or more positive (less spontaneous)?

SOLUTION

Estimate ΔG_{rxn}° at the new temperature using the calculated values of ΔH_{rxn}° and ΔS_{rxn}° from Example 19.6. For T , convert the given temperature to kelvins. Make sure to use the same units for ΔH_{rxn}° and ΔS_{rxn}° (usually joules).

$$\begin{aligned}T &= 125 + 273 = 398 \text{ K} \\ \Delta G_{rxn}^\circ &= \Delta H_{rxn}^\circ - T\Delta S_{rxn}^\circ \\ &= -98.9 \times 10^3 \text{ J} - 398 \text{ K}(-94.0 \text{ J/K}) \\ &= -61.5 \times 10^3 \text{ J} \\ &= -61.5 \text{ kJ}\end{aligned}$$

Since the value of ΔG_{rxn}° at this elevated temperature is less negative (or more positive) than the value of ΔG_{rxn}° at 25 °C (which is -70.9 kJ), the reaction is less spontaneous.

FOR PRACTICE 19.7 For the reaction in For Practice 19.6, calculate the value of -70.9 kJ , at $-55 \text{ }^\circ\text{C}$. Is the reaction more spontaneous (more negative ΔG_{rxn}°) or less spontaneous (more positive ΔG_{rxn}°) at the lower temperature?

Calculating ΔG_{rxn}° with Tabulated Values of Free Energies of Formation

Because ΔG_{rxn}° is the *change* in free energy for a chemical reaction—the difference in free energy between the products and the reactants—and because free energy is a state function, we can calculate ΔG_{rxn}° by subtracting the free energies of the reactants of the reaction from the free energies of the products of the reaction. Also, since we are interested only in *changes* in free energy (and not in absolute values of free energy), we are free to define the *zero* of free energy as conveniently as possible. By analogy with our definition of enthalpies of formation, we define the **free energy of formation (ΔG_f°)** as follows:

The free energy of formation (ΔG_f°) is the change in free energy when 1 mol of a compound in its standard state forms from its constituent elements in their standard states. The free energy of formation of pure elements in their standard states is zero.

We can measure all changes in free energy relative to pure elements in their standard states. To calculate ΔG_{rxn}° , we subtract the free energies of formation of the reactants multiplied by their stoichiometric coefficients from the free energies of formation of the products multiplied by their stoichiometric coefficients. In the form of an equation:

$$\Delta G_{rxn}^\circ = \sum n_p \Delta G_f^\circ(\text{products}) - \sum n_r \Delta G_f^\circ(\text{reactants}) \quad [19.12]$$

In Equation 19.12, n_p represents the stoichiometric coefficients of the products, n_r represents the stoichiometric coefficients of the reactants, and ΔG_f° represents the standard free energies of formation.

Table 19.3 lists ΔG_f° values for selected substances. You can find a more complete list in Appendix IIB. Notice that, by definition, *elements* have standard free energies of formation of zero. Notice also that most *compounds* have negative standard free energies of formation. This means that those compounds spontaneously form from their elements in their standard states. Compounds with positive free energies of formation do not spontaneously form from their elements and are therefore less common.

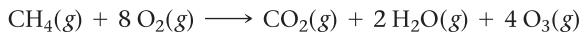
Example 19.8 demonstrates the calculation of ΔG_{rxn}° from ΔG_f° values. This method of calculating ΔG_{rxn}° works only at the temperature for which the free energies of formation are tabulated, namely, 25 °C. To estimate ΔG_{rxn}° at other temperatures we must use $\Delta G_{rxn}^\circ = \Delta H_{rxn}^\circ - T\Delta S_{rxn}^\circ$, as demonstrated previously.

**TABLE 19.3 ■ Standard Molar Free Energies of Formation
 ΔG_f° for Selected Substances at 298 K**

Substance	ΔG_f° (kJ/mol)	Substance	ΔG_f° (kJ/mol)
$\text{H}_2(g)$	0	$\text{CH}_4(g)$	-50.5
$\text{O}_2(g)$	0	$\text{H}_2\text{O}(g)$	-228.6
$\text{N}_2(g)$	0	$\text{H}_2\text{O}(l)$	-237.1
$\text{C}(s, \text{graphite})$	0	$\text{NH}_3(g)$	-16.4
$\text{C}(s, \text{diamond})$	2.900	$\text{NO}(g)$	+87.6
$\text{CO}(g)$	-137.2	$\text{NO}_2(g)$	+51.3
$\text{CO}_2(g)$	-394.4	$\text{NaCl}(s)$	-384.1

EXAMPLE 19.8 Calculating $\Delta G_{\text{rxn}}^\circ$ from Standard Free Energies of Formation

Ozone in the lower atmosphere is a pollutant that can form by the following reaction involving the oxidation of unburned hydrocarbons:



Use the standard free energies of formation to determine $\Delta G_{\text{rxn}}^\circ$ for this reaction at 25 °C.

SOLUTION

Begin by looking up (in Appendix IIB) the standard free energies of formation for each reactant and product. Remember that the standard free energy of formation of a pure element in its standard state is zero.

Reactant or product	ΔG_f° (in kJ/mol)
$\text{CH}_4(g)$	-50.5
$\text{O}_2(g)$	0.0
$\text{CO}_2(g)$	-394.4
$\text{H}_2\text{O}(g)$	-228.6
$\text{O}_3(g)$	163.2

Calculate $\Delta G_{\text{rxn}}^\circ$ by substituting into Equation 19.12.

$$\begin{aligned} \Delta G_{\text{rxn}}^\circ &= \sum n_p \Delta G_f^\circ(\text{products}) - \sum n_r \Delta G_f^\circ(\text{reactants}) \\ &= [\Delta G_f^\circ, \text{CO}_2(g) + 2(\Delta G_f^\circ, \text{H}_2\text{O}(g)) + 4(\Delta G_f^\circ, \text{O}_3(g))] - [\Delta G_f^\circ, \text{CH}_4(g) + 8(\Delta G_f^\circ, \text{O}_2(g))] \\ &= [-394.4 \text{ kJ} + 2(-228.6 \text{ kJ}) + 4(163.2 \text{ kJ})] - [-50.5 \text{ kJ} + 8(0.0 \text{ kJ})] \\ &= -198.8 \text{ kJ} + 50.5 \text{ kJ} \\ &= -148.3 \text{ kJ} \end{aligned}$$

FOR PRACTICE 19.8 One of the reactions that occurs within a catalytic converter in the exhaust pipe of a car is the simultaneous oxidation of carbon monoxide and reduction of NO (both of which are harmful pollutants):



Use standard free energies of formation to determine $\Delta G_{\text{rxn}}^\circ$ for this reaction at 25 °C. Is the reaction spontaneous at standard conditions?

FOR MORE PRACTICE 19.8 In For Practice 19.8, you calculated $\Delta G_{\text{rxn}}^\circ$ for the simultaneous oxidation of carbon monoxide and reduction of NO using standard free energies of formation. Calculate $\Delta G_{\text{rxn}}^\circ$ for that reaction again at 25 °C, only this time use $\Delta G_{\text{rxn}}^\circ = \Delta H_{\text{rxn}}^\circ - T\Delta S_{\text{rxn}}^\circ$. How do the two values compare? Use your results to calculate $\Delta G_{\text{rxn}}^\circ$ at 500.0 K and explain why you could not calculate $\Delta G_{\text{rxn}}^\circ$ at 500.0 K using tabulated standard free energies of formation.

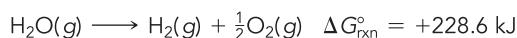


CHEMISTRY IN YOUR DAY

Making a Nonspontaneous Process Spontaneous

A process that is nonspontaneous can be made spontaneous by coupling it with another process that is highly spontaneous. For example, hydrogen gas is a potential future fuel because it can be used in a fuel cell (a type of battery in which the reactants are constantly supplied—see Chapter 20) to generate electricity. The main problem with switching to hydrogen is securing a source. Where can we get the huge amounts of hydrogen gas that would be needed to meet our world's energy needs?

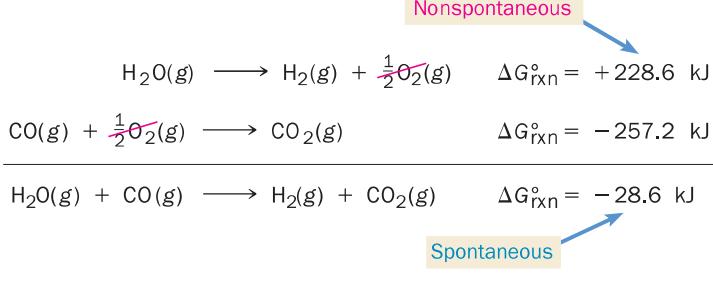
Earth's oceans and lakes, of course, contain vast amounts of hydrogen. But that hydrogen is locked up in water molecules, and the decomposition of water into hydrogen and oxygen has a positive ΔG_{rxn}° and is therefore nonspontaneous:



To obtain hydrogen from water, we need to find another reaction with a highly negative ΔG_{rxn}° that can couple with the decomposition reaction to give an overall reaction with a negative ΔG_{rxn}° . For example, the oxidation of carbon monoxide to carbon dioxide has a large negative ΔG_{rxn}° and is highly spontaneous:



If we add the two reactions together, we get a negative ΔG_{rxn}° :

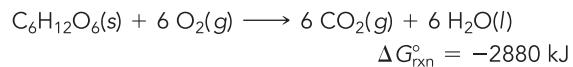


Nonspontaneous

Spontaneous

The reaction between water and carbon monoxide is thus a spontaneous way to generate hydrogen gas.

The coupling of nonspontaneous reactions with highly spontaneous ones is also important in biological systems. The synthesis reactions that create the complex biological molecules (such as proteins and DNA) needed by living organisms, for example, are themselves nonspontaneous. Living systems grow and reproduce by coupling these nonspontaneous reactions to highly spontaneous ones. The main spontaneous reaction that ultimately drives the nonspontaneous ones is the metabolism of food. The oxidation of glucose, for example, is highly spontaneous:



Spontaneous reactions such as these ultimately drive the nonspontaneous reactions necessary to sustain life.



Calculating ΔG_{rxn}° for a Stepwise Reaction from the Changes in Free Energy for Each of the Steps

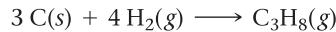
Recall from Section 7.8 that because enthalpy is a state function, we can calculate ΔH_{rxn}° for a stepwise reaction from the sum of the changes in enthalpy for each step (according to Hess's law). Since free energy is also a state function, the same relationships that we covered in Chapter 7 for enthalpy also apply to free energy:

1. If a chemical equation is multiplied by some factor, then ΔG_{rxn} is also multiplied by the same factor.
2. If a chemical equation is reversed, then ΔG_{rxn} changes sign.
3. If a chemical equation can be expressed as the sum of a series of steps, then ΔG_{rxn} for the overall equation is the sum of the free energies of reactions for each step.

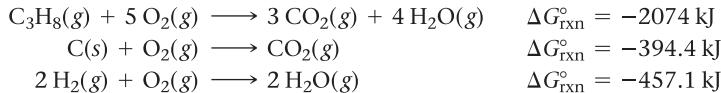
Example 19.9 illustrates the use of these relationships to calculate ΔG_{rxn}° for a stepwise reaction.

EXAMPLE 19.9 Calculating ΔG_{rxn}° for a Stepwise Reaction

Find ΔG_{rxn}° for the reaction:



Use the following reactions with known ΔG_{rxn}° values:



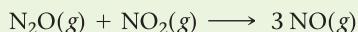
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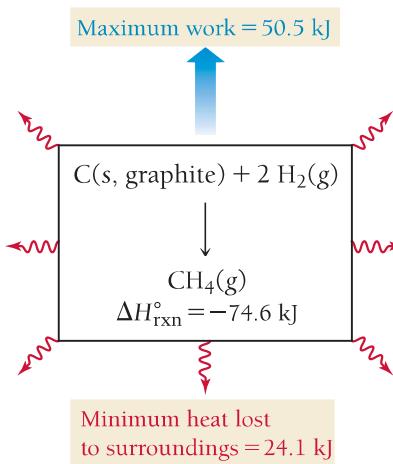
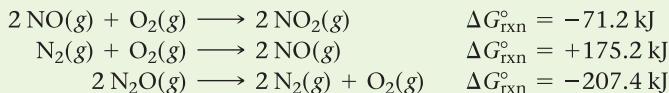
SOLUTION

To work this problem, you need to manipulate the given reactions with known values of $\Delta G_{\text{rxn}}^{\circ}$ in such a way as to get the reactants of interest on the left, the products of interest on the right, and other species to cancel.

