19—Principles of Reactivity: Entropy and Free Energy

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Waterfall by M. C. Escher, 1961. This drawing is reminiscent of Fludd's perpetual motion machine.

Perpetual Motion Machines

"You can't get something for nothing."

Economists have often said, "There is no free lunch," meaning that every desirable thing requires the expenditure of some effort, money, or energy. But people have certainly tried.

Wouldn't it be wonderful if someone could design a perpetual motion machine, one that produces energy but requires no energy itself? Over the centuries many people have attempted this feat. But, as you will see in this chapter, such a machine violates the fundamental laws of thermodynamics.

The first perpetual motion machine was apparently proposed by Villand de Honnecourt in the 13th century. Later, Leonardo da Vinci made a number of drawings of machines that would produce energy at no cost.

Among the best-known early machines was one proposed by Robert Fludd in the 1600s. Fludd, a well-known scientist, also suggested that the sun and not the earth was the center of our universe, and that blood carries the gases important to life throughout the body. But, he also believed that lightning was simply an act of God.

In 1812 Charles Redheffer of Philadelphia set up a machine that, he claimed, required no source of energy to run. He applied to the city government for funds to build an even larger version, but did not allow the city commissioners to get too close to the machine. The commissioners were suspicious, however, and asked a local engineer, Isaiah Lukens, to build a machine that worked on the same principle as Redheffer's machine. When Redheffer saw Lukens's replica, Redheffer apparently realized his fraud was exposed. He soon left town for New York City, where he tried anew to interest investors in his machine.

In New York Redheffer was again exposed as a charlatan, this time by the inventor Robert Fulton. When Fulton was invited to view

Chapter Goals

See Chapter Goals Revisited (page 933). Test your knowledge of these goals by taking the exam-prep quiz on the General ChemistryNow CD-ROM or website.

- Understand the concept of entropy and its relationship to spontaneity.
- Predict whether a process will be spontaneous.
- Understand and use a new thermodynamic function, free energy.
- Understand the relationship of a free energy change for a reaction, its equilibrium constant, and whether the reaction is product- or reactant-favored.

Chapter Outline

19.1 Spontaneous Change and Equilibrium
19.2 Heat and Spontaneity
19.3 Dispersal of Energy and Matter
19.4 Entropy and the Second Law of Thermodynamics
19.5 Entropy Changes and Spontaneity
19.6 Gibbs Free Energy
19.7 ΔG°, K, and Product Favorability
19.8 Thermodynamics, Time, and Life

the machine, he noticed that it was operating in a wobbly manner. Fulton challenged Redheffer, stating that he could expose the secret source of energy. Fulton also offered to compensate Redheffer for damages if the accusations proved to be false. Redheffer should never have agreed. When Fulton removed some boards in a wall near the machine, a thin cord of cat gut was discovered to lead to yet another room. There Fulton found an elderly gentleman, eating a crust of bread with one hand and turning a crank with the other hand—not so smoothly—to run Redheffer's machine! Upon the discovery Redheffer disappeared.

The vast majority of the so-called perpetual motion machines violate the first law of thermodynamics. Falling water in Fludd's machine can, indeed, turn a crank to perform useful work. However, then there is insufficient energy available to lift the water to the reservoir to begin the cycle again. Besides, energy losses due to friction occur in any machine.

In the 1880s John Gamgee invented an "ammonia engine" and tried to persuade the U. S. Navy to use it for ship propulsion. Even President Garfield took the time to inspect Gamgee's engine. The engine worked by using the heat of ocean water to evaporate liquid ammonia. The expanding ammonia vapor was supposed to drive a piston, in the same way that the combustion of gasoline in an automobile's engine drives its pistons. In the ammonia engine, the ammonia vapor cools when it expands, which would lead to the condensation of the ammonia. The reservoir of liquid ammonia is thereby replenished, and the cycle begins anew.

Gamgee's engine sounded good—but it violates the second law of thermodynamics, the subject of this chapter.

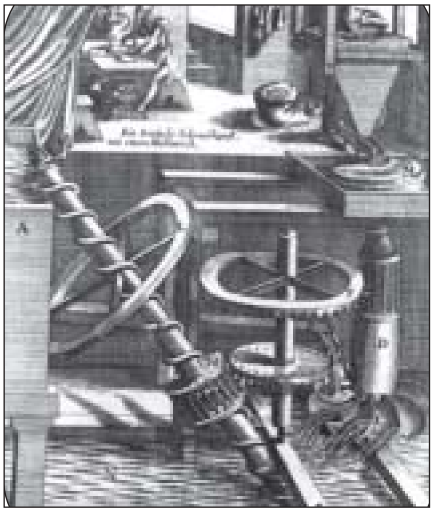
Image courtesy of University of Kentucky Library/Special Collections

A late-17th-century version of Fludd's proposed "perpetual motion machine." Water flows from a reservoir at the right, turning a water wheel. Work could be extracted from this motion, and it was also used to turn an Archimedes screw, the long rod to the left, that transported the water back to the top where it could again flow downward onto the water wheel. Can you figure out what is wrong with this device?

To Review Before You Begin

- Review enthalpy and the first law of thermodynamics (Chapter 6)
- Review the concepts underlying chemical equilibria (Chapter 16)

Chapter 6 (Energy and Chemical Reactions) and Chapter 19 (Entropy and Free Energy) together provide an introduction to the subject of thermodynamics. Chapter 6 focused on heat and heat transfer, with the discussion being guided by the first law of thermodynamics, the law of conservation of energy. In Chapter 19, we encounter two more laws of thermodynamics. These laws determine the spontaneity of chemical and physical processes, explain the driving forces that compel the changes that a system undergoes to achieve equilibrium, and guide us to understand when reactions are product-favored or reactant-favored.

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Throughout the chapter this icon introduces a list of resources on the General ChemistryNow CD-ROM or website (**http://now.brookscole.com/kotz6e**) that will:

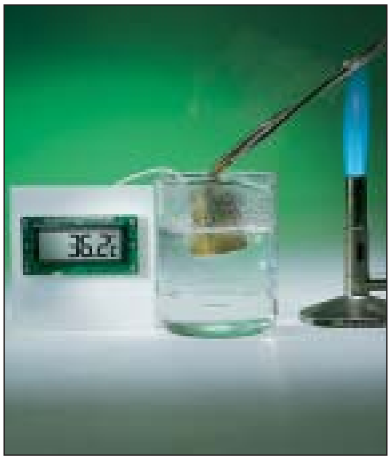
- help you evaluate your knowledge of the material
- provide homework problems
- allow you to take an exam-prep quiz
- provide a personalized Learning Plan targeting resources that address areas you should study

19.1—Spontaneous Change and Equilibrium

Change is central to chemistry, so it is important to understand the factors that determine whether a change will occur. In chemistry, we encounter many examples of both chemical changes (chemical reactions) and physical changes (the formation of mixtures, expansion of gases, and changes of state, to name a few). When describing changes, chemists use the term **spontaneous**. A spontaneous change is one that occurs without outside intervention. This statement does not say anything about the rate of the change, merely that a spontaneous change is naturally occurring and unaided. Furthermore, *a spontaneous change leads inexorably to equilibrium.*

If a piece of hot metal is placed in a beaker of cold water, heat transfer from the hot metal to the cooler water occurs spontaneously. The process of heat transfer continues until the two objects are at the same temperature and thermal equilibrium is attained. Similarly, many chemical reactions proceed spontaneously until equilibrium is reached. Some chemical reactions greatly favor products at equilibrium, as in the reaction of sodium and chlorine (page 19). In Chapters 16–18 we described them as *product-favored* reactions (page 765). In other instances, the position of the equilibrium favors the reactants. One example of such a *reactant-favored* process would be the dissolution of an insoluble substance like limestone. If you place a handful of $CaCO_3$ in a small amount of water, only a tiny fraction of the sample will dissolve spontaneously until equilibrium is reached; most of the salt will remain undissolved.

When considering both physical and chemical processes, the focus is always on the changes that must occur to achieve equilibrium. The factors that determine the directionality of the change are the topic of this chapter. Given two objects at the same temperature but isolated thermally from their surroundings, it will never happen that one will heat up while the other becomes colder. Gas molecules will never spontaneously congregate at one end of a flask. A chemical system at equilibrium will not spontaneously change in a way that results in the system no longer being in equilibrium. Neither will a chemical system not at equilibrium change in the direction that takes it farther from the equilibrium condition.



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A spontaneous process. Heat transfers spontaneously from a hotter object to a cooler object.

19.2—Heat and Spontaneity

In previous chapters, we have encountered many spontaneous chemical reactions: hydrogen and oxygen combine to form water; methane burns to give CO_2 and H_2O; Na and Cl_2 react to form NaCl; (HCl(aq) and NaOH(aq) react to form H_2O

Problem-Solving Tip 19.1

A Review of Concepts of Thermodynamics

To understand the thermodynamic concepts introduced in this chapter, be sure to review the ideas of Chapter 6.

System: The part of the universe under study.

Surroundings: The rest of the universe exclusive of the system.

Exothermic: Thermal energy transfer occurs from the system to the surroundings.

Endothermic: Thermal energy transfer occurs from the surroundings to the system.

First law of thermodynamics: The law of the conservation of energy, $\Delta E = q + w$. The change in internal energy of a system is the sum of heat transferred to or from the system and the work done on or by the system. Energy can be neither created nor destroyed.

Enthalpy change: The thermal energy transferred at constant pressure.

State function: A quantity whose value is determined only by the initial and final states of a system.

Standard conditions: Pressure of 1 bar (1 bar = 0.98692 atm) and solution concentration of 1 *m*.

Standard enthalpy of formation, ΔH_f° : The enthalpy change occurring when a compound is formed from its elements in their standard states.

and NaCl(aq). These reactions proceed spontaneously from reactants to products and have gone substantially to completion when equilibrium is reached. These chemical reactions and many others share a common feature: They are exothermic. Therefore, it might be tempting to conclude that evolution of heat is the criterion that determines whether a reaction or process is spontaneous. Further inspection, however, will reveal flaws in this reasoning. This is especially evident with the inclusion of some common physical changes, changes that are spontaneous but that are endothermic or energy-neutral:

- *Dissolving NH_4ND_3.* The ionic compound NH_4ND_3 dissolves spontaneously in water in an endothermic process with $\Delta H^\circ = +25.7$ kJ/mol (page 765).
- *Expansion of a gas into a vacuum.* A system is set up with two flasks connected by a valve (Figure 19.1). One flask is filled with a gas and the other is evacuated. When the valve is opened, the gas will flow spontaneously from one flask to the other until the pressure is the same throughout. The expansion of an ideal gas is energy-neutral, with heat being neither evolved nor required.
- *Phase changes.* Melting of ice is an endothermic process; to melt one mole of H_2O requires about 6 kJ. At temperatures above 0 °C, the melting of ice is spontaneous. Below 0 °C, however, ice does not melt; melting is not a spontaneous process under these conditions. At 0 °C, liquid water and ice coexist at equilibrium, and no net change occurs. This example illustrates that temperature can have a role in determining whether a process is spontaneous. We will return to this important issue later in this chapter.
- *Heat transfer.* The temperature of a cold soft drink sitting in a warm environment will rise until the beverage reaches the ambient temperature. The heat required for this process comes from the surroundings. The endothermic process illustrates that heat transfer from a hotter object (the surroundings) to a cooler object (the soft drink) is spontaneous.

We can gain further insight into spontaneity if we think about a specific chemical system—for example, the reaction $H_2(g) + I_2(g) \longrightarrow 2\,HI(g)$. Equilibrium in this system can be approached from either direction. The reaction of H_2 and I_2 is endothermic, but the reaction occurs spontaneously until an equilibrium mixture containing H_2, I_2, and HI forms. The reverse reaction, the decomposition of HI to form H_2 and I_2

Spontaneous Reactions
A spontaneous reaction proceeds to equilibrium without outside intervention. Such a reaction may or may not be product-favored.

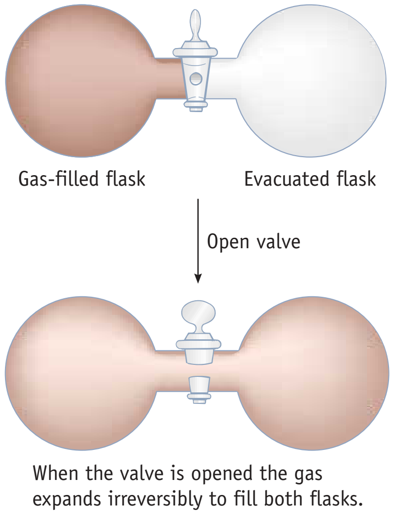

Figure 19.1 Spontaneous expansion of a gas. *(See General ChemistryNow CD-ROM or website Screen 19.3 Directionality of Reactions, to view an animation of this figure.)*

until equilibrium is achieved, is also spontaneous, but in this case the process evolves heat. Equilibrium is approached spontaneously from either direction.

From these examples, and many others, we must conclude that evolution of heat is not a sufficient criterion to determine whether a process is spontaneous. In retrospect, this conclusion makes sense. The first law of thermodynamics tells us that in any process energy must be conserved. If energy is evolved by a system, then the same amount of energy must be absorbed by the surroundings. The exothermicity of the system must be balanced by the endothermicity of the surroundings so that the energy content of the universe remains unchanged. If energy evolution were the only factor determining whether a change is spontaneous, then for every spontaneous process there would be a corresponding nonspontaneous change in the surroundings. We must search further than heat evolution and the first law to determine whether a change is spontaneous.

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See the General ChemistryNow CD-ROM or website:

- **Screen 19.2 Reaction Spontaneity,** for a description of kinetic and thermodynamic control of reactions

19.3—Dispersal of Energy and Matter

A better way to predict whether a process will be spontaneous is with a thermodynamic function called **entropy, *S***. Entropy is tied to the **second law of thermodynamics**, which states that *in a spontaneous process, the entropy of the universe increases.* Ultimately, this law allows us to predict the conditions at equilibrium as well as the direction of spontaneous change toward equilibrium.

The concept of entropy is built around the idea that *spontaneous change results in dispersal of energy.* Many times, a dispersal of matter is also involved, and it can contribute to energy dispersal in some systems. Because the logic underlying these ideas is statistical, let us examine the statistical nature of entropy more closely.