Since the first reaction has C_3H_8 as a reactant, and the reaction of interest has C_3H_8 as a product, reverse the first reaction and change the sign of $\Delta G_{\text{rxn}}^{\circ}$.	$3 \text{CO}_2(g) + 4 \text{H}_2\text{O}(g) \longrightarrow \text{C}_3\text{H}_8(g) + 5 \text{O}_2(g)$ $\Delta G_{\text{rxn}}^{\circ} = +2074 \text{ kJ}$
The second reaction has C as a reactant and CO_2 as a product, as required in the reaction of interest. However, the coefficient for C is 1, and in the reaction of interest, the coefficient for C is 3. Therefore, multiply this equation and its $\Delta G_{\text{rxn}}^{\circ}$ by 3.	$3 \times [\text{C}(s) + \text{O}_2(g) \longrightarrow \text{CO}_2(g)]$ $\Delta G_{\text{rxn}}^{\circ} = 3 \times (-394.4 \text{ kJ})$ $= -1183 \text{ kJ}$
In the third reaction $\text{H}_2(g)$ is a reactant, as required. However, the coefficient for H_2 is 2, and in the reaction of interest, the coefficient for H_2 is 4. Multiply this reaction and its $\Delta G_{\text{rxn}}^{\circ}$ by 2.	$2 \times [2 \text{H}_2(g) + \text{O}_2(g) \longrightarrow 2 \text{H}_2\text{O}(g)]$ $\Delta G_{\text{rxn}}^{\circ} = 2 \times (-457.1 \text{ kJ})$ $= -914.2 \text{ kJ}$
Lastly, rewrite the three reactions after multiplying through by the indicated factors and show how they sum to the reaction of interest. $\Delta G_{\text{rxn}}^{\circ}$ for the reaction of interest is then the sum of the ΔG 's for the steps.	$\begin{array}{l} 3 \text{CO}_2(g) + 4 \text{H}_2\text{O}(g) \longrightarrow \text{C}_3\text{H}_8(g) + 5 \text{O}_2(g) \\ 3 \text{C}(s) + 3 \text{O}_2(g) \longrightarrow 3 \text{CO}_2(g) \\ 4 \text{H}_2(g) + 2 \text{O}_2(g) \longrightarrow 4 \text{H}_2\text{O}(g) \\ \hline 3 \text{C}(s) + 4 \text{H}_2(g) \longrightarrow \text{C}_3\text{H}_8(g) \end{array}$ $\begin{array}{ll} \Delta G_{\text{rxn}}^{\circ} = +2074 \text{ kJ} & \Delta G_{\text{rxn}}^{\circ} = -1183 \text{ kJ} \\ \Delta G_{\text{rxn}}^{\circ} = -914.2 \text{ kJ} & \Delta G_{\text{rxn}}^{\circ} = -23 \text{ kJ} \end{array}$

FOR PRACTICE 19.9 Find $\Delta G_{\text{rxn}}^{\circ}$ for the reaction:

Use the following reactions with known $\Delta G_{\text{rxn}}^{\circ}$ values:

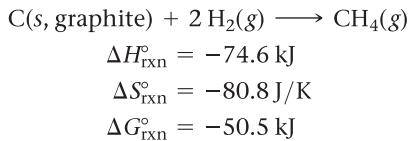


▲ FIGURE 19.8 Free Energy
Although the reaction produces 74.6 kJ of heat, only a maximum of 50.5 kJ is available to do work. The rest of the energy is lost to the surroundings.

Why Free Energy Is “Free”

We often want to use the energy released by a chemical reaction to do work. For example, in an automobile engine, we use the energy released by the combustion of gasoline to move the car forward. The change in free energy of a chemical reaction represents the maximum amount of energy available, or *free*, to do work (if $\Delta G_{\text{rxn}}^{\circ}$ is negative).

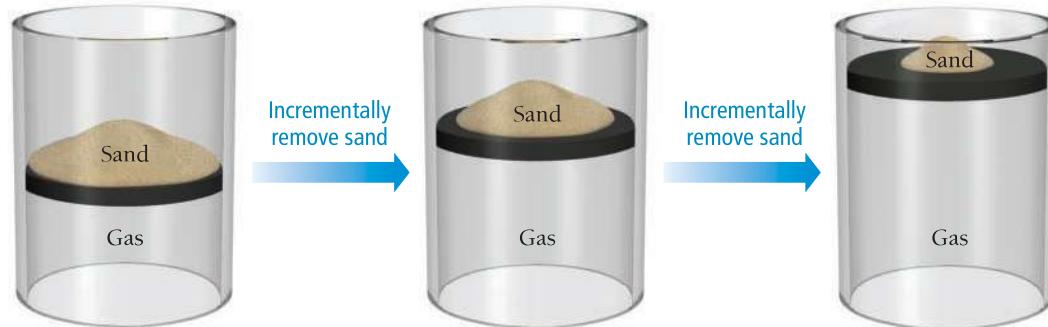
For many reactions, the change in free energy is less than the change in enthalpy for the reaction. Consider the reaction between carbon and hydrogen occurring at 25 °C:



The reaction is exothermic and gives off 74.6 kJ of heat energy. However, the maximum amount of energy available for useful work is only 50.5 kJ (Figure 19.8▲). Why? We can see that the change in entropy of the *system* is negative. Nevertheless, the reaction is spontaneous. This is possible only if some of the emitted heat goes to increase the entropy of the surroundings by an amount sufficient to make the change in entropy of the *universe* positive. The amount of energy available to do work (the free energy) is what remains after accounting for the heat that must be lost to the surroundings.

Reversible Process

Weight of sand exactly matches pressure at each increment.



▲ FIGURE 19.9 A Reversible Process In a reversible process, the free energy is drawn out in infinitesimally small increments that exactly match the amount of energy that the process is producing in that increment. In this case, grains of sand are removed one at a time, resulting in a series of small expansions in which the weight of sand almost exactly matches the pressure of the expanding gas. This process is close to reversible—each sand grain would need to have an infinitesimally small mass for the process to be fully reversible.

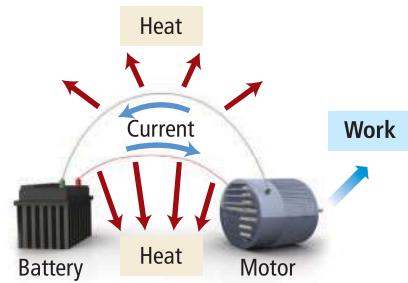
The change in free energy for a chemical reaction represents a *theoretical limit* as to how much work can be done by the reaction. In a *real* reaction, the amount of energy available to do work is even *less* than ΔG_{rxn}° because additional energy is lost to the surroundings as heat. The only reactions that reach the theoretical limit are reversible reactions (see Section 19.4 for the definition of reversible processes). A reversible chemical reaction occurs infinitesimally slowly, and the free energy is drawn out in infinitesimally small increments that exactly match the amount of energy that the reaction is producing during that increment (Figure 19.9▲).

All real reactions are irreversible and therefore do not achieve the theoretical limit of available free energy. For example, consider the discharging of a battery. A battery contains chemical reactants configured in such a way that, upon spontaneous reaction, they produce an electrical current. We can harness the free energy released by the reaction to do work. For example, an electric motor can be wired to the battery. Flowing electrical current makes the motor turn (Figure 19.10►).

Because of the resistance in the wire, the flowing electrical current also produces some heat, which is lost to the surroundings and is not available to do work. The amount of free energy lost as heat can be decreased by slowing down the rate of current flow. The slower the rate of current flow, the less free energy is lost as heat and the more is available to do work. However, only in the theoretical case of infinitesimally slow current flow is the maximum amount of work (equal to ΔG_{rxn}°) done. Any real rate of current flow results in some loss of energy as heat. This lost energy is sometimes called the “heat tax,” a loss of energy that must necessarily occur in any energy exchange. Recharging the battery necessarily requires more energy than is obtained as work because some of the energy is lost as heat. In other words, during discharging and recharging, the battery has gone through a cycle in which it returns to its original (charged) state. However, the surroundings have gained some heat during the process, and the entropy of the surroundings has increased (which makes the process spontaneous). Any real (or irreversible) cyclical process such as this suffers the same fate—the system may return to its original state, but the surroundings do not, resulting in the permanent dispersal of energy to the surroundings.

If the change in free energy of a chemical reaction is positive, then ΔG_{rxn}° represents the *minimum amount of energy required to make the reaction occur*. Again, ΔG_{rxn}° represents a theoretical limit. Making a real nonspontaneous reaction occur always requires more energy than the theoretical limit.

Applying the definition of reversibility from Section 19.4, a reversible chemical reaction is one that changes direction upon an infinitesimally small change in a variable (such as temperature or pressure) related to the reaction.



▲ FIGURE 19.10 Energy Loss in a Battery When current is drawn from a battery to do work, some energy is lost as heat due to resistance in the wire. Consequently, the quantity of energy required to recharge the battery will be more than the quantity of work done.

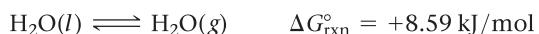
19.9

Free Energy Changes for Nonstandard States: The Relationship between ΔG_{rxn}° and ΔG_{rxn}

We have learned how to calculate the *standard* free energy change for a reaction (ΔG_{rxn}°). However, the standard free energy change applies only to a very narrow set of conditions, namely, those conditions in which the reactants and products are in their standard states.

Standard versus Nonstandard States

Consider the standard free energy change for the evaporation of liquid water to gaseous water:



▲ Spilled water spontaneously evaporates even though ΔG° for the vaporization of water is positive. Why?

The standard free energy change for this process is positive, so the process is nonspontaneous. But you know that if you spill water onto the floor under ordinary conditions, it spontaneously evaporates. Why? Because under ordinary conditions the reactants and products are not in their standard states and ΔG_{rxn}° applies only when the reactants and product are in their standard states, sometimes called *standard conditions*. For a gas (such as the water vapor in the reaction just given), the standard state is that the pure gas is present at a partial pressure of 1 atmosphere. In a flask containing liquid water and water vapor in its standard state ($P_{\text{H}_2\text{O}} = 1 \text{ atm}$) at 25 °C the water does not vaporize. In fact, since ΔG_{rxn}° is negative for the reverse reaction, the reaction spontaneously occurs in reverse—water vapor condenses.

In open air under ordinary circumstances, the partial pressure of water vapor is much less than 1 atm. The state of the water vapor is not its standard state, and therefore the value of ΔG_{rxn}° does not apply. For the nonstandard state, we must calculate ΔG_{rxn} (as opposed to ΔG_{rxn}°) to predict spontaneity.

The Free Energy Change of a Reaction under Nonstandard Conditions

We can calculate the **free energy change of a reaction under nonstandard conditions** (ΔG_{rxn}) from ΔG_{rxn}° using the relationship:

$$\Delta G_{rxn} = \Delta G_{rxn}^\circ + RT \ln Q \quad [19.13]$$

where Q is the reaction quotient (defined in Section 16.7), T is the temperature in kelvins, and R is the gas constant in the appropriate units (8.314 J/mol · K).

In Equation 19.13 and all subsequent thermodynamic equations, we use Q_p for reactions involving gases, and we use Q_c for reactions involving substances dissolved in solution. We can demonstrate the use of this equation by applying it to the liquid–vapor water equilibrium under several different conditions, as shown in Figure 19.11▶. Note that by the law of mass action, for this equilibrium, $Q = P_{\text{H}_2\text{O}}$ (where the pressure is expressed in atmospheres):

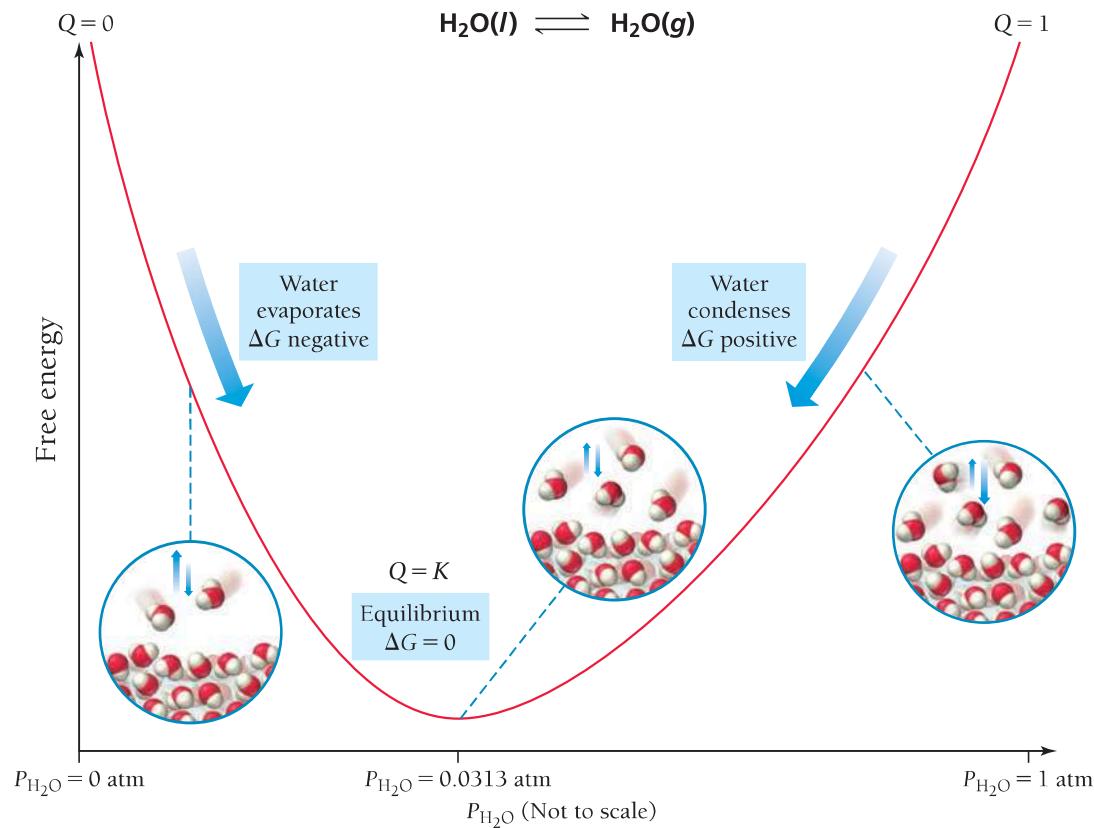


Standard Conditions

Under standard conditions, $P_{\text{H}_2\text{O}} = 1 \text{ atm}$ and therefore $Q = 1$. Substituting, we get the equation:

$$\begin{aligned} \Delta G_{rxn} &= \Delta G_{rxn}^\circ + RT \ln Q \\ &= +8.59 \text{ kJ/mol} + RT \ln(1) \\ &= +8.59 \text{ kJ/mol} \end{aligned}$$

Free Energy Change for the Vaporization of Water



▲ FIGURE 19.11 Free Energy versus Pressure for Water The free energy change for the vaporization of water is a function of pressure.

Under standard conditions, Q is always equal to 1, and since $\ln(1) = 0$, the value of ΔG_{rxn}° is therefore equal to ΔG_{rxn}° , as expected. For the liquid–vapor water equilibrium, because $\Delta G_{rxn}^\circ > 0$, the reaction is not spontaneous in the forward direction but is spontaneous in the reverse direction. As stated previously, under standard conditions water vapor condenses into liquid water.

Equilibrium Conditions

At 25.00 °C, liquid water is in equilibrium with water vapor at a pressure of 0.0313 atm; therefore, $Q = K_p = 0.0313$. Substituting:

$$\begin{aligned}\Delta G_{rxn} &= \Delta G_{rxn}^\circ + RT \ln(Q) \\ &= +8.59 \text{ kJ/mol} + 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} (298.15 \text{ K}) \ln(0.0313) \\ &= +8.59 \text{ kJ/mol} + (-8.59 \times 10^3 \text{ J/mol}) \\ &= +8.59 \text{ kJ/mol} - 8.59 \text{ kJ/mol} \\ &= 0\end{aligned}$$

Under equilibrium conditions, the value of $RT \ln Q$ is always equal in magnitude but opposite in sign to the value of ΔG_{rxn}° . Therefore, the value of ΔG_{rxn} is zero. Because $\Delta G_{rxn} = 0$, the reaction is not spontaneous in either direction, as expected for a reaction at equilibrium.

Other Nonstandard Conditions

A water partial pressure of 5.00×10^{-3} atm corresponds to a relative humidity of 16% at 25 °C.

To calculate the value of ΔG_{rxn} under any other set of nonstandard conditions, calculate Q and substitute the value into Equation 19.13. For example, the partial pressure of water vapor in the air on a dry (nonhumid) day is 5.00×10^{-3} atm, so $Q = 5.00 \times 10^{-3}$. Substituting:

$$\begin{aligned}\Delta G_{\text{rxn}} &= \Delta G_{\text{rxn}}^\circ + RT \ln(5.00 \times 10^{-3}) \\ &= +8.59 \text{ kJ/mol} + 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} (298 \text{ K}) \ln(5.00 \times 10^{-3}) \\ &= +8.59 \text{ kJ/mol} + (-13.1 \times 10^3 \text{ J/mol}) \\ &= +8.59 \text{ kJ/mol} - 13.1 \text{ kJ/mol} \\ &= -4.5 \text{ kJ/mol}\end{aligned}$$

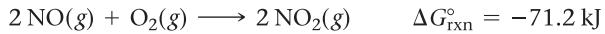
Under these conditions, the value of $\Delta G_{\text{rxn}} < 0$, so the reaction is spontaneous in the forward direction, consistent with our experience of water evaporating when spilled on the floor.

WATCH NOW!

INTERACTIVE WORKED EXAMPLE 19.10

EXAMPLE 19.10 Calculating ΔG_{rxn} under Nonstandard Conditions

Consider the reaction at 298 K:



Calculate ΔG_{rxn} under these conditions:

$$P_{\text{NO}} = 0.100 \text{ atm}; \quad P_{\text{O}_2} = 0.100 \text{ atm}; \quad P_{\text{NO}_2} = 2.00 \text{ atm}$$

Is the reaction more or less spontaneous under these conditions than under standard conditions?

SOLUTION

Use the law of mass action to calculate Q .

$$Q = \frac{(P_{\text{NO}_2})^2}{(P_{\text{NO}})^2 P_{\text{O}_2}} = \frac{(2.00)^2}{(0.100)^2 (0.100)} = 4.00 \times 10^3$$

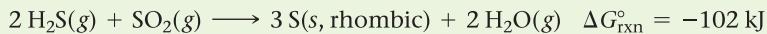
Substitute Q , T , and $\Delta G_{\text{rxn}}^\circ$ into Equation 19.13 to calculate ΔG_{rxn} . (Since the units of R include joules, write $\Delta G_{\text{rxn}}^\circ$ in joules.)

$$\begin{aligned}\Delta G_{\text{rxn}} &= \Delta G_{\text{rxn}}^\circ + RT \ln Q \\ &= -71.2 \times 10^3 \text{ J} + 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} (298 \text{ K}) \ln(4.00 \times 10^3) \\ &= -71.2 \times 10^3 \text{ J} + 20.5 \times 10^3 \text{ J} \\ &= -50.7 \times 10^3 \text{ J} \\ &= -50.7 \text{ kJ}\end{aligned}$$

The reaction is spontaneous under these conditions but less spontaneous than it would be under standard conditions (because ΔG_{rxn} is less negative than $\Delta G_{\text{rxn}}^\circ$).

CHECK The calculated result is consistent with what you would expect based on Le Châtelier's principle; increasing the concentration of the products and decreasing the concentration of the reactants relative to standard conditions should make the reaction less spontaneous than it was under standard conditions.

FOR PRACTICE 19.10 Consider the reaction at 298 K:



Calculate ΔG_{rxn} under these conditions:

$$P_{\text{H}_2\text{S}} = 2.00 \text{ atm}; \quad P_{\text{SO}_2} = 1.50 \text{ atm}; \quad P_{\text{H}_2\text{O}} = 0.0100 \text{ atm}$$

Is the reaction more or less spontaneous under these conditions than under standard conditions?

FREE ENERGY CHANGES AND LE CHÂTELIER'S PRINCIPLE

PRINCIPLE According to Le Châtelier's principle and the dependence of free energy on reactant and product concentrations, which statement is true? (Assume that both reactants and products are gaseous.)

- (a) A high concentration of reactants relative to products results in a more spontaneous reaction than one in which the reactants and products are in their standard states.
- (b) A high concentration of products relative to reactants results in a more spontaneous reaction than one in which the reactants and products are in their standard states.
- (c) A reaction in which the reactants are in standard states, but in which no products have formed, has a ΔG_{rxn} that is more positive than ΔG_{rxn}° .



ANSWER NOW!



19.10

Free Energy and Equilibrium: Relating ΔG_{rxn}° to the Equilibrium Constant (K)

We have discussed throughout this chapter that ΔG_{rxn}° determines the spontaneity of a reaction when the reactants and products are in their standard states. In Chapter 16, we learned that the equilibrium constant (K) determines how far a reaction goes toward products, a measure of spontaneity. Therefore, as you might expect, the standard free energy change of a reaction and the equilibrium constant are related—the equilibrium constant becomes larger as the standard free energy change becomes more negative. In other words, if, on the one hand, the reactants in a particular reaction undergo a large *negative* free energy change as they become products, then the reaction has a large equilibrium constant, with products strongly favored at equilibrium. If, on the other hand, the reactants in a particular reaction undergo a large *positive* free energy change as they become products, then the reaction has a small equilibrium constant, with reactants strongly favored at equilibrium.

The Relationship between ΔG_{rxn}° and K

We can derive a relationship between ΔG_{rxn}° and K from Equation 19.13. We know that at equilibrium $Q = K$ and $\Delta G_{rxn} = 0$. Making these substitutions:

$$\begin{aligned}\Delta G_{rxn} &= \Delta G_{rxn}^\circ + RT \ln Q \\ 0 &= \Delta G_{rxn}^\circ + RT \ln K \\ \Delta G_{rxn}^\circ &= -RT \ln K\end{aligned}\quad [19.14]$$

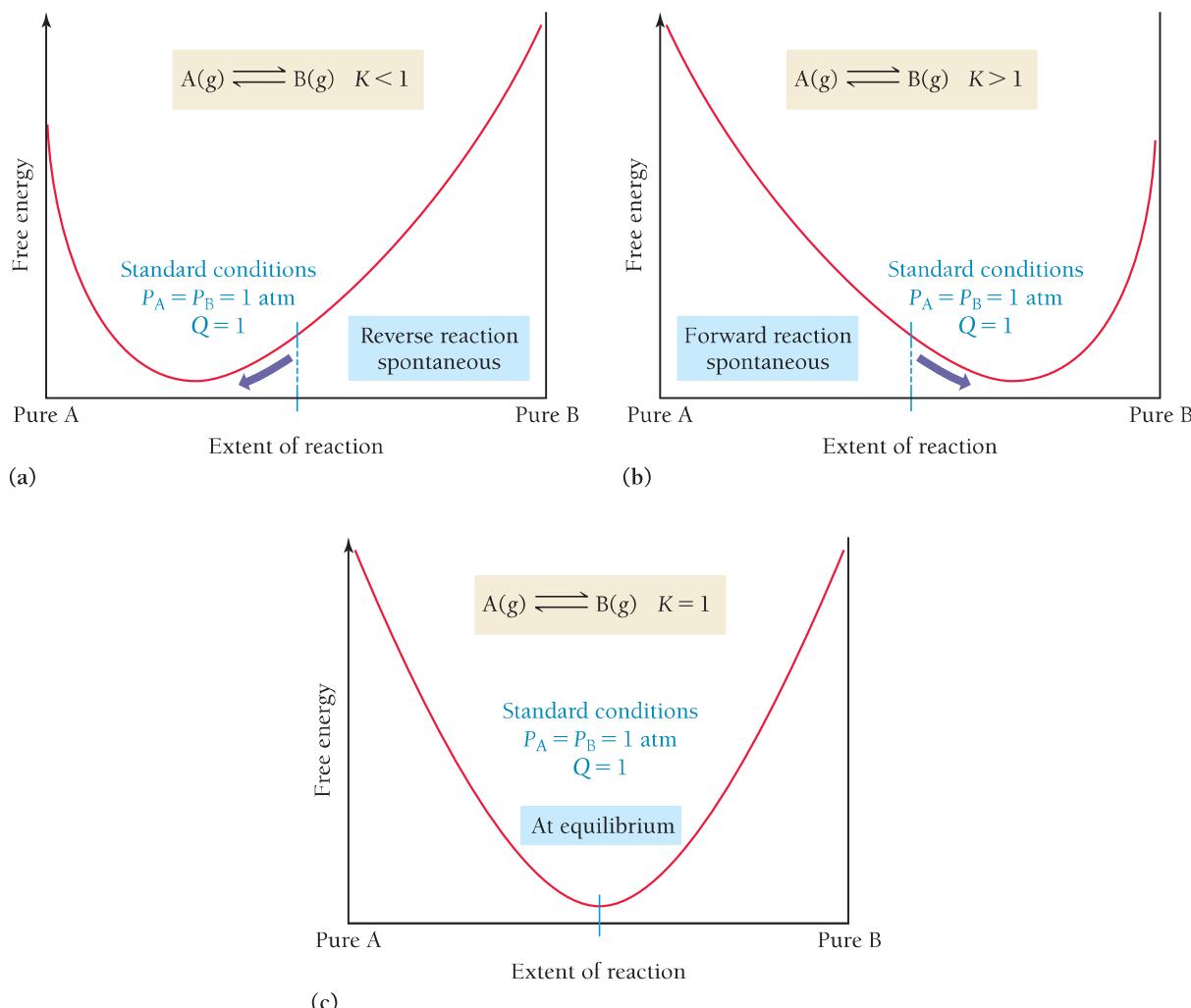
In Equation 19.14 and all subsequent thermodynamic equations, we use K_p for reactions involving gases, and we use K_c for reactions involving substances dissolved in solution.

We can better understand the relationship between ΔG_{rxn}° and K by considering the following ranges of values for K , as summarized in Figure 19.12▶:

- When $K < 1$, $\ln K$ is negative and ΔG_{rxn}° is positive. Under standard conditions (when $Q = 1$), the reaction is spontaneous in the reverse direction.
- When $K > 1$, $\ln K$ is positive and ΔG_{rxn}° is negative. Under standard conditions (when $Q = 1$), the reaction is spontaneous in the forward direction.
- When $K = 1$, $\ln K$ is zero and ΔG_{rxn}° is zero. The reaction happens to be at equilibrium under standard conditions.

The relationship between ΔG_{rxn}° and K is logarithmic—small changes in ΔG_{rxn}° have a large effect on K .

Free Energy and the Equilibrium Constant



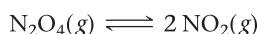
▲ FIGURE 19.12 Free Energy and the Equilibrium Constant (a) Free energy curve for a reaction with a small equilibrium constant. (b) Free energy curve for a reaction with a large equilibrium constant. (c) Free energy curve for a reaction in which $K = 1$.

WATCH NOW!

INTERACTIVE WORKED EXAMPLE 19.11

EXAMPLE 19.11 The Equilibrium Constant and ΔG_{rxn}°

Use tabulated free energies of formation to calculate the equilibrium constant for the reaction at 298 K:



SOLUTION

Look up (in Appendix IIB) the standard free energies of formation for each reactant and product.

Calculate ΔG_{rxn}° by substituting into Equation 19.12.

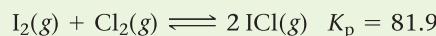
Reactant or product	ΔG_f° (in kJ/mol)
$\text{N}_2\text{O}_4(g)$	99.8
$\text{NO}_2(g)$	51.3

$$\begin{aligned}\Delta G_{rxn}^\circ &= \sum n_p \Delta G_f^\circ(\text{products}) - \sum n_r \Delta G_f^\circ(\text{reactants}) \\ &= 2[\Delta G_f^\circ, \text{NO}_2(g)] - \Delta G_f^\circ, \text{N}_2\text{O}_4(g) \\ &= 2(51.3 \text{ kJ}) - 99.8 \text{ kJ} \\ &= 2.8 \text{ kJ}\end{aligned}$$

Calculate K from $\Delta G_{\text{rxn}}^{\circ}$ by solving Equation 19.14 for K and substituting the values of $\Delta G_{\text{rxn}}^{\circ}$ and temperature.

$$\begin{aligned}\Delta G_{\text{rxn}}^{\circ} &= -RT \ln K \\ \ln K &= \frac{-\Delta G_{\text{rxn}}^{\circ}}{RT} \\ &= \frac{-2.8 \times 10^3 \text{ J/mol}}{8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}} (298 \text{ K}) \\ &= -1.13 \\ K &= e^{-1.13} \\ &= 0.32\end{aligned}$$

FOR PRACTICE 19.11 Calculate $\Delta G_{\text{rxn}}^{\circ}$ at 298 K for the reaction:



K AND $\Delta G_{\text{rxn}}^{\circ}$ The reaction $\text{A}(g) \rightleftharpoons \text{B}(g)$ has an equilibrium constant that is less than one. What can you conclude about $\Delta G_{\text{rxn}}^{\circ}$ for the reaction?

- (a) $\Delta G_{\text{rxn}}^{\circ} = 0$ (b) $\Delta G_{\text{rxn}}^{\circ} < 0$ (c) $\Delta G_{\text{rxn}}^{\circ} > 0$



ANSWER NOW!