Dispersal of Energy

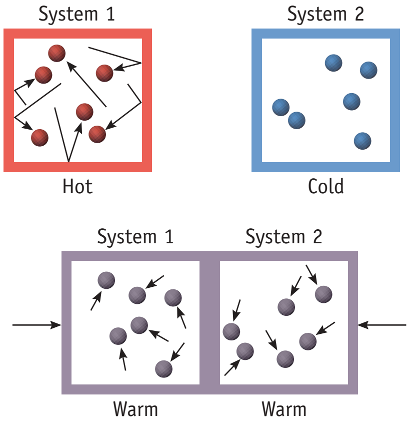


Figure 19.2 Energy transfer between molecules in the gas phase.

The dispersal of energy over as many different energy states as possible is the key contribution to entropy. We can explore a simple example of this phenomenon in which heat flows from a hot object to a cold object until both have the same temperature. A model involving gaseous atoms provides a basis for this analysis (Figure 19.2). Start by placing a sample of hot atoms in contact with a sample of cold atoms. The atoms move randomly in each container and collide with the walls. When the containers come in contact with each other, thermal energy is transferred from the warmer container to the cooler one, and the energy is thus transferred through wall collisions from the warmer atoms to the cooler atoms. Eventually the system stabilizes at an average temperature so that each sample of gas has the same molecular distribution of energies [◀ Section 12.6].

We can also use a statistical explanation to show how energy is dispersed in a system. With statistical arguments, systems must include large numbers of particles for the arguments to be accurate. We will look first at a simple example to understand the underlying concept, and then build up to a larger system.

Consider a system in which there are two atoms (1 and 2) with one discrete packet, or quantum, of energy each, and two other atoms (3 and 4) with no energy

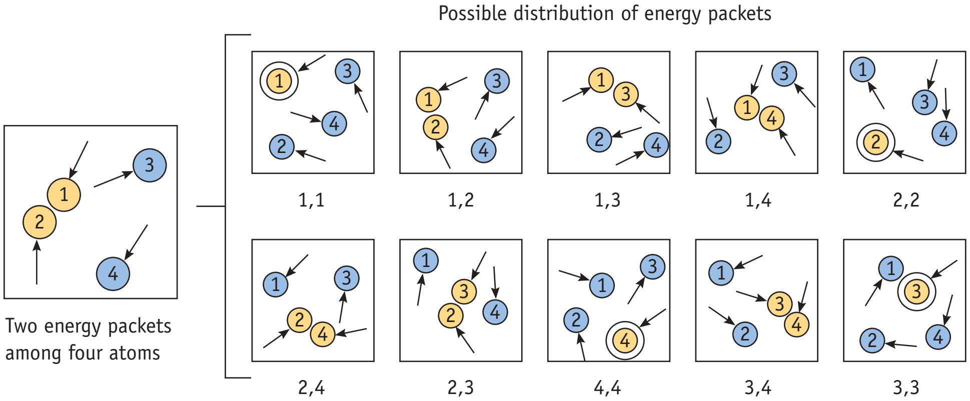


Figure 19.3 **Energy dispersal.** Possible ways of distributing two packets of energy among four atoms. Here there are two atoms (1 and 2) with one quantum of energy apiece, and two other atoms (3 and 4) that have no energy initially. The figure shows there are 10 different ways to distribute the two quanta of energy over the four atoms.

initially (Figure 19.3). When these four atoms are brought together, the total energy in the system is simply the total of the two quanta. Collisions among the atoms allow energy to be transferred so that all distributions of the two packets of energy over the four atoms are eventually achieved. There are 10 different ways to distribute these two quanta of energy over the four atoms. In only 4 of the 10 cases [1, 1; 2, 2; 3, 3; and 4,4], is the energy concentrated on a single particle. In the majority of the cases, 6 out of 10, the energy is distributed to two different particles. Thus, even in a simple example with only two packets of energy to consider, it is more likely that the energy will be found distributed over multiple particles than concentrated in one place.

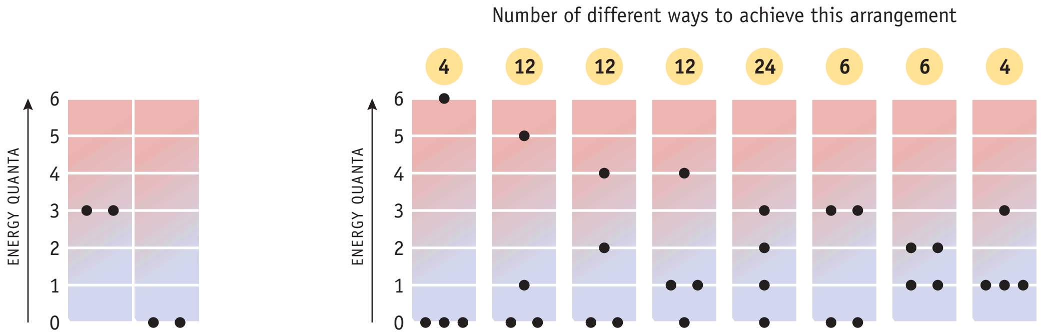
Now let's consider a slightly larger sample. Assume we have four particles again, but this time two of them each begin with three quanta of energy (Figure 19.4). The other two particles initially have zero energy. When these four particles are brought together, the total energy of the system is six quanta. There are eight different arrangements for distributing six quanta of energy among four particles (Figure 19.4). For example, one particle can have all six quanta of energy, and the others can have none. In a different arrangement, two particles can have two quanta of energy each and the other two can have one each.

As in our previous example (Figure 19.3), if we label the particles we will find that some arrangements are more likely than others. Figure 19.4 shows the number of different ways to distribute four particles with a total of six quanta of energy in each of the arrangements indicated. The arrangement that occurs most often is one in which the energy is distributed over all four particles and to a large number of states (four distinct levels are occupied). As the number of particles and the number of energy levels grows, one arrangement turns out to be vastly more probable than all the others.

Dispersal of Matter

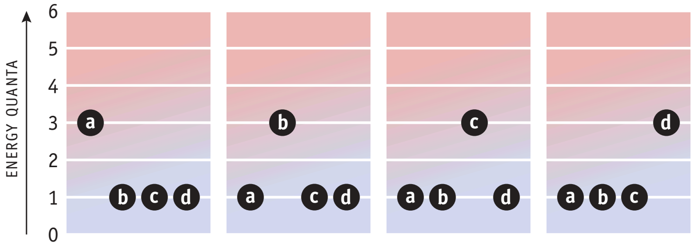
It is rarely obvious how to calculate the different energy levels of a system and how to discern the distribution of the total energy among them. Therefore, it is useful to look at the dispersal of matter, because matter dispersal often contributes to energy dispersal. Let us examine a system qualitatively to gain insight into the likely distribution of energy from the distribution of matter.

Matter dispersal is illustrated in Figure 19.1 by the expansion of a gas into a vacuum. Let us consider this same arrangement—a flask containing two molecules of a gas connected by a valve to an evacuated flask having the same volume (Figure 19.5). Assume that, when the valve connecting the flasks is opened, the two molecules originally in flask A can move randomly throughout flasks A and B. At any given instant, the molecules will be in one of four possible configurations: two molecules in flask A,



(a) Initially four particles are separated from each other. Two particles each have three quanta of energy, and the other two have none. A total of six quanta of energy will be distributed once the particles interact.

(b) Once the particles begin to interact, there are several different ways to distribute the six available quanta. Each of these arrangements will have multiple ways of distributing the energy among the four atoms. Part (c) shows why the right most arrangement can be achieved 4 ways.



(c) There are four different ways to arrange four particles (a, b, c, and d) such that one particle has three quanta of energy and the other three each have one quantum of energy.

Figure 19.4 **Energy dispersal.** Possible ways of distributing four packets of energy among four atoms.

two molecules in flask B, or one molecule in each flask. The probability of having one molecule in each flask is 50%. There is a 25% probability that the two molecules will be simultaneously in flask A and a 25% probability that they will be in flask B.

If we next consider a system having three molecules originally in flask A, we would find there is only a one in eight chance that the three molecules will remain in the original flask. With 10 molecules, there is only one chance in 1024 of finding all the molecules in flask A. The probability of n molecules remaining in the initial flask in this two-flask system is $(\frac{1}{2})^n$, where n is the number of molecules. If flask A contained one mole of a gas, the probability of all the molecules being found in that flask when the connecting valve is opened is $(\frac{1}{2})^N$, where N is Avogadro's number—a probability almost too small to comprehend! If we calculate the probabilities for all the other possible arrangements of the mole of molecules in this scenario, we would find that the most probable arrangement, by a huge margin, is the one in which the molecules are, on average, evenly distributed over the entire two-flask volume.

This analysis shows that, in a system such as is depicted in Figure 19.1 or 19.5, it is highly probable that gas molecules will flow from one flask into an evacuated flask until the pressures in the two flasks are equal. Conversely, the opposite process, in which all the gas molecules in the apparatus congregate in one of the two flasks, is highly improbable.

As stated earlier, matter dispersal contributes to energy dispersal, so let us next describe the experiment in Figure 19.5 in terms of energy dispersal. To do so, we need to remember an idea introduced in Chapter 7, that all energy is quantized. Schrödinger's model [◀ Section 7.5], and the equation that he developed, was applied to the atom to derive the three quantum numbers and the orbitals for elec-

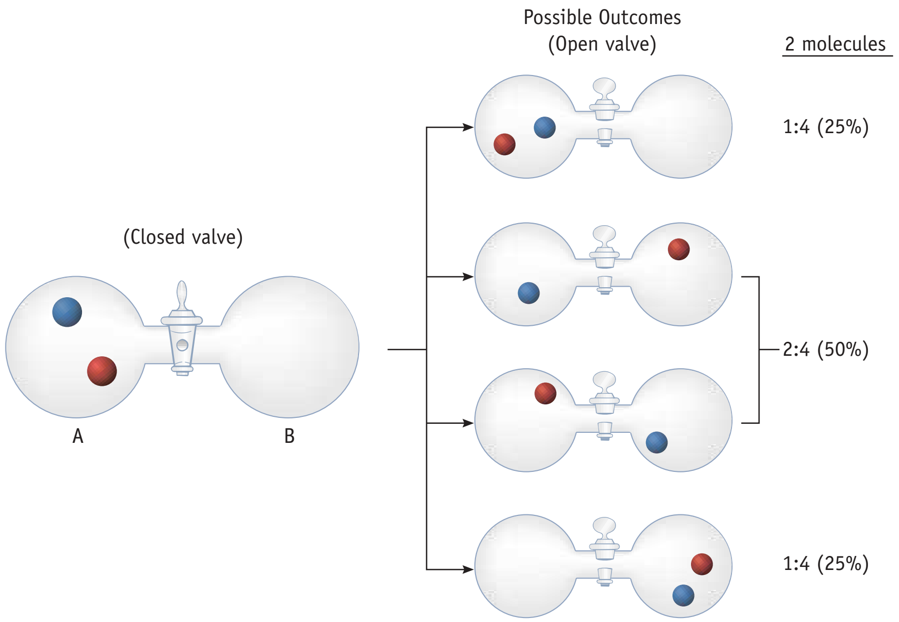


Figure 19.5 **Dispersal of matter.** The expansion of a gas into a vacuum. There are four possible arrangements for two molecules in this apparatus. There is a 50% probability that there will be one molecule in each flask at any instant of time. *(See General ChemistryNow CD-ROM or website Screen 19.3 Reaction Directionality, to view an animation of the expansion of a gas.)*

trons around a nucleus. It turns out that Schrödinger's equation is universal and can be applied to any system, including gas molecules in a room or in a reaction flask. When we do this, we find that *all* systems have quantized energies, just as we found for electrons in an atom.

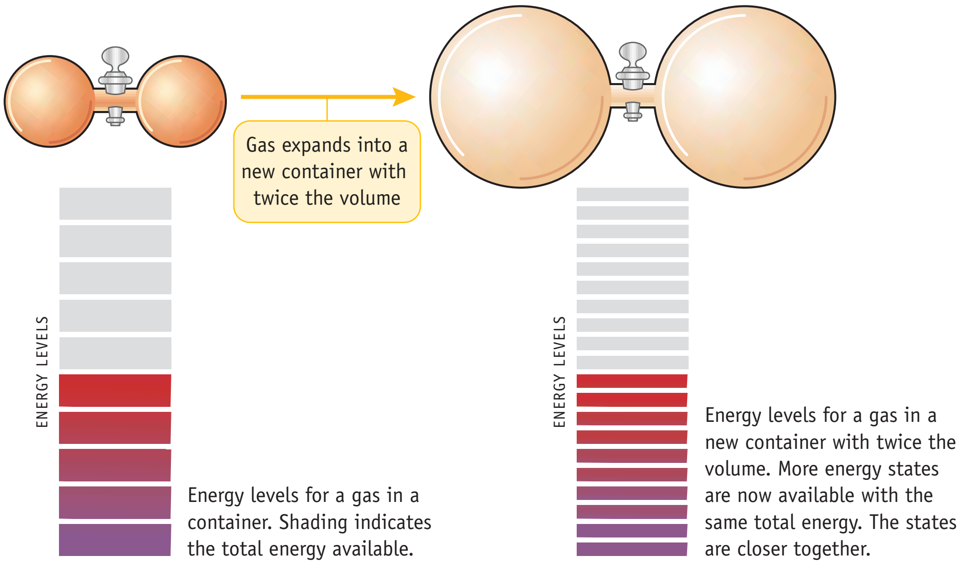
Recall from Chapter 7 that the energy levels in an atom get closer together as the principal quantum number, *n,* gets larger (Figure 7.12). It is also true that the average radius of the atom increases with the primary quantum number (page 321). If we apply the Schrödinger equation to other systems, we find the same general trends: the size of the system affects the size of *n,* and energy levels get closer together as *n* gets larger.

In a macroscopic system such as the example of a gas inside a flask, the principal quantum number is very large (because the system is much larger that the size of an atom), and the energy levels are infinitesimally close together as a result of *n* being so large. Nonetheless, they are still separate, quantized, energy levels. However, because they are so close together, we often simply treat gas samples as though the energies are continuous, such as when we discuss the Maxwell-Boltzmann distribution (see Section 12.6). If we increase the size of the vessel holding the gas, the corresponding quantum number will increase, and the energies will get even closer together. In our statistical discussion of matter and energy dispersal, a decreased spacing between energy levels means a larger number of energy levels is available to our system. Because the total energy available to our system has not changed (only the volume has changed), the number of ways of distributing the total energy within those energy levels increases (Figure 19.6). That is, when matter is dispersed into a larger volume, energy is dispersed over more energy levels.

Applications of the Dispersal of Matter Ideas

The logic applied to the expansion of a gas into a vacuum can be used to rationalize the mixing of two gases. If flasks containing O_2 and N_2 are connected (in an experimental set-up like that in Figure 19.5), the two gases will diffuse together, eventually leading to a mixture in which molecules of O_2 and N_2 are evenly distributed throughout the total volume. A mixture of N_2 and O_2 will never separate into samples

Figure 19.6 **Energy dispersal.** As the size of the container for the chemical or physical change increases, the number of energy states accessible to the molecules of the system increases and the states come closer together.



of each component of its own accord. The important point is that what began as a relatively orderly system with N_2 and O_2 molecules in separate flasks spontaneously moves toward a system in which each gas is maximally dispersed. For gases at room temperature, the entropy-driven dispersal of matter is equivalent to an increase in disorder of the system.

The equivalence of matter and energy dispersal with disorder is true for some solutions as well. For example, when a water-soluble compound is placed in water, it is highly probable that the molecules or ions of the compound will ultimately become distributed evenly throughout the solution. The tendency to move from order to disorder explains why the $KMnO_4$ sample in Figure 19.7 eventually disperses over the entire container. The process leads to a mixture, a system in which the solute and solvent molecules are more widely dispersed.

It is also evident from these examples of matter dispersal that if we wanted to put all of the gas molecules in Figure 19.5 back into one flask, or recover the $KMnO_4$ crystals, we would have to intervene in some way. For example, we could use a pump to force all of the gas molecules from one side to the other or we could lower the temperature drastically (Figure 19.8). In the latter case, the molecules would move "downhill" energetically to a place of very low kinetic energy.

Does the formation of a mixture always lead to greater disorder? It does when gases are mixed. With liquids and solids this is usually the case as well, but not always. Exceptions can be found, especially when considering aqueous solutions. For example, Li^+ and OH^- ions are highly ordered in the solid lattice [◀ Section 13.6], but they become more disordered when they enter into solution. However, the solution process is accompanied by solvation, a process in which water molecules become tightly bound to the ions. As a result, the water molecules are constrained to a more ordered arrangement than in pure water. Thus, two opposing effects are at work here: a decrease in order for the Li^+ and OH^- ions when dispersed in the water, and an increased order for water. The higher degree of ordering due to solvation dominates, and the result is a higher degree of order overall in the system.

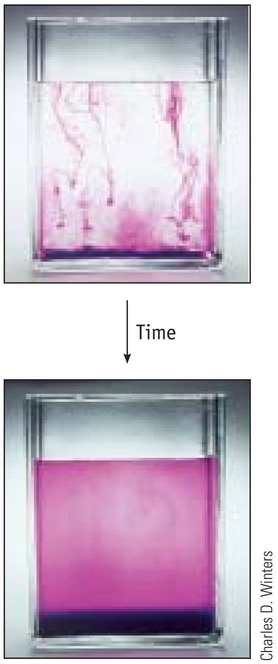


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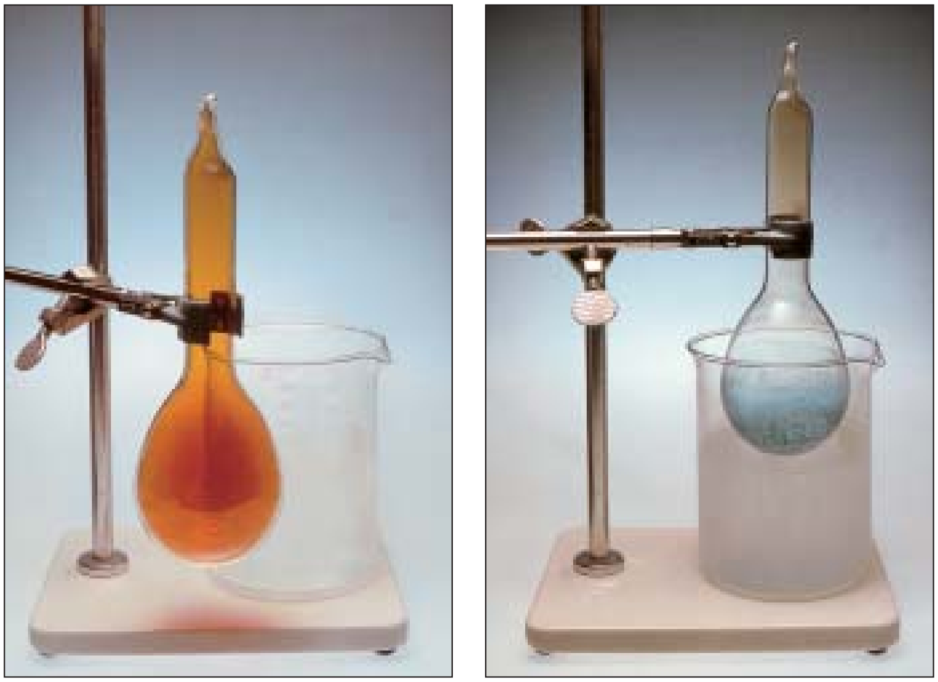
Figure 19.7 **Matter dispersal.** A small quantity of purple $KMnO_4$ is added to water (*top*). With time, the solid dissolves and the highly colored MnO_4^- ion (and the K^+ ions) become dispersed throughout the solution (*bottom*).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(a)

(b)

Figure 19.8 Reversing the process of matter dispersal. (a) Brown NO_2 gas is dispersed evenly throughout the flask. (b) If the flask is immersed in liquid nitrogen at −196 °C, the kinetic energy of the NO_2 molecules is reduced to the point that they become a solid and collect on the cold walls of the flask.

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See the General ChemistryNow CD-ROM or website:

- **Screen 19.3 Directionality of Reactions,** for an illustration of matter and energy dispersal

The Boltzmann Equation for Entropy

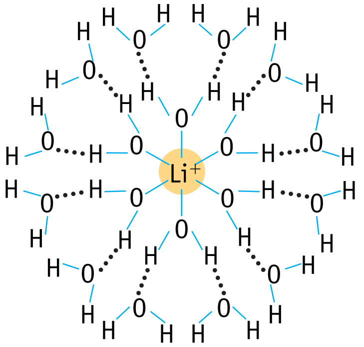
Ludwig Boltzmann (1844–1906) developed the idea of looking at the distribution of energy over different energy states as a way to calculate entropy. At the time of his death, the scientific world had not yet accepted his ideas. In spite of this, he was firmly committed to his theories and had his equation for entropy engraved on his tombstone in Vienna, Austria. The equation is

$$S = k \log W$$

where k is the Boltzmann constant, and W represents the number of different ways that the energy can be distributed over the available energy levels. Boltzmann concluded that the maximum entropy will be achieved at equilibrium, a state in which W has the maximum value.

A Summary: Matter and Energy Dispersal

In summary, the final state of a system can be more probable than the initial state in either or both of two ways: (1) the atoms and molecules can be more disordered and (2) energy can be dispersed over a greater number of atoms and molecules.



Order and disorder in solid and solution. Lithium hydroxide is a crystalline solid with an orderly arrangement of Li^+ and OH^- ions. When placed in water, it dissolves, and water molecules interact with the Li^+ cations and OH^- anions. Water molecules in pure water have a highly disordered arrangement. However, the attraction between Li^+ ions and water molecules leads to a net ordering of the system when LiOH dissolves.

Ludwig Boltzmann (1844–1906). Engraved on his tombstone in Vienna, Austria, is his equation defining entropy: $S = k \log W$. The symbol k is a constant now known as the Boltzmann constant.

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- If energy and matter are both dispersed in a process, it is spontaneous.
- If only matter is dispersed, then quantitative information is needed to decide whether the process is spontaneous.
- If energy is not dispersed after a process occurs, then that process will never be spontaneous.

19.4—Entropy and the Second Law of Thermodynamics

Entropy is used to quantify the extent of disorder resulting from dispersal of energy and matter. For any substance under a given set of conditions, a numerical value for entropy can be determined. The greater the disorder in a system, the greater the entropy and the larger the value of S.

Like internal energy (E) and enthalpy (H), entropy is a state function. This means that the *change in entropy* for any process depends only on the initial and final states of the system, and not on the pathway by which the process occurs [◀ Section 6.4]. This point is important because it has a bearing on how the value of S is determined, as we will see later.

The point of reference for entropy values is established by the **third law of thermodynamics**. Defined by Ludwig Boltzmann, the third law states that there is no disorder in a perfect crystal at 0 K; that is, $S = 0$. The entropy of an element or compound under any set of conditions is the entropy gained by converting the substance from 0 K to the defined conditions. The entropy of a substance at any temperature can be obtained by measuring the heat required to raise the temperature from 0 K, but with a specific provision that the conversion must be carried out by a reversible process. Adding heat slowly and in very small increments approximates a reversible process. The entropy added by each incremental change is calculated using Equation 19.1:

$$\Delta S = \frac{q_{\text{rev}}}{T} \tag{19.1}$$

In this equation, q_{rev} is the heat absorbed and T is the Kelvin temperature at which the change occurs. Adding the entropy changes for the incremental steps gives the total entropy of a substance. (Because it is necessary to add heat to raise the temperature, *all substances have positive entropy values at temperatures above 0 K*. Based on the third law of thermodynamics, negative values of entropy cannot occur.)

	$S°$ (J/K · mol)
 methane	186.3
 ethane	229.2
 propane	270.3

The standard entropy, $S°$, of a substance, is the entropy gained by converting it from a perfect crystal at 0 K to standard state conditions (1 bar, 1 molal solution). The units for entropy are J/K · mol. A few values of $S°$ are given in Table 19.1. Generally, values of $S°$ found in tables of data refer to a temperature of 298 K.

Some interesting and useful generalizations can be drawn from the data given in Table 19.1 (and Appendix L).

- *When comparing the same or similar substances, entropies of gases are much larger than those for liquids, and entropies of liquids are larger than those for solids.* In a solid the particles have fixed positions in the solid lattice. When a solid melts, its particles have more freedom to assume different positions, resulting in an increase in disorder (Figure 19.9). When a liquid evaporates, restrictions due to forces between the particles nearly disappear, and another large entropy increase occurs. For example, the standard entropies of $I_2(s)$, $Br_2(\ell)$, and $Cl_2(g)$ are 116.1, 152.2, and 223.1 J/K · mol, respectively, and the standard entropies of C(s, graphite) and C(g) are 5.6 and 158.1 J/K · mol, respectively.

Table 19.1 Some Standard Molar Entropy Values at 298 K

Element	Entropy, $S°$ (J/K mol)	Compound	Entropy, $S°$ (J/K mol)
C(graphite)	5.6	CH_4(g)	186.3
C(diamond)	2.377	C_2H_6(g)	229.2
C(vapor)	158.1	C_3H_8(g)	270.3
Ca(s)	41.59	$CH_3OH(\ell)$	127.2
Ar(g)	154.9	CO(g)	197.7
H_2(g)	130.7	CO_2(g)	213.7
O_2(g)	205.1	H_2O(g)	188.84
N_2(g)	191.6	$H_2O(\ell)$	69.95
F_2(g)	202.8	HCl(g)	186.2
Cl_2(g)	223.1	NaCl(s)	72.11
$Br_2(\ell)$	152.2	MgO(s)	26.85
I_2(s)	116.1	$CaCO_3$(s)	91.7

■ **Entropy Values**
A longer list of entropy values appears in Appendix L. Extensive lists of $S°$ values can be found in standard chemical reference sources such as the NIST tables (**http://webbook.nist.gov**).

- As a general rule, *larger molecules have a larger entropy that smaller molecules, and molecules with more complex structures have larger entropies than simpler molecules.* These generalizations work best in series of related compounds. With a more complicated molecule, there are more ways for the molecule to rotate, twist, and vibrate in space (which provides a larger number of internal energy states over which energy can be distributed). Entropies for methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) are 186.3, 229.2, and 270.3 J/K · mol, respectively. The effect of molecular structure can be seen with atoms or molecules of similar molar mass: Ar, CO_2, and C_3H_8 have entropies of 154.9, 213.7, and 270.3 J/K · mol, respectively.

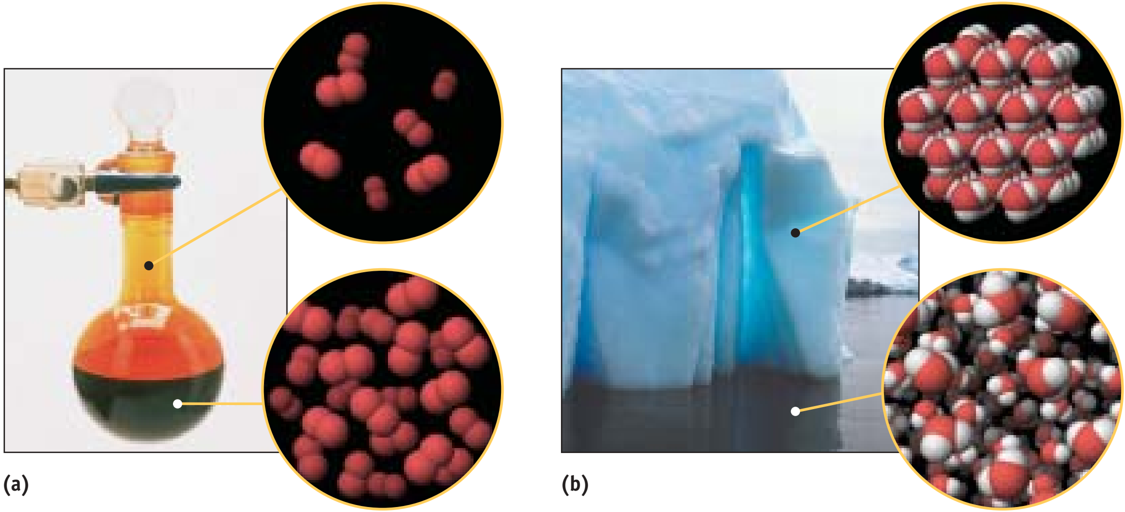
(a)
(b)

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Figure 19.9 **Entropy and states of matter.** (a) The entropy of liquid bromine, $Br_2(\ell)$, is 152.2 J/K · mol, and that for more disordered bromine vapor is 245.47 J/K · mol. (b) The entropy of ice, which has a highly ordered molecular arrangement, is smaller than that for disordered liquid water. *(See General ChemistryNow CD-ROM or website Screen 19.4 Entropy, to view animations of the relationship of entropy and molecular state or molecular properties.)*

A Closer Look

Reversible and Irreversible Processes

To determine the entropy change experimentally, the heat transfer must be measured for a reversible process. But what is a reversible process, and why is this constraint important in this discussion?