THE CONDITIONS OF SPONTANEITY A reaction is spontaneous under a certain set of conditions. What can you conclude about ΔG_{rxn} and Q ?

- | | |
|--|--|
| (a) $\Delta G_{\text{rxn}} < 0, Q > K$ | (b) $\Delta G_{\text{rxn}} < 0, Q < K$ |
| (c) $\Delta G_{\text{rxn}} > 0, Q < K$ | (d) $\Delta G_{\text{rxn}} > 0, Q > K$ |



ANSWER NOW!



The Temperature Dependence of the Equilibrium Constant

We now have an equation that relates the standard free energy change for a reaction ($\Delta G_{\text{rxn}}^{\circ}$) to the equilibrium constant for a reaction (K):

$$\Delta G_{\text{rxn}}^{\circ} = -RT \ln K \quad [19.15]$$

We also have an equation for how the free energy change for a reaction ($\Delta G_{\text{rxn}}^{\circ}$) depends on temperature (T):

$$\Delta G_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} - T \Delta S_{\text{rxn}}^{\circ} \quad [19.16]$$

We can combine these two equations to obtain an equation for how the equilibrium constant depends on temperature. Combining Equations 19.15 and 19.16, we arrive at:

$$-RT \ln K = \Delta H_{\text{rxn}}^{\circ} - T \Delta S_{\text{rxn}}^{\circ} \quad [19.17]$$

We can then divide both sides of Equation 19.17 by the quantity RT :

$$-\ln K = \frac{\Delta H_{\text{rxn}}^{\circ}}{RT} - \frac{T \Delta S_{\text{rxn}}^{\circ}}{RT}$$

Canceling and rearranging, we get this important result:

$$\ln K = -\frac{\Delta H_{\text{rxn}}^{\circ}}{R} \left(\frac{1}{T} \right) + \frac{\Delta S_{\text{rxn}}^{\circ}}{R} \quad [19.18]$$

$$y = mx + b$$

Equation 19.18 is in the form of a straight line. A plot of the natural log of the equilibrium constant ($\ln K$) versus the inverse of the temperature in kelvins ($1/T$) yields a straight line with a slope of $-\Delta H_{\text{rxn}}^{\circ}/R$ and a y -intercept of $-\Delta S_{\text{rxn}}^{\circ}/R$. Such a plot is useful for obtaining thermodynamic data (namely, $\Delta H_{\text{rxn}}^{\circ}$ and $\Delta S_{\text{rxn}}^{\circ}$) from measurements of K as a function of temperature. However, since $\Delta H_{\text{rxn}}^{\circ}$ and $\Delta S_{\text{rxn}}^{\circ}$ can themselves be slightly temperature dependent, this analysis works only over a relatively limited temperature range.

The equation can also be expressed in a two-point form:

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H_{rxn}^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad [19.19]$$

We can use this equation to find ΔH_{rxn}° from a measurement of the equilibrium constant at two different temperatures or to find the equilibrium constant at some other temperature if we know the equilibrium constant at a given temperature and ΔH_{rxn}° .

QUIZ YOURSELF NOW!

Self-Assessment Quiz



Q1. Which reaction is most likely to have a positive ΔS_{sys} ?

MISSED THIS? Read Section 19.4

- a) $\text{SiO}_2(s) + 3 \text{C}(s) \longrightarrow \text{SiC}(s) + 2 \text{CO}(g)$
- b) $6 \text{CO}_2(g) + 6 \text{H}_2\text{O}(g) \longrightarrow \text{C}_6\text{H}_{12}\text{O}_6(s) + 6 \text{O}_2(g)$
- c) $\text{CO}(g) + \text{Cl}_2(g) \longrightarrow \text{COCl}_2(g)$
- d) $3 \text{NO}_2(g) + \text{H}_2\text{O}(l) \longrightarrow 2 \text{HNO}_3(l) + \text{NO}(g)$

Q2. The sign of ΔH_{rxn} and ΔS_{rxn} for several different reactions are given. In which case is the reaction spontaneous at all temperatures?

MISSED THIS? Read Section 19.5; Watch IWE 19.3

- a) $\Delta H_{rxn} < 0; \Delta S_{rxn} < 0$
- b) $\Delta H_{rxn} > 0; \Delta S_{rxn} > 0$
- c) $\Delta H_{rxn} < 0; \Delta S_{rxn} > 0$
- d) $\Delta H_{rxn} > 0; \Delta S_{rxn} < 0$

Q3. Arrange the gases— F_2 , Ar, and CH_3F —in order of increasing standard molar entropy (S°) at 298 K.

MISSED THIS? Read Section 19.7; Watch KCV 19.7

- a) $\text{F}_2 < \text{Ar} < \text{CH}_3\text{F}$
- b) $\text{CH}_3\text{F} < \text{F}_2 < \text{Ar}$
- c) $\text{CH}_3\text{F} < \text{Ar} < \text{F}_2$
- d) $\text{Ar} < \text{F}_2 < \text{CH}_3\text{F}$

Q4. Calculate the change in entropy that occurs in the system when 1.00 mol of methanol (CH_3OH) vaporizes from a liquid to a gas at its boiling point (64.6 °C). For methanol, $\Delta H_{vap} = 35.21 \text{ kJ/mol}$.

MISSED THIS? Read Section 19.4; Watch IWE 19.2

- a) 104 J/K
- b) -104 J/K
- c) 545 J/K
- d) -545 J/K

Q5. A reaction has a $\Delta H_{rxn} = 54.2 \text{ kJ}$. Calculate the change in entropy for the surroundings (ΔS_{surr}) for the reaction at 25.0 °C. (Assume constant pressure and temperature.)

MISSED THIS? Read Section 19.5; Watch IWE 19.3

- a) $2.17 \times 10^3 \text{ J/K}$
- b) $-2.17 \times 10^3 \text{ J/K}$
- c) -182 J/K
- d) 182 J/K

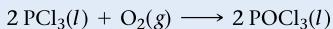
Q6. A reaction has $\Delta H_{rxn}^\circ = -255 \text{ kJ}$ and $\Delta S_{rxn}^\circ = 211 \text{ J/K}$. Calculate ΔG_{rxn}° at 55 °C.

MISSED THIS? Read Section 19.6; Watch KCV 19.6, IWE 19.4

- a) $11.9 \times 10^3 \text{ kJ}$
- b) $69.5 \times 10^3 \text{ kJ}$
- c) -267 kJ
- d) -324 kJ

Q7. Use standard entropies to calculate ΔS_{rxn}° for the balanced chemical equation:

MISSED THIS? Read Section 19.7; Watch KCV 19.7, IWE 19.5



Substance	$S^\circ \text{ (J/mol} \cdot \text{K)}$
$\text{POCl}_3(l)$	222.5
$\text{POCl}_3(g)$	325.5
$\text{PCl}_3(l)$	217.1
$\text{PCl}_3(g)$	311.8
$\text{O}_2(g)$	205.2

- a) -194.4 J/K
- b) -199.8 J/K
- c) 10.8 J/K
- d) 1084.4 J/K

Q8. Use standard free energies of formation to calculate ΔG_{rxn}° for the balanced chemical equation:

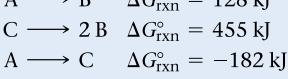
MISSED THIS? Read Section 19.8



Substance	$\Delta G_{rxn}^\circ \text{ (kJ/mol)}$
$\text{N}_2\text{O}(g)$	103.7
$\text{MgO}(s)$	-569.3

- a) 673.0 kJ
- b) -673.0 kJ
- c) -465.6 kJ
- d) 465.6 kJ

Q9. Find ΔG_{rxn}° for the reaction $2 \text{A} + \text{B} \longrightarrow 2 \text{C}$ from the given data. **MISSED THIS?** Read Section 19.8



- a) -401 kJ
- b) 509 kJ
- c) 401 kJ
- d) -509 kJ

Q10. The given reaction has a $\Delta G_{rxn}^\circ = 9.4 \text{ kJ}$ at 25 °C. Find ΔG_{rxn} when $P_{\text{NO}_2} = 0.115 \text{ atm}$ and $P_{\text{NO}} = 9.7 \text{ atm}$ at 25 °C.

MISSED THIS? Read Section 19.9; Watch IWE 19.10



- a) -12.3 kJ
- b) $21.7 \times 10^3 \text{ kJ}$
- c) 31.1 kJ
- d) 18.8 kJ

Q11. The reaction $\text{A}(g) \rightleftharpoons \text{B}(g)$ has an equilibrium constant of $K_p = 2.3 \times 10^{-5}$. What can you conclude about the sign of ΔG_{rxn}° for the reaction? **MISSED THIS?** Read Section 19.10

- a) $\Delta G_{rxn}^\circ = 0$
- b) ΔG_{rxn}° is negative
- c) ΔG_{rxn}° is positive
- d) Nothing can be concluded about the sign of ΔG_{rxn}° for the reaction.

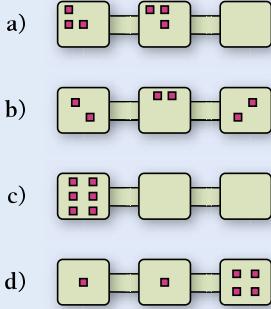
Q12. A reaction has an equilibrium constant of $K_p = 0.018$ at 25 °C. Find ΔG_{rxn}° for the reaction at this temperature.

MISSED THIS? Read Section 19.10; Watch IWE 19.11

- a) -835 J
- b) -4.32 kJ
- c) -9.95 kJ
- d) 9.95 kJ

Q13. Which distribution of six particles into three interconnected boxes has the highest entropy?

MISSED THIS? Read Section 19.3; Watch KCV 19.3

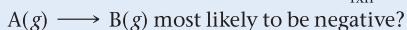


- Q14.** Which process results in the increase in entropy of the universe?

MISSED THIS? Read Section 19.3; Watch KCV 19.3

- the cooling of a hot cup of coffee in room temperature air
- the evaporation of water from a desk at room temperature
- the melting of snow above 0 °C
- all of the above

- Q15.** Under which set of conditions is ΔG_{rxn} for the reaction



most likely to be negative?

MISSED THIS? Read Section 19.9

- $P_A = 10.0 \text{ atm}; P_B = 10.0 \text{ atm}$
- $P_A = 10.0 \text{ atm}; P_B = 0.010 \text{ atm}$
- $P_A = 0.010 \text{ atm}; P_B = 10.0 \text{ atm}$
- $P_A = 0.010 \text{ atm}; P_B = 0.010 \text{ atm}$

Answers: 1. (a) 2. (c) 3. (d) 4. (a) 5. (c) 6. (a) 7. (d) 8. (b) 9. (d) 10. (c) 11. (c) 12. (d) 13. (b) 14. (d) 15. (b) 16. (b)

- Q16.** Which statement is true for the freezing of liquid water below 0 °C?

MISSED THIS? Read Section 19.6; Watch KCV 19.6

- ΔH is positive; ΔS is negative; ΔG is negative
- ΔH is negative; ΔS is negative; ΔG is negative
- ΔH is positive; ΔS is positive; ΔG is positive
- ΔH is positive; ΔS is negative; ΔG is positive

CHAPTER 19 IN REVIEW

TERMS

Section 19.2

spontaneous process (848)

Section 19.3

entropy (S) (852)

second law of

thermodynamics (854)

Section 19.4

reversible process (859)

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Gibbs free energy (G) (863)

Section 19.7

standard entropy change
for a reaction ($\Delta S_{\text{rxn}}^{\circ}$) (867)

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entropies (S°) (867)

third law of
thermodynamics (868)

free energy of

formation (ΔG_f°) (873)

Section 19.9

free energy change of a

reaction under nonstandard
conditions (ΔG_{rxn}) (878)

CONCEPTS

Spontaneous and Nonspontaneous Processes (19.2)

- Both spontaneous and nonspontaneous processes can occur, but only spontaneous processes can take place without outside intervention.
- Thermodynamics is the study of the *spontaneity* of reactions, *not* to be confused with kinetics, the study of the *rate* of reactions.

Entropy and the Second Law of Thermodynamics (19.3)

- The second law of thermodynamics states that for *any* spontaneous process, the entropy of the universe increases.
- Entropy (S) is proportional to the number of energetically equivalent ways in which the components of a system can be arranged and is a measure of energy dispersal per unit temperature.

The Entropy Changes Associated with Changes of State (19.4)

- The entropy of a substance increases as it changes state from a solid to a liquid and when it changes from a liquid to a gas.
- The change in entropy for a system undergoing a reversible change in state is $\Delta S = q_{\text{rev}}/T$.

Heat Transfer and Changes in the Entropy of the Surroundings (19.5)

- For a process to be spontaneous, the total entropy of the universe (system plus surroundings) must increase.
- The entropy of the surroundings increases when the change in *enthalpy* of the system (ΔH_{sys}) is negative (i.e., for exothermic reactions).
- The change in entropy of the surroundings for a given ΔH_{sys} depends inversely on temperature—the greater the temperature, the smaller the magnitude of ΔS_{surr} .

Gibbs Free Energy (19.6)

- Gibbs free energy, G , is a thermodynamic function that is proportional to the negative of the change in the entropy of the universe. A negative ΔG represents a spontaneous reaction, and a positive ΔG represents a nonspontaneous reaction.
- We can calculate the value of ΔG for a reaction from the values of ΔH and ΔS for the *system* using the equation $\Delta G = \Delta H - T\Delta S$.

Entropy Changes in Chemical Reactions: Calculating $\Delta S_{\text{rxn}}^{\circ}$ (19.7)

- We calculate the standard change in entropy for a reaction similarly to the way we calculate the standard change in enthalpy for a

reaction: by subtracting the sum of the standard entropies of the reactants multiplied by their stoichiometric coefficients from the sum of the standard entropies of the products multiplied by their stoichiometric coefficients.

- Standard entropies are *absolute*; an entropy of zero is established by the third law of thermodynamics as the entropy of a perfect crystal at absolute zero.
- The entropy of a substance at a given temperature depends on factors that affect the number of energetically equivalent arrangements of the substance; these include the state, size, and molecular complexity of the substance.