The melting of ice/freezing of water at 0 °C is an example of a reversible process. Given a mixture of ice and water at equilibrium, adding heat in small increments will convert ice to water; removing heat in small increments will convert water back to ice. The test for reversibility is that after carrying out a change along a given path (in this instance, heat added), it must be possible to return to the starting point by the same path (heat taken away) without altering the surroundings.

Reversibility is closely associated with equilibrium. Assume that we have a system at equilibrium. Changes can then be made by slightly perturbing the equilibrium and letting the system readjust. Melting (or freezing) water is carried out by adding (or removing) heat in small increments.

Spontaneous processes are not reversible: The process occurs in one direction. Suppose a gas is allowed to expand into a vacuum, which is clearly a spontaneous process (Figure 19.1). No work is done in this process because no force resists this expansion. To return the system to its original state, it will be necessary to compress the gas, but doing so means doing work on the system. In this process, the energy content of the surroundings will decrease by the amount of work expended by the surroundings. The system can be restored to its original state, but the surroundings will be altered in the process.

In summary, there are two important points concerning reversibility:

- At every step along a reversible pathway between two states, the system remains at equilibrium.
- Spontaneous processes follow irreversible pathways and involve nonequilibrium conditions.

To determine the entropy change for a process, it is necessary to identify a reversible pathway. Only then can an entropy change for the process be calculated from the measured heat change for the process, q_{rev}, and the temperature at which it occurs.

- For a given substance, entropy increases as the temperature is raised. Large increases in entropy accompany changes of state (Figure 19.10).

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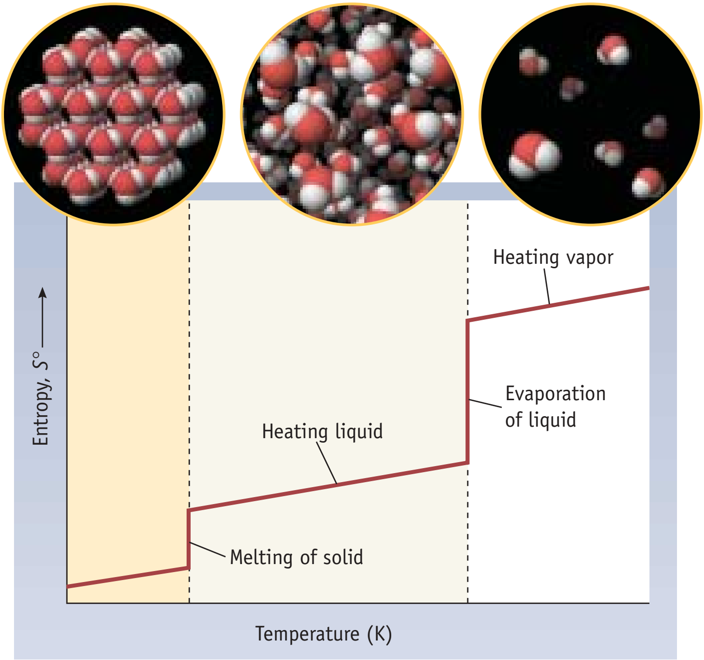
See the General ChemistryNow CD-ROM or website:

- **Screen 19.4 Entropy: Matter Dispersal and Disorder,** to view animations of the effects of molecular properties on entropy

Figure 19.10 **Entropy and temperature.** For each of the three states of matter, entropy increases with increasing temperature. An especially large increase in entropy accompanies a phase change from a solid to a liquid to a gas.



Problem-Solving Tip 19.2

Summary of Common Entropy-Favored Processes

The discussion to this point, along with the examples and exercises, allows the listing of several general principles involving entropy changes:

- A substance becomes increasingly disordered going from a solid to a liquid to a gas. Significant increases in entropy correspond to these phase changes.
- Entropy of any substance increases with temperature (Figure 19.10). Heat must be added to a system to increase its temperature (that is, $q > 0$), so q_{rev}/T is necessarily positive.
- Entropy of a gas increases with an increase in volume. A larger volume provides a larger number of energy levels over which to disperse energy.
- Reactions that increase the number of moles of gases in a system are accompanied by an increase in entropy.

Example 19.1—Entropy Comparisons

Problem Which substance has the higher entropy under standard conditions? Explain your reasoning. Check your answer against data in Appendix L.

(a) NO_2(g) or N_2O_4(g)

(b) I_2(g) or I_2(s)

Strategy Use the general guidelines on entropy listed in the text: Entropy decreases in the order gas > liquid > solid; larger molecules have greater entropy than smaller molecules.

Solution

(a) Both NO_2 and N_2O_4 are gases. Dinitrogen tetraoxide, N_2O_4, the larger molecule, is expected to have the higher standard entropy. $S°$ values (Appendix L) confirm this prediction: $S°$ for NO_2(g) is 240.04 J/K · mol; $S°$ for N_2O_4(g) is 304.38 J/K · mol.

(b) Gases have higher entropies than solids. $S°$ for I_2(g) is 260.69 J/K · mol; $S°$ for I_2(s) is 116.135 J/K · mol

Comment A prediction is a useful check on your numerical result. If an error is inadvertently made, then the prediction will alert you to reconsider your work.

Exercise 19.1—Entropy Comparisons

Predict which substance has the higher entropy and explain your reasoning.

(a) O_2(g) or O_3(g)

(b) $SnCl_4(\ell)$ or $SnCl_4$(g)

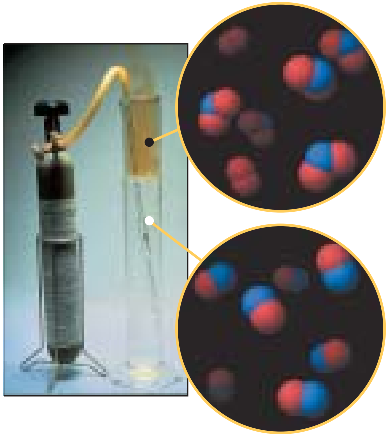
Entropy Changes in Physical and Chemical Processes

The entropy changes ($\Delta S°$) for chemical and physical changes under standard conditions can be calculated from values of $S°$. The procedure used to calculate $\Delta S°$ is similar to that used to obtain values of $\Delta H°$ [◀ Equation 6.6]. The entropy change is the sum of the entropies of the products minus the sum of the entropies of reactants:

$$\Delta S°_{system} = \sum S°(\text{products}) - \sum S°(\text{reactants}) \tag{19.2}$$

To illustrate, let us calculate $\Delta S°_{rxn}$ ($=\Delta S°_{system}$) for the oxidation of NO with O_2.

$$2\ NO(g) + O_2(g) \longrightarrow 2\ NO_2(g)$$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The reaction of NO with O_2. The entropy of the system decreases when two molecules of gas are produced from three molecules of gas.

Here we subtract the entropies of the reactants (2 mol NO and 1 mol O_2) from the entropy of the products (2 mol NO_2).

$$\begin{aligned}\Delta S^\circ_{rxn} &= (2\text{ mol }NO_2)(240.0\text{ J/K}\cdot\text{mol})\\ &\qquad - [(2\text{ mol NO})(210.8\text{ J/K mol}) + (1\text{ mol }O_2)(205.1\text{ J/K}\cdot\text{mol})]\\ &= -146.7\text{ J/K}^{-1}\end{aligned}$$

or -73.35 J/K for 1 mol of NO_2 formed. Notice that the entropy of the system decreases, as predicted for a reaction that converts three molecules of gas into two molecules of another gas.

GENERAL **ChemistryNow™**

See the General ChemistryNow CD-ROM or website:

- **Screen 19.5 Calculating ΔS for a Chemical Reaction,** for a tutorial

Example 19.2—Predicting and Calculating ΔS°

Problem Calculate the standard entropy changes for the following processes. Do the calculations match prediction?

(a) Evaporation of 1.00 mol of liquid ethanol to ethanol vapor

$$C_2H_5OH(\ell) \longrightarrow C_2H_5OH(g)$$

(b) Oxidation of 1 mol of ethanol vapor

$$C_2H_5OH(g) + 3\ O_2(g) \longrightarrow 2\ CO_2(g) + 3\ H_2O(g)$$

Strategy Entropy changes are calculated from values of standard entropies (Appendix L) using Equation 19.2. Predictions are made using the guidelines given in the text: Entropy increases going from solid to liquid to gas (see Figure 19.10), and entropy increases in a chemical reaction if there is an increase in the number of moles of gases in the system.

Solution

(a) Evaporating ethanol

$$\begin{aligned}\Delta S^\circ &= \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants})\\ &= S^\circ[C_2H_5OH(g)] - S^\circ[C_2H_5OH(\ell)]\\ &= 1\text{ mol }(282.70\text{ J/K}\cdot\text{mol}) - 1\text{ mol }(160.7\text{ J/K}\cdot\text{mol})\\ &= +\ 122.0\text{ J/K}\end{aligned}$$

The large positive value for the entropy change is expected because the process converts ethanol from a more ordered state (liquid) to a less ordered state (vapor).

(b) Oxidation of ethanol vapor

$$\begin{aligned}\Delta S^\circ &= 2\ S^\circ[CO_2(g)] + 3\ S^\circ[H_2O(g)] - \{S^\circ[C_2H_5OH(g)] + 3\ S^\circ[O_2(g)]\}\\ &= 2\text{ mol }(213.74\text{ J/K}\cdot\text{mol}) + 3\text{ mol }(188.84\text{ J/K}\cdot\text{mol})\\ &\qquad - \{1\text{ mol }(282.70\text{ J/K}\cdot\text{mol}) + 3\text{ mol }(205.07\text{ J/K}\cdot\text{mol})\}\\ &= +\ 96.09\text{ J/K}\end{aligned}$$

An increase in entropy is predicted for this reaction because the number of moles of gases increases from four to five.

Comment Values of entropies in tables are based on 1 mol of the compound. In part (b), the number of moles of reactants and products is defined by the stoichiometric coefficients in the balanced chemical equation.

Exercise 19.2—Calculating $\Delta S°$

Calculate the standard entropy changes for the following processes using the entropy values in Appendix L. Do the calculated values of $\Delta S°$ match predictions?

(a) Dissolving 1 mol of $NH_4Cl(s)$ in water: $NH_4Cl(s) \longrightarrow NH_4Cl(aq)$
(b) Forming 2.0 mol of $NH_3(g)$ from $N_2(g)$ and $H_2(g)$: $N_2(g) + 3\ H_2(g) \longrightarrow 2\ NH_3(g)$

■ **Spontaneity and the Second Law** Spontaneous change is always accompanied by an increase in entropy in the universe. This is in contrast to enthalpy and internal energy. According to the first law, the energy contained in the universe is constant.

19.5—Entropy Changes and Spontaneity

Which processes are spontaneous, and how is spontaneity predicted? Entropy is the basis for this determination. But how can it be useful when, as you have seen earlier, the entropy of a system may either decrease (oxidation of NO) or increase (evaporation and oxidation of ethanol). The second law of thermodynamics provides an answer. The **second law of thermodynamics** states that *a spontaneous process is one that results in an increase of entropy in the universe.* This criterion requires assessing entropy changes in both the system under study and the surroundings.

At first glance, the statement of the second law may seem curious. Ordinarily our thinking is not so expansive as to consider the whole universe; we think mainly about a given system. Recall that the term "system" is defined as "that part of the universe being studied." As we continue, however, it will become apparent that this view is not so complicated as it might first sound.

The "universe" (= univ) has two parts: the system (= sys) and its surroundings (= surr) [◀ Section 6.1]. The entropy change for the universe is the sum of the entropy changes for the system and the surroundings:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \tag{19.3}$$

The second law states that ΔS_{univ} is positive for a spontaneous process. Conversely, a negative value of ΔS_{univ} means the process cannot be spontaneous as written. If $\Delta S_{\text{univ}} = 0$, the system is at equilibrium.

A similar equation can be written for the entropy change for a process under standard conditions:

$$\Delta S°_{\text{univ}} = \Delta S°_{\text{sys}} + \Delta S°_{\text{surr}} \tag{19.4}$$

■ **Using $\Delta S°$universe**
For a spontaneous process:
$\Delta S°_{\text{univ}} > 0$
For a system at equilibrium:
$\Delta S°_{\text{univ}} = 0$
For a nonspontaneous process:
$\Delta S°_{\text{univ}} < 0$

The value of $\Delta S°_{\text{univ}}$ represents the entropy change for a process in which all of the reactants and products are in their standard states.

The standard entropy change for a chemical reaction can be calculated from standard entropy values found in tables such as Appendix L. The value of $\Delta S°_{\text{univ}}$ calculated in this way is the entropy change when reactants are converted *completely* to products, with all species at standard conditions. The sign of $\Delta S°_{\text{univ}}$ carries with it the same connotation concerning spontaneity as ΔS_{univ}.

As an example of the calculation of $\Delta S°_{\text{univ}}$, consider the reaction currently used to manufacture methanol, CH_3OH.

$$CO(g) + 2\ H_2(g) \longrightarrow CH_3OH(\ell)$$

If the change in entropy for the universe is positive, the conversion of 1 mol of CO and 2 mol of H_2 to 1 mol of CH_3OH will be spontaneous under standard conditions.

Calculating ΔS°_{sys}, the Entropy Change for the System

To calculate ΔS°_{sys}, we start by defining the system to include the reactants and products. This means that dispersal of matter in this process occurs entirely within the system. That is, to evaluate the entropy change for matter dispersal, we need to look only at ΔS°_{sys}. Calculation of the entropy change follows the procedure given in Example 19.2.

$$\begin{aligned}\Delta S^\circ_{sys} &= \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants})\\ &= S^\circ[\text{CH}_3\text{OH}(\ell)] - \{S^\circ[\text{CO(g)}] + 2\ S^\circ[\text{H}_2\text{(g)}]\}\\ &= (1\ \text{mol})(127.2\ \text{J/K}\cdot\text{mol}) - \{(1\ \text{mol})(197.7\ \text{J/K mol}) + (2\ \text{mol})(130.7\ \text{J/K}\cdot\text{mol})\}\\ &= -331.9\ \text{J/K}\end{aligned}$$

A decrease in entropy for the system is expected because three moles of gaseous reactants are converted to one mole of a liquid product.