Free Energy Changes in Chemical Reactions: Calculating ΔG_{rxn}° (19.8)

- There are three ways to calculate ΔG_{rxn}° : (1) from ΔH° and ΔS° , (2) from free energies of formation (only at 25 °C), and (3) from the ΔG° 's of reactions that sum to the reaction of interest.
- The magnitude of a negative ΔG_{rxn}° represents the theoretical amount of energy available to do work, while a positive ΔG_{rxn}° represents the minimum amount of energy required to make a nonspontaneous process occur.

EQUATIONS AND RELATIONSHIPS

The Definition of Entropy (19.3)

$$S = k \ln W \quad k = 1.38 \times 10^{-23} \text{ J/K}$$

Change in Entropy (19.3, 19.4)

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

$$\Delta S = q_{rev}/T \quad (\text{Isothermal, reversible process})$$

Change in the Entropy of the Universe (19.5)

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

Change in the Entropy of the Surroundings (19.5)

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

Change in Gibbs Free Energy (19.6)

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

The Relationship between Spontaneity and ΔH , ΔS , and T (19.6)

ΔH	ΔS	Low Temperature	High Temperature
—	+	Spontaneous	Spontaneous
+	—	Nonspontaneous	Nonspontaneous
—	—	Spontaneous	Nonspontaneous
+	+	Nonspontaneous	Spontaneous

Free Energy Changes for Nonstandard States: The Relationship between ΔG_{rxn}° and ΔG_{rxn} (19.9)

- The value of ΔG_{rxn}° applies only to standard conditions, and most real conditions are not standard.
- Under nonstandard conditions, we can calculate ΔG_{rxn} from the equation $\Delta G_{rxn} = \Delta G_{rxn}^\circ + RT \ln Q$.

Free Energy and Equilibrium: Relating ΔG_{rxn}° to the Equilibrium Constant (K) (19.10)

- Under standard conditions, the free energy change for a reaction is directly proportional to the negative of the natural log of the equilibrium constant, K ; the more negative the free energy change (i.e., the more spontaneous the reaction), the larger the equilibrium constant.
- We can use the temperature dependence of ΔG_{rxn}° , as given by $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, to derive an equation for the temperature dependence of the equilibrium constant.

Standard Change in Entropy (19.7)

$$\Delta S_{rxn}^\circ = \sum n_p S^\circ(\text{products}) - \sum n_r S^\circ(\text{reactants})$$

Methods for Calculating the Free Energy of Formation (ΔG_{rxn}°) (19.8)

1. $\Delta G_{rxn}^\circ = \Delta H_{rxn}^\circ - T\Delta S_{rxn}^\circ$
2. $\Delta G_{rxn}^\circ = \sum n_p \Delta G_f^\circ(\text{products}) - \sum n_r \Delta G_f^\circ(\text{reactants})$
3. $\Delta G_{rxn(\text{overall})}^\circ = \Delta G_{rxn(\text{step 1})}^\circ + \Delta G_{rxn(\text{step 2})}^\circ + \Delta G_{rxn(\text{step 3})}^\circ + \dots$

The Relationship between ΔG_{rxn}° and ΔG_{rxn} (19.9)

$$\Delta G_{rxn} = \Delta G_{rxn}^\circ + RT \ln Q \quad R = 8.314 \text{ J/mol} \cdot \text{K}$$

The Relationship between ΔG_{rxn}° and K (19.10)

$$\Delta G_{rxn}^\circ = -RT \ln K$$

The Temperature Dependence of the Equilibrium Constant (19.10)

$$\ln K = -\frac{\Delta H_{rxn}^\circ}{R} \left(\frac{1}{T} \right) + \frac{\Delta S_{rxn}^\circ}{R}$$

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H_{rxn}^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

LEARNING OUTCOMES

Chapter Objectives

Identify spontaneous and nonspontaneous processes (19.2)

Analyze systems of particles and reactions in terms of entropy change (19.3)

Calculate the entropy change for a change in state (19.4)

Assessment

Exercises 27–28

Example 19.1 For Practice 19.1 Exercises 29–30

Example 19.2 For Practice 19.2 Exercises 31–34

Calculate entropy changes in the system (ΔS_{sys}), the surroundings (ΔS_{surr}), and the universe (ΔS_{univ}) (19.5)	Example 19.3 For Practice 19.3 For More Practice 19.3 Exercises 35–42
Analyze reaction spontaneity using Gibbs free energy change (ΔG), ΔH , and ΔS (19.6)	Example 19.4 For Practice 19.4 Exercises 43–47
Calculate the standard entropy change for a reaction ($\Delta S_{\text{rxn}}^{\circ}$) (19.7)	Example 19.5 For Practice 19.5 Exercises 48–58
Analyze reaction spontaneity using standard Gibbs free energy change ($\Delta G_{\text{rxn}}^{\circ}$), $\Delta H_{\text{rxn}}^{\circ}$, and $\Delta S_{\text{rxn}}^{\circ}$ (19.8)	Examples 19.6, 19.7 For Practice 19.6, 19.7 Exercises 59–62
Calculate $\Delta G_{\text{rxn}}^{\circ}$ using free energies of formation (ΔG_f°) (19.8)	Example 19.8 For Practice 19.8 For More Practice 19.8 Exercises 63–66
Calculate $\Delta G_{\text{rxn}}^{\circ}$ for a stepwise reaction (19.8)	Example 19.9 For Practice 19.9 Exercises 67–68
Calculate ΔG_{rxn} for nonstandard conditions (19.9)	Example 19.10 For Practice 19.10 Exercises 69–72
Perform $\Delta G_{\text{rxn}}^{\circ}$ calculations using equilibrium constants (K) (19.10)	Example 19.11 For Practice 19.11 Exercises 73–82

EXERCISES

Mastering Chemistry provides end-of-chapter exercises, feedback-enriched tutorial problems, animations, and interactive activities to encourage problem-solving practice and deeper understanding of key concepts and topics.

REVIEW QUESTIONS

- What is the first law of thermodynamics, and how does it relate to energy use?
- What is nature's heat tax, and how does it relate to energy use?
- What is a perpetual motion machine? Can such a machine exist given the laws of thermodynamics?
- Is it more efficient to heat your home with a natural gas furnace or an electric furnace? Explain.
- What is a spontaneous process? Provide an example.
- Explain the difference between the spontaneity of a reaction (which depends on thermodynamics) and the speed at which the reaction occurs (which depends on kinetics). Can a catalyst make a nonspontaneous reaction spontaneous?
- What is the precise definition of entropy? What is the significance of entropy being a state function?
- Why does the entropy of a gas increase when it expands into a vacuum?
- Explain the difference between macrostates (external arrangements of particles) and microstates (internal arrangements of particles).
- Based on its fundamental definition, explain why entropy is a measure of energy dispersion.
- State the second law of thermodynamics. How does the second law explain why heat travels from a substance at higher temperature to one at lower temperature?
- What happens to the entropy of a sample of matter when it changes state from a solid to a liquid? From a liquid to a gas?
- Explain why water spontaneously freezes to form ice below 0 °C even though the entropy of the water decreases during the state transition. Why is the freezing of water not spontaneous above 0 °C?
- Why do exothermic processes tend to be spontaneous at low temperatures? Why does their tendency toward spontaneity decrease with increasing temperature?
- What is the significance of the change in Gibbs free energy (ΔG) for a reaction?
- Predict the spontaneity of a reaction (and the temperature dependence of the spontaneity) for each possible combination of signs for ΔH and ΔS (for the system).
 - ΔH negative, ΔS positive
 - ΔH positive, ΔS negative
 - ΔH negative, ΔS negative
 - ΔH positive, ΔS positive
- State the third law of thermodynamics and explain its significance.
- Why is the standard entropy of a substance in the gas state greater than its standard entropy in the liquid state?
- How does the standard entropy of a substance depend on its molar mass? On its molecular complexity?
- How can you calculate the standard entropy change for a reaction from tables of standard entropies?
- What are three different methods to calculate ΔG° for a reaction? Which method would you choose to calculate ΔG° for a reaction at a temperature other than 25 °C?
- Why is free energy "free"?
- Explain the difference between ΔG° and ΔG .
- Why does water spilled on the floor evaporate even though ΔG° for the evaporation process is positive at room temperature?
- How do you calculate the change in free energy for a reaction under nonstandard conditions?
- How does the value of ΔG° for a reaction relate to the equilibrium constant for the reaction? What does a negative ΔG° for a reaction imply about K for the reaction? A positive ΔG° ?

PROBLEMS BY TOPIC

Entropy, the Second Law of Thermodynamics, and the Direction of Spontaneous Change

- 27.** Which of these processes is spontaneous?

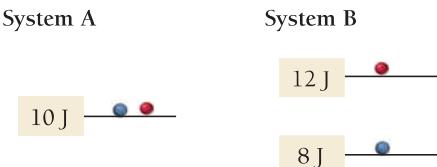
MISSED THIS? Read Section 19.2

- the combustion of natural gas
- the extraction of iron metal from iron ore
- a hot drink cooling to room temperature
- drawing heat energy from the ocean's surface to power a ship

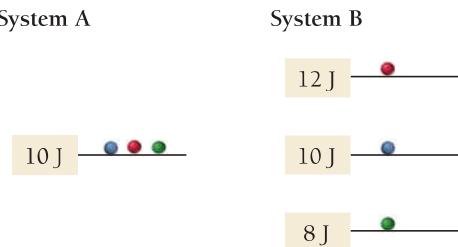
- 28.** Which of these processes are nonspontaneous? Are the nonspontaneous processes impossible?

- a bike going up a hill
- a meteor falling to Earth
- obtaining hydrogen gas from liquid water
- a ball rolling down a hill

- 29.** Two systems, each composed of two particles represented by circles, have 20 J of total energy. Which system, A or B, has the greater entropy? Why? **MISSED THIS? Read Section 19.3**



- 30.** Two systems, each composed of three particles represented by circles, have 30 J of total energy. In how many energetically equivalent ways can you distribute the particles in each system? Which system has greater entropy?



- 31.** Calculate the change in entropy that occurs in the system when 1.00 mole of isopropyl alcohol (C_3H_8O) melts at its melting point (-89.5°C). See Table 12.9 for heats of fusion.

MISSED THIS? Read Section 19.4; Watch IWE 19.2

- 32.** Calculate the change in entropy that occurs in the system when 1.00 mole of diethyl ether ($C_4H_{10}O$) condenses from a gas to a liquid at its normal boiling point (34.6°C). See Table 12.7 for heats of vaporization.

- 33.** Calculate the change in entropy that occurs in the system when 45.0 g of acetone (C_3H_6O) freezes at its melting point (-94.8°C). See Table 12.9 for heats of fusion.

MISSED THIS? Read Section 19.4; Watch IWE 19.2

- 34.** Calculate the change in entropy that occurs in the system when 55.0 g of water vaporizes from a liquid to a gas at its boiling point (100.0°C). See Table 12.7 for heats of vaporization.

- 35.** Without doing any calculations, determine the sign of ΔS_{sys} for each chemical reaction. **MISSED THIS? Read Section 19.4**

- $2 \text{KClO}_3(s) \longrightarrow 2 \text{KCl}(s) + 3 \text{O}_2(g)$
- $\text{CH}_2=\text{CH}_2(g) + \text{H}_2(g) \longrightarrow \text{CH}_3\text{CH}_3(g)$

- $\text{Na}(s) + 1/2 \text{Cl}_2(g) \longrightarrow \text{NaCl}(s)$
- $\text{N}_2(g) + 3 \text{H}_2(g) \longrightarrow 2 \text{NH}_3(g)$

- 36.** Without doing any calculations, determine the sign of ΔS_{sys} for each chemical reaction.

- $\text{Mg}(s) + \text{Cl}_2(g) \longrightarrow \text{MgCl}_2(s)$
- $2 \text{H}_2\text{S}(g) + 3 \text{O}_2(g) \longrightarrow 2 \text{H}_2\text{O}(g) + 2 \text{SO}_2(g)$
- $2 \text{O}_3(g) \longrightarrow 3 \text{O}_2(g)$
- $\text{HCl}(g) + \text{NH}_3(g) \longrightarrow \text{NH}_4\text{Cl}(s)$

- 37.** Without doing any calculations, determine the signs of ΔS_{sys} and ΔS_{surr} for each chemical reaction. In addition, predict under what temperatures (all temperatures, low temperatures, or high temperatures), if any, the reaction is spontaneous.

MISSED THIS? Read Sections 19.4, 19.5; Watch IWE 19.3

- $\text{C}_3\text{H}_8(g) + 5 \text{O}_2(g) \longrightarrow 3 \text{CO}_2(g) + 4 \text{H}_2\text{O}(g)$
 $\Delta H_{\text{rxn}}^\circ = -2044 \text{ kJ}$
- $\text{N}_2(g) + \text{O}_2(g) \longrightarrow 2 \text{NO}(g)$ $\Delta H_{\text{rxn}}^\circ = +182.6 \text{ kJ}$
- $2 \text{N}_2(g) + \text{O}_2(g) \longrightarrow 2 \text{N}_2\text{O}(g)$ $\Delta H_{\text{rxn}}^\circ = +163.2 \text{ kJ}$
- $4 \text{NH}_3(g) + 5 \text{O}_2(g) \longrightarrow 4 \text{NO}(g) + 6 \text{H}_2\text{O}(g)$
 $\Delta H_{\text{rxn}}^\circ = -906 \text{ kJ}$

- 38.** Without doing any calculations, determine the signs of ΔS_{sys} and ΔS_{surr} for each chemical reaction. In addition, predict under what temperatures (all temperatures, low temperatures, or high temperatures), if any, the reaction is spontaneous.

- $2 \text{CO}(g) + \text{O}_2(g) \longrightarrow 2 \text{CO}_2(g)$ $\Delta H_{\text{rxn}}^\circ = -566.0 \text{ kJ}$
- $2 \text{NO}_2(g) \longrightarrow 2 \text{NO}(g) + \text{O}_2(g)$ $\Delta H_{\text{rxn}}^\circ = +113.1 \text{ kJ}$
- $2 \text{H}_2(g) + \text{O}_2(g) \longrightarrow 2 \text{H}_2\text{O}(g)$ $\Delta H_{\text{rxn}}^\circ = -483.6 \text{ kJ}$
- $\text{CO}_2(g) \longrightarrow \text{C}(s) + \text{O}_2(g)$ $\Delta H_{\text{rxn}}^\circ = +393.5 \text{ kJ}$

- 39.** Calculate ΔS_{surr} at the indicated temperature for each reaction.

MISSED THIS? Read Section 19.5; Watch IWE 19.3

- $\Delta H_{\text{rxn}}^\circ = -385 \text{ kJ}; 298 \text{ K}$ b. $\Delta H_{\text{rxn}}^\circ = -385 \text{ kJ}; 77 \text{ K}$
- $\Delta H_{\text{rxn}}^\circ = +114 \text{ kJ}; 298 \text{ K}$ d. $\Delta H_{\text{rxn}}^\circ = +114 \text{ kJ}; 77 \text{ K}$

- 40.** A reaction has $\Delta H_{\text{rxn}}^\circ = -112 \text{ kJ}$ and $\Delta S_{\text{rxn}}^\circ = 354 \text{ J/K}$. At what temperature is the change in entropy for the reaction equal to the change in entropy for the surroundings?

- 41.** Given the values of $\Delta H_{\text{rxn}}^\circ$, $\Delta S_{\text{rxn}}^\circ$, and T , determine ΔS_{univ} and predict whether or not each reaction is spontaneous. (Assume that all reactants and products are in their standard states.) **MISSED THIS? Read Section 19.5; Watch IWE 19.3**

- $\Delta H_{\text{rxn}}^\circ = +115 \text{ kJ}; \Delta S_{\text{rxn}}^\circ = -263 \text{ J/K}; T = 298 \text{ K}$
- $\Delta H_{\text{rxn}}^\circ = -115 \text{ kJ}; \Delta S_{\text{rxn}}^\circ = +263 \text{ J/K}; T = 298 \text{ K}$
- $\Delta H_{\text{rxn}}^\circ = -115 \text{ kJ}; \Delta S_{\text{rxn}}^\circ = -263 \text{ J/K}; T = 298 \text{ K}$
- $\Delta H_{\text{rxn}}^\circ = -115 \text{ kJ}; \Delta S_{\text{rxn}}^\circ = -263 \text{ J/K}; T = 615 \text{ K}$

- 42.** Given the values of $\Delta H_{\text{rxn}}^\circ$, and T , determine ΔS_{rxn} , and predict whether or not each reaction is spontaneous. (Assume that all reactants and products are in their standard states.)

- $\Delta H_{\text{rxn}}^\circ = -95 \text{ kJ}; \Delta S_{\text{rxn}}^\circ = -157 \text{ J/K}; T = 298 \text{ K}$
- $\Delta H_{\text{rxn}}^\circ = -95 \text{ kJ}; \Delta S_{\text{rxn}}^\circ = -157 \text{ J/K}; T = 855 \text{ K}$
- $\Delta H_{\text{rxn}}^\circ = +95 \text{ kJ}; \Delta S_{\text{rxn}}^\circ = -157 \text{ J/K}; T = 298 \text{ K}$
- $\Delta H_{\text{rxn}}^\circ = -95 \text{ kJ}; \Delta S_{\text{rxn}}^\circ = +157 \text{ J/K}; T = 398 \text{ K}$

Standard Entropy Changes and Gibbs Free Energy

- 43.** Calculate the change in Gibbs free energy for each of the sets of $\Delta H_{\text{rxn}}^\circ$, $\Delta S_{\text{rxn}}^\circ$, and T given in Problem 41. Predict whether or not each reaction is spontaneous at the temperature indicated. (Assume that all reactants and products are in their standard states.)

MISSED THIS? Read Section 19.6; Watch KCV 19.6, IWE 19.4

44. Calculate the change in Gibbs free energy for each of the sets of ΔH_{rxn} , ΔS_{rxn} , and T given in Problem 42. Predict whether or not each reaction is spontaneous at the temperature indicated. (Assume that all reactants and products are in their standard states.)

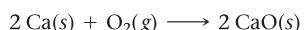
45. Calculate the free energy change for this reaction at 25 °C. Is the reaction spontaneous? (Assume that all reactants and products are in their standard states.)

MISSED THIS? Read Section 19.6; Watch KCV 19.6, IWE 19.4



$$\Delta H_{rxn}^\circ = -2217 \text{ kJ}; \Delta S_{rxn}^\circ = 101.1 \text{ J/K}$$

46. Calculate the free energy change for this reaction at 25 °C. Is the reaction spontaneous? (Assume that all reactants and products are in their standard states.)



$$\Delta H_{rxn}^\circ = -1269.8 \text{ kJ}; \Delta S_{rxn}^\circ = -364.6 \text{ J/K}$$

47. Fill in the blanks in the table. Both ΔH and ΔS refer to the system.

MISSED THIS? Read Section 19.6; Watch KCV 19.6

ΔH	ΔS	ΔG	Low Temperature	High Temperature
—	+	—	Spontaneous	_____
—	—	Temperature dependent	_____	_____
+	+	_____	_____	Spontaneous
_____	—	_____	Nonspontaneous	Nonspontaneous

48. Predict the conditions (high temperature, low temperature, all temperatures, or no temperatures) under which each reaction is spontaneous.

- a. $\text{H}_2\text{O}(g) \longrightarrow \text{H}_2\text{O}(l)$
- b. $\text{CO}_2(s) \longrightarrow \text{CO}_2(g)$
- c. $\text{H}_2(g) \longrightarrow 2 \text{H}(g)$
- d. $2 \text{NO}_2(g) \longrightarrow 2 \text{NO}(g) + \text{O}_2(g)$ (endothermic)

49. How does the molar entropy of a substance change with increasing temperature?

MISSED THIS? Read Section 19.7; Watch KCV 19.7

50. What is the molar entropy of a pure crystal at 0 K? What is the significance of the answer to this question?

51. For each pair of substances, choose the one that you expect to have the higher standard molar entropy (S°) at 25 °C. Explain your choices. **MISSED THIS?** Read Section 19.7; Watch KCV 19.7

- | | |
|---|---|
| a. $\text{CO}(g); \text{CO}_2(g)$ | b. $\text{CH}_3\text{OH}(l); \text{CH}_3\text{OH}(g)$ |
| c. $\text{Ar}(g); \text{CO}_2(g)$ | d. $\text{CH}_4(g); \text{SiH}_4(g)$ |
| e. $\text{NO}_2(g); \text{CH}_3\text{CH}_2\text{CH}_3(g)$ | f. $\text{NaBr}(s); \text{NaBr}(aq)$ |

52. For each pair of substances, choose the one that you expect to have the higher standard molar entropy (S°) at 25 °C. Explain your choices.

- | | |
|--|--|
| a. $\text{NaNO}_3(s); \text{NaNO}_3(aq)$ | b. $\text{CH}_4(g); \text{CH}_3\text{CH}_3(g)$ |
| c. $\text{Br}_2(l); \text{Br}_2(g)$ | d. $\text{Br}_2(g); \text{F}_2(g)$ |
| e. $\text{PCl}_3(g); \text{PCl}_5(g)$ | f. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3(g); \text{SO}_2(g)$ |

53. Rank each set of substances in order of increasing standard molar entropy (S°). Explain your reasoning.

MISSED THIS? Read Section 19.7; Watch KCV 19.7

- a. $\text{NH}_3(g); \text{Ne}(g); \text{SO}_2(g); \text{CH}_3\text{CH}_2\text{OH}(g); \text{He}(g)$
- b. $\text{H}_2\text{O}(s); \text{H}_2\text{O}(l); \text{H}_2\text{O}(g)$
- c. $\text{CH}_4(g); \text{CF}_4(g); \text{CCl}_4(g)$

54. Rank each set of substances in order of increasing standard molar entropy (S°). Explain your reasoning.

- a. $\text{I}_2(g); \text{F}_2(g); \text{Br}_2(g); \text{Cl}_2(g)$
- b. $\text{H}_2\text{O}(g); \text{H}_2\text{O}_2(g); \text{H}_2\text{S}(g)$
- c. $\text{C}(s, \text{graphite}); \text{C}(s, \text{diamond}); \text{C}(s, \text{amorphous})$

55. Use data from Appendix IIB to calculate ΔS_{rxn}° for each of the reactions. In each case, try to rationalize the sign of ΔS_{rxn}° .

MISSED THIS? Read Section 19.7; Watch IWE 19.5

- a. $\text{C}_2\text{H}_4(g) + \text{H}_2(g) \longrightarrow \text{C}_2\text{H}_6(g)$
- b. $\text{C}(s) + \text{H}_2\text{O}(g) \longrightarrow \text{CO}(g) + \text{H}_2(g)$
- c. $\text{CO}(g) + \text{H}_2\text{O}(g) \longrightarrow \text{H}_2(g) + \text{CO}_2(g)$
- d. $2 \text{H}_2\text{S}(g) + 3 \text{O}_2(g) \longrightarrow 2 \text{H}_2\text{O}(l) + 2 \text{SO}_2(g)$

56. Use data from Appendix IIB to calculate ΔS_{rxn}° for each of the reactions. In each case, try to rationalize the sign of ΔS_{rxn}° .

- a. $3 \text{NO}_2(g) + \text{H}_2\text{O}(l) \longrightarrow 2 \text{HNO}_3(aq) + \text{NO}(g)$
- b. $\text{Cr}_2\text{O}_3(s) + 3 \text{CO}(g) \longrightarrow 2 \text{Cr}(s) + 3 \text{CO}_2(g)$
- c. $\text{SO}_2(g) + \frac{1}{2} \text{O}_2(g) \longrightarrow \text{SO}_3(g)$
- d. $\text{N}_2\text{O}_4(g) + 4 \text{H}_2(g) \longrightarrow \text{N}_2(g) + 4 \text{H}_2\text{O}(g)$

57. Find ΔS° for the formation of $\text{CH}_2\text{Cl}_2(g)$ from its gaseous elements in their standard states. Rationalize the sign of ΔS° .

MISSED THIS? Read Section 19.7; Watch IWE 19.5

58. Find ΔS° for the reaction between nitrogen gas and fluorine gas to form nitrogen trifluoride gas. Rationalize the sign of ΔS° .

59. Methanol (CH_3OH) burns in oxygen to form carbon dioxide and water. Write a balanced equation for the combustion of liquid methanol and calculate ΔH_{rxn}° , ΔS_{rxn}° , and ΔG_{rxn}° at 25 °C. Is the combustion of methanol spontaneous?

MISSED THIS? Read Section 19.8; Watch IWE 19.6

60. In photosynthesis, plants form glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) and oxygen from carbon dioxide and water. Write a balanced equation for photosynthesis and calculate ΔH_{rxn}° , ΔS_{rxn}° , and ΔG_{rxn}° at 25 °C. Is photosynthesis spontaneous?

61. For each reaction, calculate ΔH_{rxn}° , ΔS_{rxn}° , and ΔG_{rxn}° at 25 °C and state whether or not the reaction is spontaneous. If the reaction is not spontaneous, would a change in temperature make it spontaneous? If so, should the temperature be raised or lowered from 25 °C? **MISSED THIS?** Read Section 19.8; Watch IWE 19.6

- a. $\text{N}_2\text{O}_4(g) \longrightarrow 2 \text{NO}_2(g)$
- b. $\text{NH}_4\text{Cl}(s) \longrightarrow \text{HCl}(g) + \text{NH}_3(g)$
- c. $3 \text{H}_2(g) + \text{Fe}_2\text{O}_3(s) \longrightarrow 2 \text{Fe}(s) + 3 \text{H}_2\text{O}(g)$
- d. $\text{N}_2(g) + 3 \text{H}_2(g) \longrightarrow 2 \text{NH}_3(g)$

62. For each reaction, calculate ΔH_{rxn}° , ΔS_{rxn}° , and ΔG_{rxn}° at 25 °C and state whether or not the reaction is spontaneous. If the reaction is not spontaneous, would a change in temperature make it spontaneous? If so, should the temperature be raised or lowered from 25 °C?

- a. $2 \text{CH}_4(g) \longrightarrow \text{C}_2\text{H}_6(g) + \text{H}_2(g)$
- b. $2 \text{NH}_3(g) \longrightarrow \text{N}_2\text{H}_4(g) + \text{H}_2(g)$
- c. $\text{N}_2(g) + \text{O}_2(g) \longrightarrow 2 \text{NO}(g)$
- d. $2 \text{KClO}_3(s) \longrightarrow 2 \text{KCl}(s) + 3 \text{O}_2(g)$

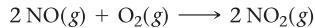
63. Use standard free energies of formation to calculate ΔG° at 25 °C for each reaction in Problem 61. How do the values of ΔG° calculated this way compare to those calculated from ΔH° and ΔS° ? Which of the two methods could be used to determine how ΔG° changes with temperature?

MISSED THIS? Read Section 19.8

64. Use standard free energies of formation to calculate ΔG° at 25 °C for each reaction in Problem 62. How well do the values of ΔG° calculated this way compare to those calculated from ΔH° and ΔS° ? Which of the two methods could be used to determine how ΔG° changes with temperature?

65. Consider the reaction:

MISSED THIS? Read Section 19.8; Watch IWE 19.6



Estimate ΔG° for this reaction at each temperature and predict whether or not the reaction is spontaneous. (Assume that ΔH° and ΔS° do not change too much within the given temperature range.)

- a. 298 K b. 715 K c. 855 K

66. Consider the reaction:



Estimate ΔG° for this reaction at each temperature and predict whether or not the reaction is spontaneous. (Assume that ΔH° and ΔS° do not change too much within the given temperature range.)