Calculating ΔS°_{surr}, the Entropy Change for the Surroundings

The entropy change resulting from the dispersal of energy produced in this exothermic chemical reaction is evaluated from the enthalpy change for the reaction. The heat evolved in this reaction is transferred to the surroundings, so $q_{surr} = -\Delta H^\circ_{sys}$, and

$$\Delta S^\circ_{surr} = \frac{q_{surr}}{T} = -\frac{\Delta H^\circ_{sys}}{T}$$

According to this equation, an exothermic reaction ($\Delta H^\circ_{sys} < 0$) is accompanied by an increase in entropy in the surroundings. For the synthesis of methanol, the enthalpy change is −127.9 kJ.

$$\begin{aligned}\Delta H^\circ_{sys} &= \sum \Delta H^\circ_f(\text{products}) - \sum \Delta H^\circ_f(\text{reactants})\\ &= \Delta H^\circ_f[\text{CH}_3\text{OH}(\ell)] - \{\Delta H^\circ_f[\text{CO(g)}] + 2\ \Delta H^\circ_f[\text{H}_2\text{(g)}]\}\\ &= (1\ \text{mol})(-238.4\ \text{kJ/mol}) - \{(1\ \text{mol})(-110.5\ \text{kJ/mol}) + (2\ \text{mol})(0)\}\\ &= -127.9\ \text{kJ}\end{aligned}$$

Therefore, if we make the simplifying assumption that the process is reversible and occurs at a constant temperature, the entropy change for the surroundings in the methanol synthesis is +429.2 J/K.

$$\Delta S^\circ_{surr} = -\frac{\Delta H^\circ_{sys}}{T} = -\frac{-127.9\ \text{kJ}}{298\ \text{K}}(1000\ \text{J/kJ}) = +429.2\ \text{J/K}$$

Calculating ΔS°_{univ}, the Total Entropy Change for the System and Surroundings

The pieces are now in place to calculate the entropy change in the universe. For the formation of $CH_3OH(\ell)$ from CO(g) and $H_2(g)$, ΔS°_{univ} is

$$\begin{aligned}\Delta S^\circ_{univ} &= \Delta S^\circ_{sys} + \Delta S^\circ_{surr}\\ &= -331.9\ \text{J/K} + 429.2\ \text{J/K}\\ &= +97.3\ \text{J/K}\end{aligned}$$

The positive value indicates an increase in the entropy of the universe. It follows from the second law of thermodynamics that this reaction is spontaneous.

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See the General ChemistryNow CD-ROM or website:

- **Screen 19.6 The Second Law of Thermodynamics,** for a simulation and tutorial to explore entropy changes in reactions

Example 19.3—Determining whether a Process Is Spontaneous

Problem Show that ΔS°_{univ} is positive (> 0) for dissolving NaCl in water.

Strategy The problem is divided into two parts: determining ΔS°_{sys} and determining ΔS°_{surr} (calculated from ΔH° for the process). The sum of these two entropy changes is ΔS°_{univ}. Values of ΔH°_f and S° for NaCl(s) and NaCl(aq) are obtained from Appendix L.

Solution The process occurring is $\text{NaCl(s)} \longrightarrow \text{NaCl(aq)}$. Its entropy change, ΔS°_{sys}, can be calculated from values of S° for the two species using Equation 19.2. The calculation is based on 1 mol of NaCl.

$$\begin{aligned}\Delta S^\circ_{sys} &= S^\circ[\text{NaCl(aq)}] - S^\circ[\text{NaCl(s)}]\\ &= (1\text{ mol})(115.5\text{ J/K}\cdot\text{mol}) - (1\text{ mol})(72.11\text{ J/K}\cdot\text{mol})\\ &= +43.4\text{ J/K}\end{aligned}$$

The heat of solution is determined from values of ΔH°_f for solid and aqueous sodium chloride. The solution process is slightly endothermic, indicating heat transfer occurs from the surroundings to the system:

$$\begin{aligned}\Delta H^\circ_{sys} &= \Delta H^\circ_f[\text{NaCl(aq)}] - \Delta H^\circ_f[\text{NaCl(s)}]\\ &= (1\text{ mol})(-407.27\text{ kJ/mol}) - (1\text{ mol})(-411.12\text{ kJ/mol})\\ &= +3.85\text{ kJ}\end{aligned}$$

The enthalpy change of the surroundings has the same numerical value but is opposite in sign:

$$q_{surr} = -\Delta H^\circ_{sys} = -3.85\text{ kJ}.$$

The entropy change of the surroundings is determined by dividing q_{surr} by the Kelvin temperature.

$$\Delta S^\circ_{surr} = \frac{q_{surr}}{T} = \frac{-3.85\text{ kJ}}{298\text{ K}}(1000\text{ J/kJ}) = -12.9\text{ J/K}$$

We see that ΔS°_{surr} has a negative sign. Heat was transferred from the surroundings to the system in this endothermic process.

The overall entropy change—the change of entropy in the universe—is the sum of the values for the system and the surroundings.

$$\Delta S^\circ_{univ} = \Delta S^\circ_{sys} + \Delta S^\circ_{surr} = (+43.4\text{ J/K}) + (-12.9\text{ J/K}) = 30.5\text{ J/K}$$

Comment The sum of the two entropy quantities is positive, indicating that, overall, entropy in the universe increases. Dissolving NaCl is product-favored. Notice that the process is favored based on dispersal of matter ($\Delta S^\circ_{sys} > 0$) and disfavored based on dispersal of energy ($\Delta S^\circ_{surr} < 0$).

In Summary: Spontaneous or Not?

In the preceding examples, predictions were made using values of ΔS°_{sys} and ΔH°_{sys} calculated from tables of thermodynamic data. It will be useful to look at the possibilities that result from the interplay of these two quantities. There are four possible

Table 19.2 Predicting Whether a Process Will Be Spontaneous

Type	ΔH°_{sys}	ΔS°_{sys}	Spontaneous Process?
1	Exothermic process $\Delta H^\circ_{sys} < 0$	Less order $\Delta S^\circ_{sys} > 0$	Spontaneous under all conditions $\Delta S^\circ_{univ} > 0$.
2	Exothermic process $\Delta H^\circ_{sys} < 0$	more order $\Delta S^\circ_{sys} < 0$	Depends on relative magnitudes of ΔH and ΔS. More favorable at *lower* temperatures.
3	Endothermic process $\Delta H^\circ_{sys} > 0$	Less order $\Delta S^\circ_{sys} > 0$	Depends on relative magnitudes of ΔH and ΔS. More favorable at *higher* temperatures.
4	Endothermic process $\Delta H^\circ_{sys} > 0$	More order $\Delta S^\circ_{sys} < 0$	Not spontaneous under any conditions $\Delta S^\circ_{univ} < 0$

outcomes when these two quantities are matched (Table 19.2). In two, ΔH°_{sys} and ΔS°_{sys} work in concert (Types 1 and 4 in Table 19.2). In the other two, the two quantities are opposed (Types 2 and 3).

Processes in which both enthalpy and entropy favor energy dispersal (Type 1) are always spontaneous. Processes disfavored by both enthalpy and entropy (Type 4) can never be spontaneous. Let us consider examples that illustrate each situation.

Combustion reactions are always exothermic and often produce a larger number of product molecules from a few reactant molecules. They are Type 1 reactions. The equation for the combustion of butane is an example.

$$2\ C_4H_{10}(g) + 13\ O_2(g) \longrightarrow 8\ CO_2(g) + 10\ H_2O(g)$$

For this reaction $\Delta H^\circ = -5315.1$ kJ and $\Delta S^\circ = 312.4$ J/K. Both values indicate that this reaction, like all combustion reactions, is spontaneous.

Hydrazine, N_2H_4, is used as a high-energy rocket fuel. Synthesis of N_2H_4 from gaseous N_2 and H_2 would be attractive because these reactants are inexpensive.

$$N_2(g) + 2\ H_2(g) \longrightarrow N_2H_4(\ell)$$

However, this reaction fits into the Type 4 category. The reaction is endothermic ($\Delta H^\circ = +50.63$ kJ/mol), and the entropy change ΔS° is negative ($\Delta S^\circ = -331.4$ J/K (1 mol of liquid is produced from 3 mol of gases).

In the two other possible outcomes, entropy and enthalpy changes oppose each other. A process could be favored by the enthalpy change but disfavored by the entropy change (Type 2), or vice versa (Type 3). In either instance, whether a process is spontaneous depends on which factor is more important.

Temperature also influences the value of ΔS°_{univ} because ΔS°_{surr} (the dispersal of energy) varies with temperature. Because the enthalpy change for the surroundings is divided by the temperature to obtain ΔS°_{surr}, the numerical value of ΔS°_{surr} is smaller (either less positive or less negative) at higher temperatures. In contrast, ΔS°_{sys} does not depend on temperature. Thus, the effect of ΔS°_{surr} relative to ΔS°_{sys} diminishes at higher temperature. Stated another way, at higher temperatures the enthalpy change becomes less of a factor relative to the entropy change. Consider the two cases where ΔH°_{sys} and ΔS°_{sys} are in opposition (Table 19.2):

- Type 2: *Exothermic processes that are entropy-disfavored.* Such processes become less favorable with an increase in temperature.
- Type 3: *Endothermic processes that are entropy-favored.* These processes become more favorable as the temperature increases.

The effect of temperature is illustrated by two examples. The first is the reaction of N_2 and H_2 to form NH_3, one of the most important industrial chemical processes. The reaction is exothermic; that is, it is favored by energy dispersal. The entropy change for the system is unfavorable, however, because the reaction, $N_2(g) + 3\ H_2(g) \longrightarrow 2\ NH_3(g)$, converts four moles of gaseous reactants to two moles of gaseous products. To maximize the yield of ammonia, the lowest possible temperature should be used [◀ Section 16.7].

The second example considers the thermal decomposition of NH_4Cl (Figure 19.11). At room temperature, NH_4Cl is a stable, white, crystalline salt. When heated strongly, it decomposes to $NH_3(g)$ and $HCl(g)$. The reaction is endothermic (enthalpy-disfavored) but entropy-favored because of the formation of two moles of gas from one mole of a solid reactant.

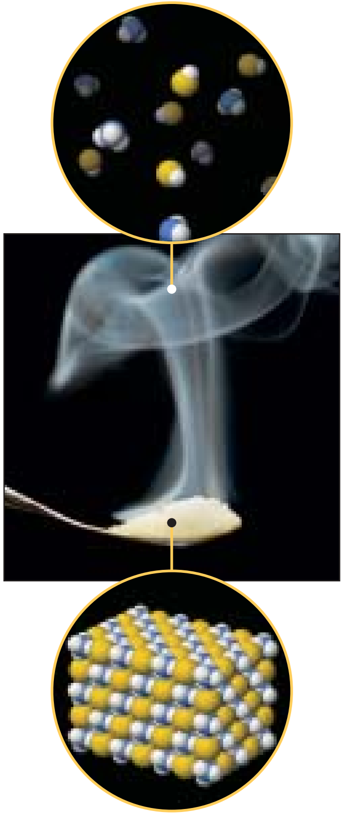

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Figure 19.11 Thermal decomposition of $NH_4Cl(s)$. White, solid ammonium chloride is heated in a spoon. At high temperatures, $NH_4Cl(s)$ decomposes to $NH_3(g)$ and $HCl(g)$ in a spontaneous reaction. At lower temperatures, the reverse reaction, forming $NH_4Cl(s)$, is spontaneous. As $HCl(g)$ and $NH_3(g)$ above the heated solid cool, they recombine to form solid NH_4Cl, the white "smoke" seen in this photo.

Exercise 19.3—Is a Reaction Spontaneous?

Classify the following reactions as one of the four types of reactions summarized in Table 19.2.

Reaction	ΔH°_{rxn} (at 298 K) (kJ)	ΔS°_{sys} (at 298 K) (J/K)
(a) $CH_4(g) + 2\ O_2(g) \longrightarrow 2\ H_2O(\ell) + CO_2(g)$	−890.6	−242.8
(b) $2\ Fe_2O_3(s) + 3\ C(graphite) \longrightarrow 4\ Fe(s) + 3\ CO_2(g)$	+467.9	+560.7
(c) $C(graphite) + O_2(g) \longrightarrow CO_2(g)$	−393.5	+3.1
(d) $N_2(g) + 3\ F_2(g) \longrightarrow 2\ NF_3(g)$	−264.2	−277.8

Exercise 19.4—Is a Reaction Spontaneous?

Is the direct reaction of hydrogen and chlorine to give hydrogen chloride gas predicted to be spontaneous?

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

Answer the question by calculating the values for ΔS°_{sys} and ΔS°_{surr} (at 298 K) and then summing them to determine ΔS°_{univ}.

Exercise 19.5—Effect of Temperature on Spontaneity

Iron is produced in a blast furnace by reducing iron oxide using carbon. For this reaction, $2\ Fe_2O_3(s) + 3\ C(graphite) \longrightarrow 4\ Fe(s) + 3\ CO_2(g)$, the following parameters are determined: $\Delta H^\circ_{rxn} = +467.9$ kJ and $\Delta S^\circ_{rxn} = +560.7$ J/K. Show that it is necessary that this reaction be carried out at a high temperature.

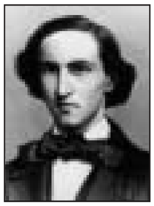
Courtesy of Bethlehem Steel

A reaction requiring a higher temperature so that ΔS°_{univ} is positive. Iron is obtained in a blast furnace by heating iron ore and coke (carbon). See Exercise 19.5.

19.6—Gibbs Free Energy

The method used so far to determine whether a process is spontaneous required evaluation of two quantities, ΔS°_{sys} and ΔS°_{surr}. Wouldn't it be convenient to have a single thermodynamic function that serves the same purpose? A function associated with a system only—one that does not require assessment of the surroundings—would be even better. In fact, such a function exists. It is called Gibbs free energy, with the name honoring J. Willard Gibbs (1839–1903). **Gibbs free energy**, ***G***, often referred to simply as "free energy," is defined mathematically as

$$G = H - TS$$



J. Willard Gibbs (1839–1903) Gibbs received a Ph.D. from Yale University in 1863. His was the first Ph.D. in science awarded from an American university.

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where H is enthalpy, T is the Kelvin temperature, and S is entropy. In this equation, G, H, and S all refer to a system. Because enthalpy and entropy are state functions [◀ Section 6.4], free energy is also a state function.

Every substance possesses a specific quantity of free energy. The actual quantity of free energy is seldom known, however, or even of interest. Instead, we are concerned with *changes* in free energy, ΔG, in the course of a chemical or physical process. We do not need to know the free energy of a substance to determine ΔG. In this sense, free energy and enthalpy are similar. A substance possesses some amount of enthalpy, but we do not have to know what the actual value of H is to obtain or use ΔH.