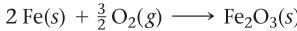
- a. 298 K b. 1055 K c. 1455 K

67. Determine ΔG° for the reaction:

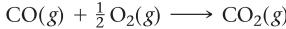
MISSED THIS? Read Section 19.8



Use the following reactions with known $\Delta G_{\text{rxn}}^\circ$ values:



$$\Delta G_{\text{rxn}}^\circ = -742.2 \text{ kJ}$$

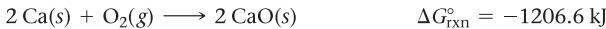
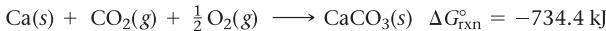


$$\Delta G_{\text{rxn}}^\circ = -257.2 \text{ kJ}$$

68. Calculate $\Delta G_{\text{rxn}}^\circ$ for the reaction:



Use the following reactions and given $\Delta G_{\text{rxn}}^\circ$ values:



Free Energy Changes, Nonstandard Conditions, and the Equilibrium Constant

69. Consider the sublimation of iodine at 25.0 °C:

MISSED THIS? Read Section 19.9; Watch IWE 19.10



- a. Find $\Delta G_{\text{rxn}}^\circ$ at 25.0 °C.

- b. Find $\Delta G_{\text{rxn}}^\circ$ at 25.0 °C under the following nonstandard conditions:

i. $P_{\text{I}_2} = 1.00 \text{ mmHg}$

ii. $P_{\text{I}_2} = 0.100 \text{ mmHg}$

- c. Explain why iodine spontaneously sublimes in open air at 25.0 °C.

70. Consider the evaporation of methanol at 25.0 °C:



- a. Find ΔG_r° at 25.0 °C.

- b. Find ΔG_r° at 25.0 °C under the following nonstandard conditions:

i. $P_{\text{CH}_3\text{OH}} = 150.0 \text{ mmHg}$

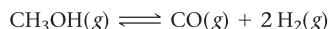
ii. $P_{\text{CH}_3\text{OH}} = 100.0 \text{ mmHg}$

iii. $P_{\text{CH}_3\text{OH}} = 10.0 \text{ mmHg}$

- c. Explain why methanol spontaneously evaporates in open air at 25.0 °C.

71. Consider the reaction:

MISSED THIS? Read Section 19.9; Watch IWE 19.10



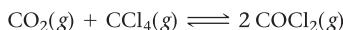
Calculate ΔG for this reaction at 25 °C under the following conditions:

i. $P_{\text{CH}_3\text{OH}} = 0.855 \text{ atm}$

ii. $P_{\text{CO}} = 0.125 \text{ atm}$

iii. $P_{\text{H}_2} = 0.183 \text{ atm}$

72. Consider the reaction:



Calculate ΔG for this reaction at 25 °C under the following conditions:

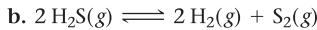
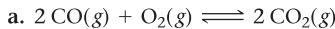
i. $P_{\text{CO}_2} = 0.112 \text{ atm}$

ii. $P_{\text{CCl}_4} = 0.174 \text{ atm}$

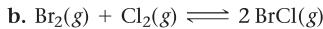
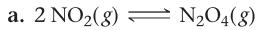
iii. $P_{\text{COCl}_2} = 0.744 \text{ atm}$

73. Use data from Appendix IIB to calculate the equilibrium constants at 25 °C for each reaction.

MISSED THIS? Read Section 19.10; Watch IWE 19.11

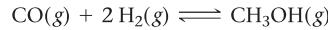


74. Use data from Appendix IIB to calculate the equilibrium constants at 25 °C for each reaction. ΔG_f° for $\text{BrCl}(g)$ is -1.0 kJ/mol .



75. Consider the reaction:

MISSED THIS? Read Sections 19.9, 19.10; Watch IWE 19.10, 19.11



$$K_p = 2.26 \times 10^4 \text{ at } 25^\circ\text{C}$$

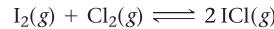
Calculate $\Delta G_{\text{rxn}}^\circ$ for the reaction at 25 °C under each of the following conditions:

- a. standard conditions

- b. at equilibrium

c. $P_{\text{CH}_3\text{OH}} = 1.0 \text{ atm}; P_{\text{CO}} = P_{\text{H}_2} = 0.010 \text{ atm}$

76. Consider the reaction:



$$K_p = 81.9 \text{ at } 25^\circ\text{C}$$

Calculate $\Delta G_{\text{rxn}}^\circ$ for the reaction at 25 °C under each of the following conditions:

- a. standard conditions

- b. at equilibrium

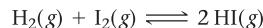
c. $P_{\text{ICl}} = 2.55 \text{ atm}; P_{\text{I}_2} = 0.325 \text{ atm}; P_{\text{Cl}_2} = 0.221 \text{ atm}$

77. Estimate the value of the equilibrium constant at 525 K for each reaction in Problem 73.

MISSED THIS? Read Sections 19.8, 19.10; Watch IWE 19.11

78. Estimate the value of the equilibrium constant at 655 K for each reaction in Problem 74. (ΔH_f° for BrCl is 14.6 kJ/mol .)

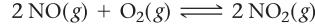
79. Consider the reaction: **MISSED THIS?** Read Section 19.10



The following data show the equilibrium constant for this reaction measured at several different temperatures. Use the data to find $\Delta H_{\text{rxn}}^\circ$ and $\Delta S_{\text{rxn}}^\circ$ for the reaction.

Temperature	K_p
150 K	1.4×10^{-6}
175 K	4.6×10^{-4}
200 K	3.6×10^{-2}
225 K	1.1
250 K	15.5

80. Consider the reaction:



The following data show the equilibrium constant for this reaction measured at several different temperatures. Use the data to find $\Delta H_{\text{rxn}}^\circ$ and $\Delta S_{\text{rxn}}^\circ$ for the reaction.

Temperature	K_p
170 K	3.8×10^{-3}
180 K	0.34
190 K	18.4
200 K	681

CUMULATIVE PROBLEMS

83. Determine the sign of ΔS_{sys} for each process.

- a. water boiling
- b. water freezing

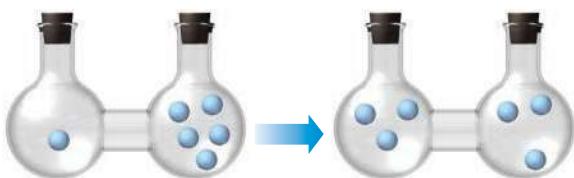
c.



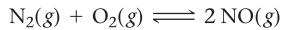
84. Determine the sign of ΔS_{sys} for each process.

- a. dry ice subliming
- b. dew forming

c.

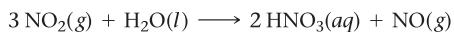


85. Our atmosphere is composed primarily of nitrogen and oxygen, which coexist at 25 °C without reacting to any significant extent. However, the two gases can react to form nitrogen monoxide according to the reaction:

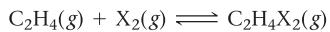


- a. Calculate ΔG° and K_p for this reaction at 298 K. Is the reaction spontaneous?
- b. Estimate ΔG° at 2000 K. Does the reaction become more spontaneous as temperature increases?

86. Nitrogen dioxide, a pollutant in the atmosphere, can combine with water to form nitric acid. One of the possible reactions is shown here. Calculate ΔG° and K_p for this reaction at 25 °C and comment on the spontaneity of the reaction.



87. Ethene (C_2H_4) can be halogenated by the reaction:



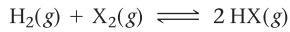
where X_2 can be Cl_2 , Br_2 , or I_2 . Use the thermodynamic data given to calculate ΔH° , ΔS° , ΔG° , and K_p for the halogenation reaction by each of the three halogens at 25 °C. Which reaction is most spontaneous? Least spontaneous? What is the main factor responsible for the difference in the spontaneity of the three reactions? Does higher temperature make the reactions more spontaneous or less spontaneous?

Compound	$\Delta H_f^\circ(\text{kJ/mol})$	$S^\circ(\text{J/mol} \cdot \text{K})$
$\text{C}_2\text{H}_4\text{Cl}_2(g)$	-129.7	308.0
$\text{C}_2\text{H}_4\text{Br}_2(g)$	+38.3	330.6
$\text{C}_2\text{H}_4\text{I}_2(g)$	+66.5	347.8

81. The change in enthalpy (ΔH_{rxn}°) for a reaction is -25.8 kJ/mol. The equilibrium constant for the reaction is 1.4×10^3 at 298 K. What is the equilibrium constant for the reaction at 655 K?
MISSED THIS? Read Section 19.10

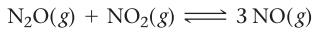
82. A reaction has an equilibrium constant of 8.5×10^3 at 298 K. At 755 K, the equilibrium constant is 0.65. Find ΔH_{rxn}° for the reaction.

88. H_2 reacts with the halogens (X_2) according to the reaction:



where X_2 can be Cl_2 , Br_2 , or I_2 . Use the thermodynamic data in Appendix IIB to calculate ΔH° , ΔS° , ΔG° , and K_p for the reaction between hydrogen and each of the three halogens. Which reaction is most spontaneous? Least spontaneous? What is the main factor responsible for the difference in the spontaneity of the three reactions? Does higher temperature make the reactions more spontaneous or less spontaneous?

89. Consider this reaction occurring at 298 K:



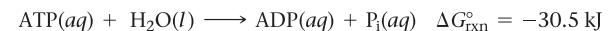
- a. Show that the reaction is not spontaneous under standard conditions by calculating ΔG_{rxn}° .
- b. If a reaction mixture contains only N_2O and NO_2 at partial pressures of 1.0 atm each, the reaction will be spontaneous until some NO forms in the mixture. What maximum partial pressure of NO builds up before the reaction ceases to be spontaneous?
- c. Can the reaction be made more spontaneous by an increase or decrease in temperature? If so, what temperature is required to make the reaction spontaneous under standard conditions?

90. Consider this reaction occurring at 298 K:



- a. Show that the reaction is not spontaneous under standard conditions by calculating ΔG_{rxn}° .
- b. If BaCO_3 is placed in an evacuated flask, what is the partial pressure of CO_2 when the reaction reaches equilibrium?
- c. Can the reaction be made more spontaneous by an increase or decrease in temperature? If so, at what temperature is the partial pressure of carbon dioxide 1.0 atm?

91. Living organisms use energy from the metabolism of food to create an energy-rich molecule called adenosine triphosphate (ATP). The ATP acts as an energy source for a variety of reactions that the living organism must carry out to survive. ATP provides energy through its hydrolysis, which can be symbolized as follows:



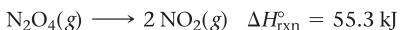
where ADP represents adenosine diphosphate and P_i represents an inorganic phosphate group (such as HPO_4^{2-}).

- a. Calculate the equilibrium constant, K , for the given reaction at 298 K.
- b. The free energy obtained from the oxidation (reaction with oxygen) of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) to form carbon dioxide and water can be used to re-form ATP by driving the given reaction in reverse. Calculate the standard free energy change for the oxidation of glucose and estimate the maximum number of moles of ATP that can be formed by the oxidation of one mole of glucose.

- 92.** The standard free energy change for the hydrolysis of ATP was given in Problem 91. In a particular cell, the concentrations of ATP, ADP, and P_i are 0.0031 M, 0.0014 M, and 0.0048 M, respectively. Calculate the free energy change for the hydrolysis of ATP under these conditions. (Assume a temperature of 298 K.)
- 93.** These reactions are important in catalytic converters in automobiles. Calculate ΔG° for each at 298 K. Predict the effect of increasing temperature on the magnitude of ΔG° .
- $2 \text{CO}(g) + 2 \text{NO}(g) \longrightarrow \text{N}_2(g) + 2 \text{CO}_2(g)$
 - $5 \text{H}_2(g) + 2 \text{NO}(g) \longrightarrow 2 \text{NH}_3(g) + 2 \text{H}_2\text{O}(g)$
 - $2 \text{H}_2(g) + 2 \text{NO}(g) \longrightarrow \text{N}_2(g) + 2 \text{H}_2\text{O}(g)$
 - $2 \text{NH}_3(g) + 2 \text{O}_2(g) \longrightarrow \text{N}_2\text{O}(g) + 3 \text{H}_2\text{O}(g)$
- 94.** Calculate ΔG° at 298 K for these reactions and predict the effect on ΔG° of lowering the temperature.
- $\text{NH}_3(g) + \text{HBr}(g) \longrightarrow \text{NH}_4\text{Br}(s)$
 - $\text{CaCO}_3(s) \longrightarrow \text{CaO}(s) + \text{CO}_2(g)$
 - $\text{CH}_4(g) + 3 \text{Cl}_2(g) \longrightarrow \text{CHCl}_3(g) + 3 \text{HCl}(g)$
(ΔG_f° for $\text{CHCl}_3(g)$ is -70.4 kJ/mol)
- 95.** All the oxides of nitrogen have positive values of ΔG_f° at 298 K, but only one common oxide of nitrogen has a positive ΔS_f° . Identify that oxide of nitrogen without reference to thermodynamic data and explain.
- 96.** The values of ΔG_f° for the hydrogen halides become less negative with increasing atomic number. The ΔG_f° of HI is slightly positive. However, the trend in ΔS_f° is to become more positive with increasing atomic number. Explain.
- 97.** Consider the reaction $\text{X}_2(g) \longrightarrow 2 \text{X}(g)$. When a vessel initially containing 755 torr of X_2 comes to equilibrium at 298 K, the equilibrium partial pressure of X is 103 torr. The same reaction

is repeated with an initial partial pressure of 748 torr of X_2 at 755 K; the equilibrium partial pressure of X is 532 torr. Find ΔH° for the reaction.

- 98.** Dinitrogen tetroxide decomposes to nitrogen dioxide:



At 298 K, a reaction vessel initially contains 0.100 atm of N_2O_4 . When equilibrium is reached, 58% of the N_2O_4 has decomposed to NO_2 . What percentage of N_2O_4 decomposes at 388 K? Assume that the initial pressure of N_2O_4 is the same (0.100 atm).

- 99.** Indicate and explain the sign of ΔS_{univ} for each process.