Let us see first how to use free energy as a way to determine whether a reaction is spontaneous. We can then ask further questions about the meaning of the term "free" energy and its use in deciding whether a reaction is product- or reactant-favored.

$\Delta G°$ and Spontaneity

Recall the equation defining the entropy change for the universe (Equation 19.3):

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

On page 918 we noted that the entropy change of the surroundings equals the negative of the change in enthalpy of the system divided by T. Thus

$$\Delta S_{\text{univ}} = (-\Delta H_{\text{sys}}/T) + \Delta S_{\text{sys}}$$

Multiplying through this equation by $-T$, we have

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

Gibbs defined the free energy function so that

$$\Delta G_{\text{sys}} = -T\Delta S_{\text{univ}}$$

Therefore, we have

$$\Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$$

The connection between ΔG_{rxn} ($= \Delta G_{\text{sys}}$) and spontaneity is the following:

- If $\Delta G_{\text{rxn}} < 0$, a reaction is spontaneous.
- If $\Delta G_{\text{rxn}} = 0$, the reaction is at equilibrium with $K = 1$.
- If $\Delta G_{\text{rxn}} > 0$, the reaction is not spontaneous.

The free energy change can also be defined under standard conditions.

$$\Delta G°_{\text{sys}} = \Delta H°_{\text{sys}} - T\Delta S°_{\text{sys}} \quad (19.5)$$

$\Delta G°_{\text{sys}}$ is generally used as a criterion of reaction spontaneity, and, as you shall see, *it is directly related to the value of the equilibrium constant and hence to product favorability.*

What Is "Free" Energy?

The term "free energy" was not arbitrarily chosen. In any given process, *the free energy represents the maximum energy available to do useful work* (or, mathematically, $\Delta G = w_{\text{max}}$). In this context, the word "free" means "available."

To illustrate the reasoning behind this relationship, consider a reaction in which heat is evolved ($\Delta H_{\mathrm{rxn}} < 0$) and entropy decreases ($\Delta S_{\mathrm{rxn}} < 0$).

$$\mathrm{C(graphite)} + 2\ \mathrm{H_2(g)} \longrightarrow \mathrm{CH_4(g)}$$
$$\Delta H^\circ_{\mathrm{rxn}} = -74.9\ \mathrm{kJ} \quad \text{and} \quad \Delta S^\circ_{\mathrm{rxn}} = -80.7\ \mathrm{J/K}$$
$$\Delta G^\circ_{\mathrm{rxn}} = -50.8\ \mathrm{kJ}$$

At first glance, it might seem that all the energy available from the reaction could be transferred to the surroundings and would thus be available to do work, but this is not the case. The negative entropy change means that the system is becoming more ordered. A portion of the energy from the reaction was used to create this more ordered system, so this energy is not available to do work. The energy left over is "free," or available, to do work. Here that free energy amounts to 50.8 kJ, as shown in Example 19.4.

The analysis of the enthalpy and entropy changes for the carbon and hydrogen reaction applies to any combination of ΔH° and ΔS°. The "free" energy is the sum of the energies available from dispersal of energy and matter. In a process that is favored by both the enthalpy and entropy changes, the free energy available exceeds what is available based on enthalpy alone.

Calculating $\Delta G^\circ_{\mathrm{rxn}}$, the Free Energy Change for a Reaction

Enthalpy and entropy changes at standard conditions can be calculated for chemical reactions using values of ΔH°_f and S° for substances in the reaction. Then, $\Delta G^\circ_{\mathrm{rxn}}$ ($= \Delta G^\circ_{\mathrm{sys}}$) can be found from the resulting values of $\Delta H^\circ_{\mathrm{rxn}}$ and $\Delta S^\circ_{\mathrm{rxn}}$ using Equation 19.5, as illustrated in the following example and exercise.

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See the General ChemistryNow CD-ROM or website:

- **Screen 19.7 Gibbs Free Energy,** for tutorials on calculating $\Delta G^\circ_{\mathrm{rxn}}$

Example 19.4—Calculating $\Delta G^\circ_{\mathrm{rxn}}$ from $\Delta H^\circ_{\mathrm{rxn}}$ and $\Delta S^\circ_{\mathrm{rxn}}$

Problem Calculate the standard free energy change, ΔG°, for the formation of methane at 298 K:

$$\mathrm{C(graphite)} + 2\ \mathrm{H_2(g)} \longrightarrow \mathrm{CH_4(g)}$$

Strategy Values for ΔH°_f and S° are provided in Appendix L. These are first combined to find $\Delta H^\circ_{\mathrm{rxn}}$ and $\Delta S^\circ_{\mathrm{rxn}}$. With these values known, $\Delta G^\circ_{\mathrm{rxn}}$ can be calculated using Equation 19.5. When doing so, recall that S° values in tables are given in units of J/K · mol, whereas ΔH° values are given in units of kJ/mol.

Solution

	C(graphite)	H_2(g)	CH_4(g)
ΔH°_f (kJ/mol)	0	0	−74.9
S° (J/K · mol)	+5.6	+130.7	+186.3

From these values, we can find both $\Delta H°$ and $\Delta S°$ for the reaction:

$$\begin{aligned}\Delta H°_{rxn} &= \Delta H°_f[CH_4(g)] - \{\Delta H°_f[C(graphite)] + 2\Delta H°_f[H_2(g)]\}\\ &= -74.9 \text{ kJ} - (0 + 0)\\ &= -74.9 \text{ kJ}\end{aligned}$$

$$\begin{aligned}\Delta S°_{rxn} &= S°[CH_4(g)] - \{S°[C(graphite)] + 2S°[H_2(g)]\}\\ &= (1 \text{ mol})186.3 \text{ J/K} \cdot \text{mol} - [(1 \text{ mol})(5.6 \text{ J/K} \cdot \text{mol}) + (2 \text{ mol})(130.7 \text{ J/K} \cdot \text{mol})]\\ &= -80.7 \text{ J/K}\end{aligned}$$

Both the enthalpy change and the entropy change for this reaction are negative. In this case, the reaction is predicted to be spontaneous at "low temperature" (see Table 19.2). These values alone do not tell us whether the temperature is low enough, however. By combining them in the Gibbs free energy equation, and calculating $\Delta G°_{rxn}$ for a temperature of 298 K, we can predict with certainty the outcome of the reaction.

$$\begin{aligned}\Delta G°_{rxn} &= \Delta H°_{rxn} - T\Delta S°_{rxn}\\ &= -74.9 \text{ kJ} - (298 \text{ K})(-80.7 \text{ J/K})(1 \text{ kJ/1000 J})\\ &= -74.9 \text{ kJ} - (-24.1 \text{ kJ})\\ &= -50.8 \text{ kJ}\end{aligned}$$

$\Delta G°_{rxn}$ is negative at 298 K, so the reaction is predicted to be spontaneous.

Comment In this case the product $T\Delta S°$ is negative and smaller than $\Delta H°_{rxn}$ because the entropy change is relatively small. Chemists call this situation an "enthalpy-driven reaction" because the exothermic nature of the reaction overcomes the decrease in entropy of the system.

Exercise 19.6—Calculating $\Delta G°_{rxn}$ from $\Delta H°_{rxn}$ and $\Delta S°_{rxn}$

Using values of $\Delta H°_f$ and $S°$ to find $\Delta H°_{rxn}$ and $\Delta S°_{rxn}$, respectively, calculate the free energy change, $\Delta G°$, for the formation of 2 mol of $NH_3(g)$ from the elements at standard conditions (and 25 °C): $N_2(g) + 3\ H_2(g) \longrightarrow 2\ NH_3(g)$.

Standard Free Energy of Formation

The **standard free energy of formation** of a compound, $\Delta G°_f$, is the free energy change when forming one mole of the compound from the component elements, with products and reactants in their standard states. By defining $\Delta G°_f$ in this way, *the free energy of formation of an element in its standard states is zero* (Table 19.3).

Table 19.3 Standard Molar Free Energies of Formation of Some Substances at 298 K

Element/Compound	$\Delta G°_f$ (kJ/mol)	Element/Compound	$\Delta G°_f$ (kJ/mol)
$H_2(g)$	0	$CO_2(g)$	−394.4
$O_2(g)$	0	$CH_4(g)$	−50.8
$N_2(g)$	0	$H_2O(g)$	−228.6
C(graphite)	0	$H_2O(\ell)$	−237.2
C(diamond)	2.900	$NH_3(g)$	−16.4
CO(g)	−137.2	$Fe_2O_3(s)$	−742.2

Just as the standard enthalpy change for a reaction can be calculated using values of ΔH_f°, the standard free energy change for a reaction can be calculated from values of ΔG_f°:

$$\Delta G^\circ = \sum \Delta G_f^\circ(\text{products}) - \sum \Delta G_f^\circ(\text{reactants}) \tag{19.6}$$

Example 19.5—Calculating $\Delta G^\circ_{\text{rxn}}$ from ΔG_f°

Problem Calculate the standard free energy change for the combustion of one mole of methane from the standard free energies of formation of the products and reactants.

Strategy Use Equation 19.6 with values obtained from Table 19.3 or Appendix L.

Solution First, write a balanced equation for the reaction. Then, find values of ΔG_f° for each reactant and product (in Appendix L).

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

	$CH_4(g)$	$2\,O_2(g)$	$2\,H_2O(g)$	$CO_2(g)$
ΔG_f° (kJ/mol)	−50.8	0	−228.6	−394.4

Because ΔG_f° values are given for 1 mol of each substance (the units are kJ/mol), each value of ΔG_f° must be multiplied by the number of moles defined by the stoichiometric coefficient in the balanced chemical equation.

$$\begin{aligned}\Delta G^\circ_{\text{rxn}} &= 2\Delta G_f^\circ[H_2O(g)] + \Delta G_f^\circ[CO_2(g)] - \{\Delta G_f^\circ[CH_4(g)] + 2\Delta G_f^\circ[O_2(g)]\}\\ &= (2\text{ mol})(-228.6\text{ kJ/mol}) + (1\text{ mol})(-394.4\text{ kJ/mol})\\ &\qquad - [(1\text{ mol})(-50.8\text{ kJ/mol}) + (2\text{ mol})(0\text{ kJ/mol})]\\ &= -801.0\text{ kJ}\end{aligned}$$

The large negative value of $\Delta G^\circ_{\text{rxn}}$ indicates that the reaction is spontaneous under standard conditions.

Comment The most common errors made by students in this calculation are (1) ignoring the stoichiometric coefficients in the equation and (2) confusing the signs for the terms when using Equation 19.6.

Exercise 19.7—Calculating $\Delta G^\circ_{\text{rxn}}$ From ΔG_f°

Calculate the standard free energy change for the oxidation of 1.00 mol of $SO_2(g)$ to form $SO_3(g)$.

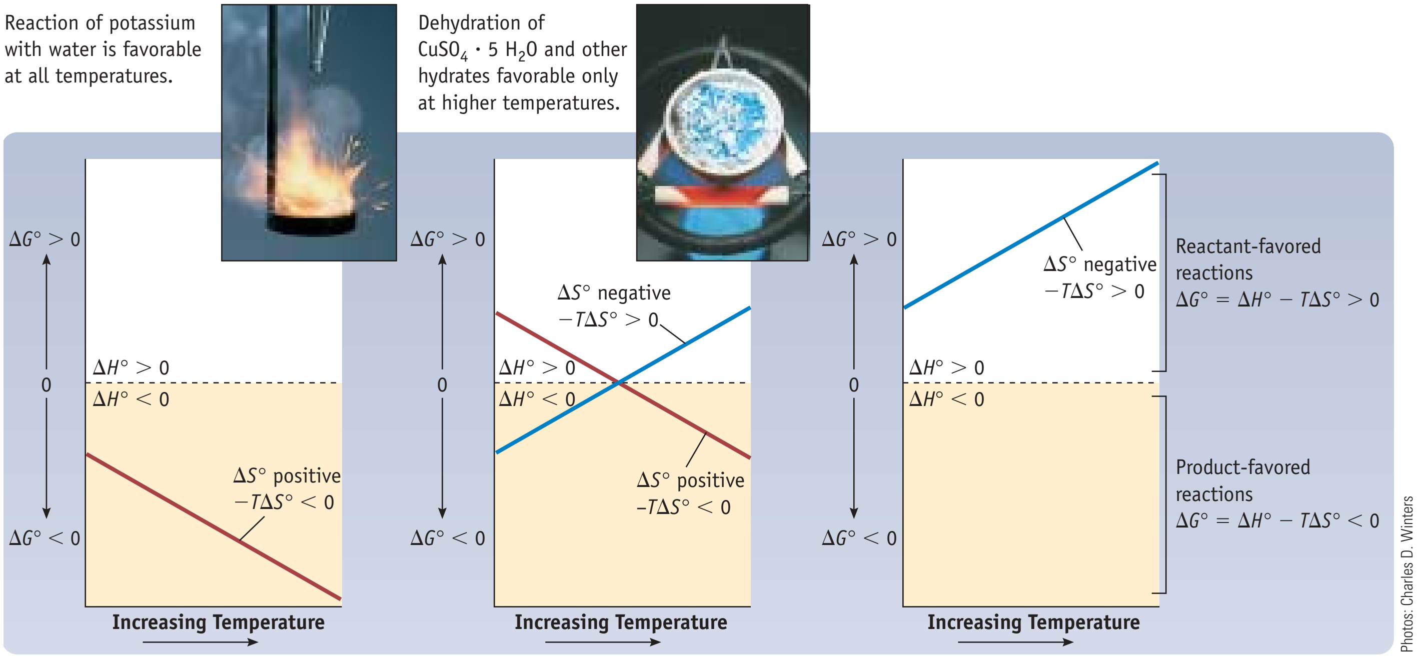
Free Energy and Temperature

The definition for free energy, $G = H - TS$, states that free energy is a function of temperature, so ΔG will change as the temperature changes (Figure 19.12).

A consequence of this dependence on temperature is that, in certain instances, reactions can be spontaneous at one temperature and not spontaneous at another. Those instances arise when the ΔH° and $T\Delta S^\circ$ terms work in opposite directions:

- Processes that are entropy-favored ($\Delta S^\circ > 0$) and enthalpy-disfavored ($\Delta H^\circ > 0$)
- Processes that are enthalpy-favored ($\Delta H^\circ < 0$) and entropy-disfavored ($\Delta S^\circ < 0$)

Let us explore the relationship of ΔG° and T further and illustrate how it can be used to advantage.



$\Delta H° < 0$ and $\Delta S° > 0$. Product-favored at all temperatures.

Blue line: $\Delta H° < 0$ and $\Delta S° < 0$. Favored at low *T*. Red line: $\Delta H° > 0$ and $\Delta S° > 0$. Favored at high *T*.

$\Delta H° > 0$ and $\Delta S° < 0$. Reactant-favored at all temperatures.

Active Figure 19.12 **Changes in $\Delta G°$ with temperature.**

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Calcium carbonate is a common substance. Among other things, it is the primary component of limestone, marble, and seashells. Heating $CaCO_3$ produces lime, CaO, along with gaseous CO_2. The data below are from Appendix L.

	$CaCO_3(s)$	$\longrightarrow$	$CaO(s)$	+	$CO_2(g)$
$\Delta G_f°$ (kJ/mol)	−1129.16		−603.42		−394.36
$\Delta H_f°$ (kJ/mol)	−1207.6		−635.09		−393.51
$S°$ (J/K · mol)	91.7		38.2		213.74

For the conversion of limestone, $CaCO_3(s)$, to lime, CaO(s), $\Delta G°_{rxn} = +131.38$ kJ, $\Delta H°_{rxn} = +179.0$ kJ, and $\Delta S°_{rxn} = +160.2$ kJ/K. Although the reaction is entropy-favored, the large positive and unfavorable enthalpy change dominates at this temperature. Thus, the free energy change is positive at 298 K and 1 bar, indicating that overall the reaction is not spontaneous under these conditions.

Although the formation of CaO from $CaCO_3$ is unfavorable at 298 K, the temperature dependence of $\Delta G°$ provides a means to turn it into a product-favored reaction. Notice that the entropy change in the reaction is positive as a result of the formation of CO_2 gas in the reaction. Thus, raising the temperature results in the value of $T\Delta S°$ becoming increasingly large. At a high enough temperature, the effect of $\Delta S°$ will outweigh the enthalpy effect and the process will become favorable.

How high must the temperature be for this reaction to become spontaneous? An estimate of the temperature can be obtained using Equation 19.5. To do this, let us calculate the temperature at which $\Delta G° = 0$. Above that temperature, $\Delta G°$ will have a negative value. (Note that in this calculation the enthalpy must be in joules, not kilojoules, to match the units used in the entropy term. Keeping track of the units will show that the temperature will have the units of kelvins.)

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ\\ 0 &= 179.0\text{ kJ }(1000\text{ J/K}) - T(160.2\text{ J/K})\\ T &= 1117\text{ K (or 844 °C)}\end{aligned}$$

How accurate is this result? As noted earlier, we can obtain only an approximate answer from this calculation. The biggest source of error is the assumption that ΔH° and ΔS° do not vary with temperature, which is not strictly true. There is usually a small variation in these values when the temperature changes—not too important if the temperature range is narrow, but potentially creating a problem over wider temperature ranges. As an estimate, however, a temperature in the 850 °C range for this reaction is reasonable. In fact, the pressure of CO_2 in an equilibrium system $[CaCO_3(s) \longrightarrow CaO(s) + CO_2(g);\ \Delta G^\circ = 0]$ is 1 bar at about 900 °C, very close to our estimated temperature.

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See the General ChemistryNow CD-ROM or website:

- **Screen 19.8 Free Energy and Temperature,** for a simulation and tutorial on the relationship of ΔH°, ΔS°, and T.

Example 19.6—Effect of Temperature on ΔG°

Problem Use thermodynamic parameters to estimate the boiling point of methanol.

Strategy At the boiling point, liquid and gas exist at equilibrium, and the condition for equilibrium is $\Delta G^\circ = 0$. Values of ΔH_f° and S° from Appendix L for the process $CH_3OH(\ell) \longrightarrow CH_3OH(g)$, are used to calculate ΔH° and ΔS°. T is the unknown in Equation 19.5.

Solution Values for ΔG_f°, ΔH_f°, and S° are obtained from Appendix L for CH_3OH liquid and vapor.

	$CH_3OH(\ell)$	$CH_3OH(g)$
ΔG_f° (kJ/mol)	−166.14	−162.5
ΔH_f° (kJ/mol)	−238.4	−201.0
S° (J/K · mol)	+127.19	+239.7

For a process in which 1 mol of liquid is converted to 1 mol of gas, $\Delta G^\circ_{rxn} = +3.6$ kJ, $\Delta H^\circ_{rxn} = +37.4$ kJ, and $\Delta S^\circ_{rxn} = +112.5$ J/K. The process is endothermic (as expected, heat being required to convert a liquid to a gas), and entropy favors the process (the vapor has a higher degree of disorder than the liquid). These two quantities oppose each other. The free energy change per mole for this process under standard conditions is +3.6 kJ. The positive value indicates that this process is not spontaneous under standard conditions (298 K and 1 bar).

If we use the values of ΔH°_{rxn} and ΔS°_{rxn}, along with the criterion that $\Delta G^\circ = 0$ at equilibrium (at the boiling point), we have

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ\\ 0 &= +37{,}400\text{ J} - [T(+112.5\text{ J/K})]\\ T &= 332\text{ K (or 59 °C)}\end{aligned}$$

Comment The calculated boiling temperature is close to the observed value of 65.0 °C.

Exercise 19.8—Effect of Temperature on $\Delta G°$

Oxygen was first prepared by Joseph Priestley (1733–1804), who heated HgO. Use the thermodynamic data in Appendix L to estimate the temperature required to decompose HgO(s) into Hg(ℓ) and O_2(g).

19.7—$\Delta G°$, K, and Product Favorability

The terms *product-favored* and *reactant-favored* were introduced in Chapter 5, and in Chapter 16 we described how these terms are related to the values of equilibrium constants. *Reactions for which K is large are product-favored and those for which K is small are reactant-favored.* We now return to this important topic, to relate the value of the equilibrium constant K_c, and thus the product or reactant favorability, to the standard free energy change, $\Delta G°$, for a chemical reaction.

The standard free energy change for a reaction, $\Delta G°$, is the increase or decrease in free energy as the reactants in their standard states are converted *completely* to the products in their standard states. But complete conversion is not always observed in practice. A product-favored reaction proceeds largely to products, but some reactants may remain when equilibrium is achieved. A reactant-favored reaction proceeds only partially to products before achieving equilibrium.

To discover the relationship of $\Delta G°$ and the equilibrium constant K, let us use Figure 19.13. The free energy of the pure reactants in their standard states is indicated at the left, and the free energy of the pure products in their standard states is at the right. The difference in these values is $\Delta G°$. In this example $\Delta G° = G°_{\text{products}} - G°_{\text{reactants}}$ has a negative value, and the reaction is product-favored.

When the reactants are mixed in a chemical system, the system will proceed spontaneously to a position of lower free energy, and the system will eventually achieve equilibrium. At any point along the way from the pure reactants to equilibrium, the reactants are not at standard conditions. The change in free energy under these nonstandard conditions, ΔG, is related to $\Delta G°$ by the equation

$$\Delta G = \Delta G° + RT \ln Q \qquad (19.7)$$

where R is the universal gas constant, T is the temperature in kelvins, and Q is the reaction quotient [◀ Section 16.2]. Recall that, for the general reaction of A and B giving products C and D,

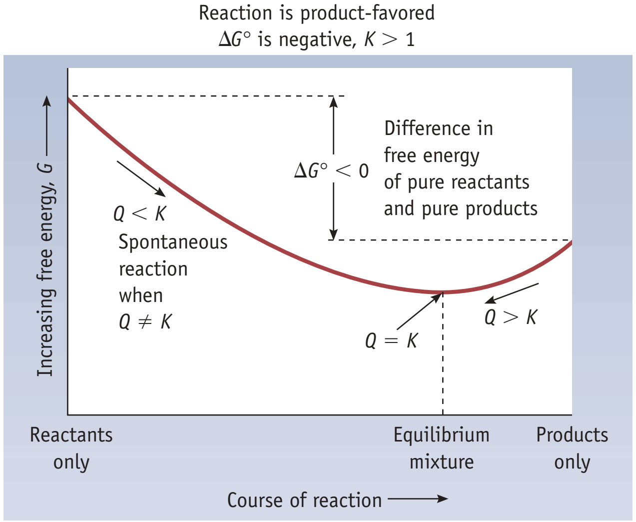
$$a\,\text{A} + b\,\text{B} \longrightarrow c\,\text{C} + d\,\text{D}$$

the reaction quotient, Q, is

$$Q = \frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b}$$

Equation 19.7 informs us that, at a given temperature, the difference in free energy between that of the pure reactants and that of a mixture of reactants and products is determined by the values of $\Delta G°$ and Q. Further, as long as ΔG is negative—that is, the reaction is "descending" from the free energy of the pure reactants to the equilibrium position—the reaction is spontaneous.

Eventually the system reaches equilibrium. Because no further change in concentration of reactants and products is seen at this point, ΔG must be zero; that is,



Active Figure 19.13 **Free energy changes as a reaction approaches equilibrium.** Equilibrium represents a minimum in the free energy for a system. The reaction portrayed here has $\Delta G° < 0$, $K > 1$, and is product-favored.

General ChemistryNow™ See the General ChemistryNow CD-ROM or website to explore an interactive version of this figure accompanied by an exercise.

there is no further change in free energy in the system. Substituting $\Delta G = 0$ and $Q = K$ into Equation 19.7 gives

$$0 = \Delta G° + RT \ln K \text{ (at equilibrium)}$$

Rearranging this equation leads to a useful relationship between the standard free energy change for a reaction and the equilibrium constant, K:

$$\boxed{\Delta G°_{rxn} = -RT \ln K} \qquad (19.8)$$

From Equation 19.8 we learn that, *when $\Delta G°_{rxn}$ is negative, K must be greater than 1, and the reaction is product-favored.* The more negative the value of $\Delta G°$, the larger the equilibrium constant. This makes sense because, as described in Chapter 16, large equilibrium constants are associated with product-favored reactions. *For reactant-favored reactions, $\Delta G°$ is positive and K is less than 1.* If $K = 1$, then $\Delta G° = 0$. (This is a rare situation, requiring that $[C]^c[D]^d/[A]^a[B]^b = 1$ for the reaction $a\text{A} + b\text{B} \longrightarrow c\text{C} + d\text{D}$.)


Charles D. Winters

Spontaneous but not product-favored. If a sample of yellow lead iodide is placed in pure water, the compound will begin to dissolve. The dissolving process will be spontaneous ($\Delta G < 0$) until equilibrium is reached. However, because PbI_2 is insoluble, with $K_{sp} = 9.8 \times 10^{-9}$, the process of dissolving the compound is strongly reactant-favored, and the value of $\Delta G°$ is positive.

Free Energy, the Reaction Quotient, and the Equilibrium Constant

Let us summarize the relationships among $\Delta G°$, ΔG, Q, and K.

- The solid line in Figure 19.13 shows how free energy decreases to a minimum as a system approaches equilibrium. *The free energy at equilibrium is lower than the free energy of the pure reactants and of the pure products.*

- $\Delta G^\circ_{\text{rxn}}$ gives the position of equilibrium and may be calculated from

$$\begin{aligned}\Delta G^\circ_{\text{rxn}} &= \sum \Delta G^\circ_f(\text{products}) - \sum \Delta G^\circ_f(\text{reactants})\\ &= \Delta H^\circ_{\text{rxn}} - T\Delta S^\circ_{\text{rxn}}\\ &= -RT \ln K\end{aligned}$$

- ΔG_{rxn} describes the direction in which a reaction proceeds to reach equilibrium and may be calculated from

$$\Delta G_{\text{rxn}} = \Delta G^\circ_{\text{rxn}} + RT \ln Q$$

When $\Delta G_{\text{rxn}} < 0$, $Q < K$ and the reaction proceeds spontaneously to convert reactants to products until equilibrium is attained.

When $\Delta G_{\text{rxn}} > 0$, $Q > K$ and the reaction proceeds spontaneously to convert products to reactants until equilibrium is attained.

When $\Delta G_{\text{rxn}} = 0$, $Q = K$, and the reaction is at equilibrium.

Using the Relationship Between $\Delta G^\circ_{\text{rxn}}$ and K

Equation 19.8 provides a direct route to determine the standard free energy change from experimentally determined equilibrium constants. Alternatively, it allows calculation of an equilibrium constant from thermochemical data contained in tables or obtained from an experiment.

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See the General ChemistryNow CD-ROM or website:

- **Screen 19.9 Thermodynamics and the Equilibrium Constant,** for a simulation and tutorial on ΔG° and K

Example 19.7—Calculating K_p from $\Delta G^\circ_{\text{rxn}}$

Problem Determine the standard free energy change, $\Delta G^\circ_{\text{rxn}}$, for the formation of 1.00 mol of ammonia from nitrogen and hydrogen, and use this value to calculate the equilibrium constant for this reaction at 25 °C.

Strategy The free energy of formation of ammonia represents the free energy change to form 1.00 mol of $NH_3(g)$ from the elements. The equilibrium constant for this reaction is calculated from ΔG° using Equation 19.8. Because the reactants and products are gases, the calculated value will be K_p.

Solution Begin by specifying a balanced equation for the chemical reaction under investigation.

$$\tfrac{1}{2}\,N_2(g) + \tfrac{3}{2}\,H_2(g) \longrightarrow NH_3(g)$$

The free energy change for this reaction is −16.37 kJ/mol ($\Delta G^\circ_{\text{rxn}} = \Delta G^\circ_f$ for $NH_3(g)$; Appendix L). In a calculation of K_p using Equation 19.8, we will need consistent units. The gas constant, R, is 8.3145 J/K · mol, so the value of ΔG° must be in joules/mol (not kilojoules/mol). The temperature is 298 K.

$$\begin{aligned}\Delta G^\circ &= -RT \ln K\\ -16{,}370 \text{ J/mol} &= -(8.3145 \text{ J/K}\cdot\text{mol})\,(298.15 \text{ K}) \ln K_p\\ \ln K_p &= 6.604\\ K_p &= 7.38 \times 10^2\end{aligned}$$

Comment As illustrated by this example, it is possible to calculate equilibrium constants from thermodynamic data. This gives us another use for these valuable tables. For the reaction of N_2 and H_2 to form NH_3, at 298 K (25 °C), the value of the equilibrium constant is quite large, indicating that the reaction is product-favored.

Example 19.8—Calculating ΔG°_{rxn} from K_c

Problem The value of K_{sp} for AgCl(s) at 25 °C is 1.8×10^{-10}. Use this value in Equation 19.8 to determine ΔG° for the process $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$ at 25 °C.