- $2 \text{H}_2(g) + \text{O}_2(g) \longrightarrow 2 \text{H}_2\text{O}(l)$ at 298 K
- the electrolysis of $\text{H}_2\text{O}(l)$ to $\text{H}_2(g)$ and $\text{O}_2(g)$ at 298 K
- the growth of an oak tree from a little acorn

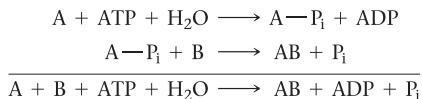
- 100.** The Haber process is very important for agriculture because it converts $\text{N}_2(g)$ from the atmosphere into bound nitrogen, which can be taken up and used by plants. The Haber process reaction is $\text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g)$. The reaction is exothermic but is carried out at relatively high temperatures. Why?

- 101.** A metal salt with the formula MCl_2 crystallizes from water to form a solid with the composition $\text{MCl}_2 \cdot 6 \text{H}_2\text{O}$. The equilibrium vapor pressure of water above this solid at 298 K is 18.3 mmHg. What is the value of ΔG for the reaction $\text{MCl}_2 \cdot 6 \text{H}_2\text{O}(s) \rightleftharpoons \text{MCl}_2(s) + 6 \text{H}_2\text{O}(g)$ when the pressure of water vapor is 18.3 mmHg? When the pressure of water vapor is 760 mmHg?

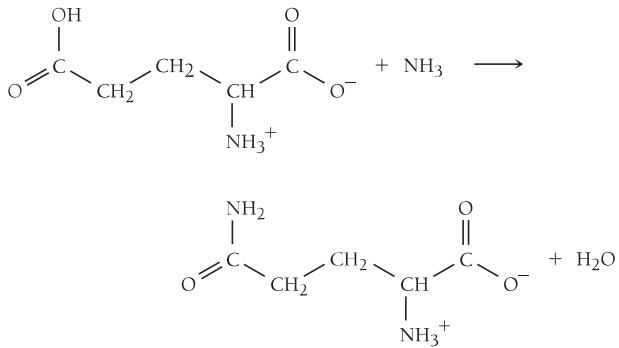
- 102.** The solubility of $\text{AgCl}(s)$ in water at 25 °C is $1.33 \times 10^{-5} \text{ mol/L}$ and its ΔH° of solution is 65.7 kJ/mol. What is its solubility at 50.0 °C?

CHALLENGE PROBLEMS

- 103.** Review the box in this chapter entitled *Chemistry in Your Day: Making a Nonspontaneous Process Spontaneous*. The hydrolysis of ATP, shown in Problem 91, is often used to drive nonspontaneous processes—such as muscle contraction and protein synthesis—in living organisms. The nonspontaneous process to be driven must be coupled to the ATP hydrolysis reaction. For example, suppose the nonspontaneous process is $A + B \longrightarrow AB$ (ΔG° positive). The coupling of a nonspontaneous reaction such as this one to the hydrolysis of ATP is often accomplished by the mechanism:



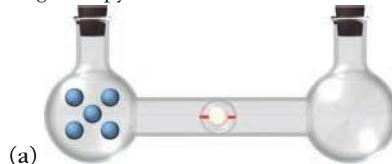
As long as $\Delta G_{\text{rxn}}^\circ$ for the nonspontaneous reaction is less than 30.5 kJ, the reaction can be made spontaneous by coupling in this way to the hydrolysis of ATP. Suppose that ATP is to drive the reaction between glutamate and ammonia to form glutamine:



- a. Calculate K for the reaction between glutamate and ammonia. (The standard free energy change for the reaction is +14.2 kJ/mol. Assume a temperature of 298 K.)

- b. Write a set of reactions such as those given showing how the glutamate and ammonia reaction can couple with the hydrolysis of ATP. What are $\Delta G_{\text{rxn}}^\circ$ and K for the coupled reaction?

- 104.** Calculate the entropy of each state and rank the states in order of increasing entropy.



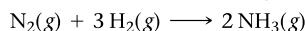
- 105.** Suppose we redefine the standard state as $P = 2$ atm. Find the new standard ΔG_f° values of each substance.

a. $\text{HCl}(g)$ b. $\text{N}_2\text{O}(g)$ c. $\text{H}(g)$

Explain the results in terms of the relative entropies of reactants and products of each reaction.

- 106.** The ΔG for the freezing of $\text{H}_2\text{O}(l)$ at -10°C is -210 J/mol, and the heat of fusion of ice at this temperature is 5610 J/mol. Find the entropy change of the universe when 1 mol of water freezes at -10°C .

- 107.** Consider the reaction that occurs during the Haber process:



The equilibrium constant is 3.9×10^5 at 300 K and 1.2×10^{-1} at 500 K . Calculate $\Delta H_{\text{rxn}}^\circ$ and $\Delta S_{\text{rxn}}^\circ$ for this reaction.

- 108.** The salt ammonium nitrate can follow three modes of decomposition: (a) to $\text{HNO}_3(g)$ and $\text{NH}_3(g)$, (b) to $\text{N}_2\text{O}(g)$ and $\text{H}_2\text{O}(g)$, and (c) to $\text{N}_2(g)$, $\text{O}_2(g)$, and $\text{H}_2\text{O}(g)$. Calculate $\Delta G_{\text{rxn}}^\circ$ for each mode of decomposition at 298 K . Explain in light of these results how it is

still possible to use ammonium nitrate as a fertilizer and identify the precautions that should be taken when it is used.

- 109.** Given the data, calculate ΔS_{vap} for each of the first four liquids. ($\Delta S_{\text{vap}} = \Delta H_{\text{vap}}/T$, where T is in K)

Compound	Name	BP (°C)	ΔH_{vap} (kJ/mol) at BP
$\text{C}_4\text{H}_{10}\text{O}$	Diethyl ether	34.6	26.5
$\text{C}_3\text{H}_6\text{O}$	Acetone	56.1	29.1
$\text{C}_6\text{H}_6\text{O}$	Benzene	79.8	30.8
CHCl_3	Chloroform	60.8	29.4
$\text{C}_2\text{H}_5\text{OH}$	Ethanol	77.8	38.6
H_2O	Water	100	40.7

All four values should be close to each other. Predict whether the last two liquids in the table have ΔS_{vap} in this same range. If not, predict whether it is larger or smaller and explain. Verify your prediction.

CONCEPTUAL PROBLEMS

- 110.** Which is more efficient, a butane lighter or an electric lighter (such as the ones traditionally found on the dashboard of automobiles)? Explain.

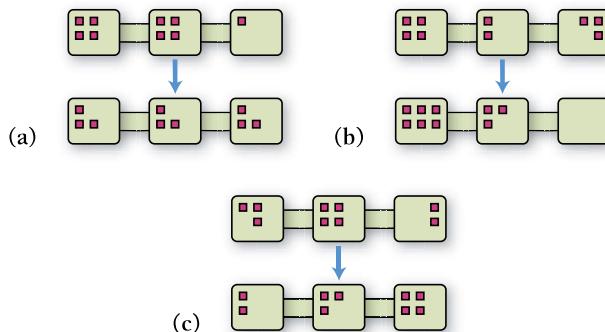
- 111.** Which statement is true?

- a. A spontaneous reaction is always a fast reaction.
- b. A spontaneous reaction is always a slow reaction.
- c. The spontaneity of a reaction is not necessarily related to the speed of a reaction.

- 112.** Which process is necessarily driven by an increase in the entropy of the surroundings?

- a. the condensation of water
- b. the sublimation of dry ice
- c. the freezing of water

- 113.** Consider the changes in the distribution of nine particles into three interconnected boxes shown here. Which has the most negative ΔS ?



- 114.** Which statement is true?

- a. A reaction in which the entropy of the system increases can be spontaneous only if it is exothermic.
- b. A reaction in which the entropy of the system increases can be spontaneous only if it is endothermic.
- c. A reaction in which the entropy of the system decreases can be spontaneous only if it is exothermic.

- 115.** Which process is spontaneous at 298 K ?

- a. $\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(g, 1\text{ atm})$
- b. $\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(g, 0.10\text{ atm})$
- c. $\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(g, 0.010\text{ atm})$

- 116.** The free energy change of the reaction $\text{A}(g) \longrightarrow \text{B}(g)$ is zero under certain conditions. The *standard* free energy change of the reaction is -42.5 kJ. Which statement must be true about the reaction?

- a. The concentration of the product is greater than the concentration of the reactant.
- b. The reaction is at equilibrium.
- c. The concentration of the reactant is greater than the concentration of the product.

- 117.** The reaction $\text{A}(g) \rightleftharpoons \text{B}(g)$ has an equilibrium constant of 5.8 and under certain conditions has $Q = 336$. What can you conclude about the sign of $\Delta G_{\text{rxn}}^\circ$ and $\Delta G_{\text{rxn}}^\circ$ for this reaction under these conditions?

QUESTIONS FOR GROUP WORK

Active Classroom Learning

Discuss these questions with the group and record your consensus answer.

- 118.** Imagine that you roll two dice. Write down all the possible rolls that sum to 2. Write all the possible rolls that sum to 12. Write all the possible rolls that sum to 7. Which configuration has the greatest entropy: 2, 12, or 7?

- 119.** If you roll 1 million dice, what will be the average of all the dice? If there is a room with 1 million dice and they all have a 1 on the top

face, and there is an earthquake strong enough to roll dice around, what is the likelihood that after the earthquake all the top faces will sum to 1 million? To 6 million? How does this thought experiment illustrate the second law of thermodynamics?

- 120.** Not all processes in which the system increases in entropy are spontaneous. How can this observation be consistent with the second law? Provide an example and explain your answer in complete sentences.

- 121.** Have each group member look up ΔH_f° and S° for one substance in the reaction: $3 \text{O}_2(g) + 6 \text{H}_2(g) + 6 \text{C(s, graphite)} \longrightarrow \text{C}_6\text{H}_{12}\text{O}_6(s, \text{glucose})$. What is ΔH° for this reaction? What is ΔS° ? When is ΔH_f° for a substance equal to zero? When is S° for a substance equal to zero?

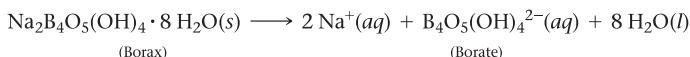
- 122.** Calculate ΔG° at 25 °C for the reaction in the previous question. Is this reaction spontaneous under standard conditions? How do you know? What is the determining factor: the change in energy or the change in entropy or both? Explain.



DATA INTERPRETATION AND ANALYSIS

Thermodynamic Functions for Borax

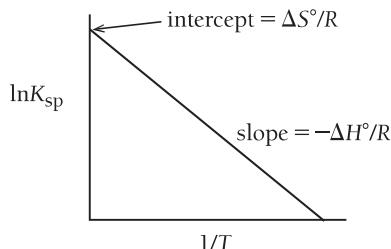
- 123.** Borax, sodium tetraborate decahydrate, is an important mineral found in dry lakebeds in California. It is used to make soap and glass, and it is also used as a preservative. You can use the values of K_{sp} of borax at different temperatures to determine ΔH° , ΔS° , and ΔG° for the dissolution of borax:



The relationship:

$$\ln(K_{\text{sp}}) = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

has the form of a linear equation $y = mx + b$, where y is the $\ln K_{sp}$ and x is $1/T$. The slope is equal to $(-\Delta H^\circ/R)$ and the y -intercept is $\Delta S^\circ/R$, where R is the gas constant, 8.314 J/K mol. If you measure K_{sp} at several different temperatures, you can plot the $\ln K$ versus $1/T$ (T in Kelvin), as shown here.



▲ Plot of $\ln K_{sp}$ versus $1/T$ where the Units of Temperature Are in Kelvin

Cc

ANSWERS TO CONCEPTUAL CONNECTIONS

The Second Law

- 19.1 (c)** The second law states that energy spontaneously disperses itself. The spontaneous concentration of energy (in a closed system) is inconsistent with the second law.

Entropy

- 19.2 (a)** The more spread out the particles are between the three boxes, the greater the entropy. Therefore, the entropy change is positive only in scheme **(a)**.

Entropy and State Changes

- 19.3 (c)** The condensation of water is a phase transition from gas to liquid, so entropy decreases.

Entropy and Biological Systems

- 19.4 (b)** Biological systems do not violate the second law of thermodynamics. The key to understanding this concept is realizing that entropy changes in the system can be negative as long as the entropy change of the universe is positive. Biological systems can decrease their own entropy, but only at the expense of creating more entropy in the surroundings (which they do primarily by emitting the heat they generate by their metabolic processes). Thus, for any biological process, ΔS_{univ} is positive.

ΔH , ΔS , and ΔG

- 19.5** (a) Sublimation is endothermic (it requires energy to overcome the intermolecular forces that hold solid carbon dioxide together), so ΔH is positive. The number of moles of gas increases when the solid turns into a gas, so the entropy of the carbon dioxide increases and ΔS is positive. Since $\Delta G = \Delta H - T\Delta S$, ΔG is positive at low temperature and negative at high temperature.

Standard Entropies

19.6 (a) $\text{Kr} < \text{Cl}_2 < \text{SO}_3$. Because krypton is a monoatomic gas, it has the least entropy. Because SO_3 is the most complex molecule, it has the most entropy. The molar masses of the three gases vary slightly, but not enough to overcome the differences in molecular complexity.

Free Energy Changes and Le Châtelier's Principle

19.7 (a) A high concentration of reactants relative to products will lead to $Q < 1$, making the term $RT \ln Q$ in Equation 19.14 negative. ΔG_{rxn} is more negative than $\Delta G_{\text{rxn}}^\circ$, and the reaction is more spontaneous.

K and $\Delta G_{\text{rxn}}^\circ$

19.8 (c) Since the equilibrium constant is less than 1, the reaction proceeds toward reactants under standard conditions (when $Q = 1$). Therefore, $\Delta G_{\text{rxn}}^\circ$ is positive.

The Conditions of Spontaneity

19.9 (b) $\Delta G_{\text{rxn}} < 0, Q < K$ If a reaction is spontaneous, then ΔG_{rxn} is negative and Q must be less than K (because a spontaneous reaction proceeds toward products).