Strategy The chemical equation given is the opposite of the equation used to define K_{sp}; therefore, its equilibrium constant is $1/K_{sp}$. This value is used to calculate ΔG°.

Solution For $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$,

$$K = \frac{1}{K_{sp}} = \frac{1}{1.8 \times 10^{-10}} = 5.6 \times 10^{9}$$

$$\Delta G^\circ = -RT \ln K = -(8.3145 \text{ J/K} \cdot \text{mol})(298.15 \text{ K}) \ln (5.6 \times 10^{9})$$

$$= -56 \text{ kJ/mol (to two significant figures)}$$

Comment The negative value of ΔG° indicates that the precipitation of AgCl from $Ag^+(aq)$ and $Cl^-(aq)$ is a product-favored process. Earlier we described the experimental determination of ΔG° values from thermochemical measurements—that is, determining ΔH and ΔS values from the measurement of heat gain or loss. Here is a second method to determine ΔG°.

Exercise 19.9—Calculating K_p from ΔG°_{rxn}

Determine the value of ΔG°_{rxn} for the reaction $C(s) + CO_2(g) \longrightarrow 2\ CO(g)$ from thermodynamic data in Appendix L. Use this result to calculate the equilibrium constant.

Exercise 19.10—Calculating ΔG°_{rxn} from K_c

The formation constant for $Ag(NH_3)_2{}^+$ is 1.6×10^{7}. Use this value to calculate ΔG° for the reaction $Ag^+(aq) + 2\ NH_3(aq) \longrightarrow [Ag(NH_3)_2]^+(aq)$.

19.8—Thermodynamics, Time and Life

Chapters 6 and 19 have brought together the three laws of thermodynamics.

First law:	The total energy of the universe is a constant.
Second law:	The total entropy of the universe is always increasing.
Third law:	The entropy of a pure, perfectly formed crystalline substance at 0 K is zero.

Some cynic long ago paraphrased the first two laws. The first law was transmuted into "You can't win!," referring to the fact that energy will always be conserved, so a process in which you get back more energy than you put in is impossible. The paraphrase of the second law? "You can't break even!" The Gibbs free energy provides a rationale for this interpretation. Only part of the energy from a chemical reaction can be converted to useful work; the rest will be committed to the redistribution of matter or energy.

■ **Time's Arrow**
If you are interested in the theories of the origin of the universe, and in "time's arrow," read *A Brief History of Time, From the Big Bang to Black Holes* by Stephen W. Hawking, New York, Bantam Books, 1988.

Chemical Perspectives

Thermodynamics and Speculation on the Origin of Life

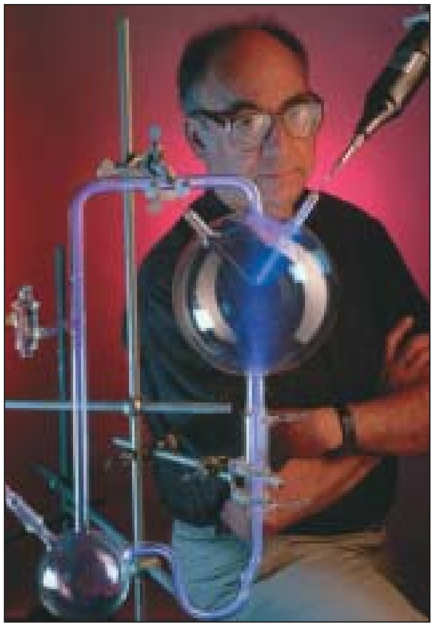
Early earth was very different than it is today. The atmosphere was made up of simple molecular substances such as N_2, H_2, CO_2, CO, NH_3, CH_4, H_2S, and H_2O. Elemental oxygen was not originally present; this atmospheric gas, now necessary for most life, would eventually be produced by plants via photosynthesis more than a billion years after earth was formed.

The crust of the planet was rocky, consisting mostly of silicon and aluminum oxides. What was available was an abundance of energy, from solar radiation (without O_2 and O_3, a high level of ultraviolet radiation reached the surface), from lightning, and from the heat in the earth's core. How did the molecules found in living organisms form under these conditions?

A classic experiment to probe the question of how more complex molecules arose was performed in the late 1950s. In the Miller–Urey experiment, a mixture of these gases was subjected to an electric discharge, where the spark simulated lightning. After a few days HCN and formaldehyde (CH_2O), along with amino acids and other organic molecules, had accumulated in this system. Although scientists no longer believe life-giving molecules may have been formed this way, it is nonetheless a starting point for new experiments in this direction.

Other theories on the formation of organic molecules have their own supporters. One theory suggests that organic molecules formed in aqueous solution on the surface of clay particles. Another posits that important molecules formed near cracks in the earth's crust on the floor of the oceans. Such processes have also been shown to occur in the laboratory.

It is, of course, a long way from small organic molecules to larger molecules, and the conversion of inanimate molecules to living beings is an even greater leap. Creating larger and larger molecules from small molecules requires energy and means that entropy must decrease in the "system." For the process to occur, however, the entropy of the universe must increase. Thus the creation of living systems means there must be a corresponding increase in the entropy of the "surroundings" elsewhere in the universe. One thing remains clear: the laws of thermodynamics must be obeyed.



James A. Sugar/© 2002 Corbis

The Miller–Urey experiment. An electric discharge through a mixture of gases leads to formation of organic molecules, including formaldehyde and amino acids.

Entropy and Time
The second law of thermodynamics requires that disorder increase with time. Because all natural processes that occur do so as time progresses and result in increased disorder, it is evident that increasing entropy and time "point" in the same direction.

The second law tells us that the entropy of the universe is continually increasing. A snowflake will melt in a warm room, but you won't see a glassful of water molecules reassemble themselves into snowflakes at any temperature above 0 °C. Molecules of perfume will diffuse throughout a room, but they won't collect again on your body. All spontaneous processes result in energy becoming more dispersed throughout the universe. This is what scientists mean when they say that the second law is an expression of time in a physical—as opposed to psychological—form. In fact, entropy has been called "time's arrow."

Neither the first nor the second law of thermodynamics has ever been proven. It is just that there never has been a single example demonstrating that either is false. Albert Einstein once remarked that thermodynamic theory "is the only physical theory of the universe content [which], within the framework of applicability of its basic concepts, will never be overthrown." Einstein's statement does not mean that people have not tried (and are continuing to try) to disprove the laws of thermodynamics. Claims to have invented machines that perform useful work without expending energy—perpetual motion machines—are frequently made. However, no perpetual motion machine has ever been shown to work (page 902). We can feel safe with the assumption that such a machine never will be built.

Roald Hoffmann, a chemist who shared the 1981 Nobel Prize in chemistry, has said, "One amusing way to describe synthetic chemistry, the making of molecules that is at the intellectual and economic center of chemistry, is that it is the local defeat of entropy" [*American Scientist*, pp. 619–621, Nov–Dec 1987]. "Local defeat" in this context refers to an unfavorable entropy change in a system because, of course, the entropy of the universe must increase if a process is to occur. An important point to make is that chemical syntheses are often entropy-disfavored. Chemists find ways to accomplish them by balancing the unfavorable changes in the system with favorable changes in the surroundings to make these reactions occur.

Finally, thermodynamics speaks to one of the great mysteries: the origin of life. Life as we know it requires the creation of extremely complex molecules such as proteins and nucleic acids. Their formation must have occurred from atoms and small molecules. Assembling thousands of atoms into a highly ordered state in biochemical compounds clearly requires a local decrease in entropy. Some have said that life is a violation of the second law of thermodynamics. A more logical view, however, is that the local decrease is offset by an increase in entropy in the rest of the universe. Here again, thermodynamics is unchallenged.

Chapter Goals—Revisited

When you have finished studying this chapter, you should ask whether you have met the chapter goals. In particular, you should be able to:

Understand the concept of entropy and its relationship to spontaneity

a. Understand that entropy is a measure of matter and energy dispersal or disorder (Section 19.3). General ChemistryNow homework: Study Question(s) 2

b. Recognize that entropy can be determined experimentally as the heat change of a reversible process (A Closer Look, Section 19.4).

c. Know how to calculate entropy changes from tables of entropy values for compounds (Section 19.4). General ChemistryNow homework: SQ(s) 6, 10, 11

d. Identify common processes that are entropy-favored (Section 19.4).

Predict whether a process will be spontaneous

a. Use entropy and enthalpy changes to predict whether a reaction will be spontaneous (Section 19.5 and Table 19.2). General ChemistryNow homework: SQ(s) 14, 18

b. Recognize how temperature influences whether a reaction is spontaneous (Section 19.5). General ChemistryNow homework: SQ(s) 20

Understand and use a new thermodynamic function, Gibbs free energy

a. Understand the connection between enthalpy and entropy changes and the Gibbs free energy change for a process (Section 19.6).

b. Calculate the change in free energy at standard conditions for a reaction from the enthalpy and entropy changes or from the standard free energy of formation of reactants and products (ΔG_f°) (Section 19.6). General ChemistryNow homework: SQ(s) 22, 24, 26, 55

c. Know how free energy changes with temperature (Section 19.5). General ChemistryNow homework: SQ(s) 30, 72

Understand the relationship of a free energy change for a reaction, its equilibrium constant, and whether the reaction is product- or reactant-favored

a. Describe the relationship between the free energy change and equilibrium constants and calculate K from $\Delta G^\circ_{\text{rxn}}$ (Section 19.7) General ChemistryNow homework: SQ(s) 36, 48, 50

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- Check your readiness for an exam by taking the exam-prep quiz and exploring the resources in the personalized Learning Plan it provides

Key Equations

Equation 19.1 (page 912):
Calculate entropy change from the heat of the process and the temperature at which it occurs.

$$\Delta S = q_{rev}/T$$

Equation 19.2 (page 915):
Calculate the standard entropy change for a process from the tabulated entropies of the products and reactants.

$$\Delta S^\circ_{\text{system}} = \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants})$$

Equation 19.4 (page 917):
Calculate the total entropy change for a system and its surroundings, to determine whether a process is product-favored.

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

Equation 19.5 (page 922):
Calculate the free energy change for a process from the enthalpy and entropy change for the process.

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

Equation 19.6 (page 925):
Calculate the free energy change for a reaction using tabulated values of ΔG°_f, the standard free energy of formation.

$$\Delta G^\circ_{\text{rxn}} = \sum \Delta G^\circ_f(\text{products}) - \sum \Delta G^\circ_f(\text{reactants})$$

Equation 19.7 (page 928):
The relationship between the free energy change under nonstandard conditions and ΔG° and the reaction quotient Q.

$$\Delta G = \Delta G^\circ + \text{RT} \ln Q$$

Equation 19.8 (page 929):
The relationship between the standard free energy change for a reaction and its equilibrium constant.

$$\Delta G^\circ = -RT \ln K$$

Study Questions

▲ denotes more challenging questions.

■ denotes questions available in the Homework and Goals section of the General ChemistryNow CD-ROM or website.

Blue numbered questions have answers in Appendix O and fully worked solutions in the *Student Solutions Manual.*

Structures of many of the compounds used in these questions are found on the General ChemistryNow CD-ROM or website in the Models folder.

General ChemistryNow™ Assess your understanding of this chapter's topics with additional quizzing and conceptual questions at http://now.brookscole.com/kotz6e

Practicing Skills

Entropy

(See Example 19.1 and General ChemistryNow CD-ROM or website Screen 19.4.)

1. Which substance has the higher entropy in each of the following pairs?
   (a) dry ice (solid CO_2) at −78 °C or CO_2 (g) at 0 °C
   (b) liquid water at 25 °C or liquid water at 50 °C
   (c) pure alumina, Al_2O_3(s), or ruby (Ruby is Al_2O_3 in which some of the Al^{3+} ions in the crystalline lattice are replaced with Cr^{3+} ions.)
   (d) one mole of N_2(g) at 1 bar pressure or one mole of N_2(g) at 10 bar pressure (both at 298 K)

2. ■ Which substance has the higher entropy in each of the following pairs?
   (a) a sample of pure silicon (to be used in a computer chip) or a piece of silicon containing a trace of some other elements such as boron or phosphorus
   (b) $O_2(g)$ at 0 °C or $O_2(g)$ at −50 °C
   (c) $I_2(s)$ or $I_2(g)$, both at room temperature
   (d) one mole of $O_2(g)$ at 1 bar pressure or one mole of $O_2(g)$ at 0.01 bar pressure (both at 298 K)

3. By comparing the formulas for each pair of compounds, decide which is expected to have the higher entropy. Assume both are at the same temperature. Check your answers using data in Appendix L.
   (a) $O_2(g)$ or $CH_3OH(g)$ (two substances with the same molar mass)
   (b) $HF(g)$, $HCl(g)$, or $HBr(g)$
   (c) $NH_4Cl(s)$ or $NH_4Cl(aq)$
   (d) $HNO_3(g)$, $HNO_3(\ell)$, or $HNO_3(aq)$

4. By comparing the formulas for each pair of compounds, decide which is expected to have the higher entropy. Assume both are at the same temperature. Check your answers using data in Appendix L.
   (a) $NaCl(s)$, $NaCl(g)$, or $NaCl(aq)$
   (b) $H_2O(g)$ or $H_2S(g)$
   (c) $C_2H_4(g)$ or $N_2(g)$ (two substances with the same molar mass)
   (d) $H_2SO_4(\ell)$ or $H_2SO_4(aq)$

Predicting and Calculating Entropy Changes

(See Example 19.2 and General ChemistryNow CD-ROM or website Screen 19.5.)

5. Use $S°$ values to calculate the entropy change, $\Delta S°$, for each of the following processes and comment on the sign of the change.
   (a) $KOH(s) \longrightarrow KOH(aq)$
   (b) $Na(g) \longrightarrow Na(s)$
   (c) $Br_2(\ell) \longrightarrow Br_2(g)$
   (d) $HCl(g) \longrightarrow HCl(aq)$

6. ■ Use $S°$ values to calculate the entropy change, $\Delta S°$, for each of the following changes and comment on the sign of the change.
   (a) $NH_4Cl(s) \longrightarrow NH_4Cl(aq)$
   (b) $C_2H_5OH(\ell) \longrightarrow C_2H_5OH(g)$
   (c) $CCl_4(g) \longrightarrow CCl_4(\ell)$
   (d) $NaCl(s) \longrightarrow NaCl(g)$

7. Calculate the standard entropy change for the formation of one mole of gaseous ethane (C_2H_6) at 25 °C.

$$2\,C(\text{graphite}) + 3\,H_2(g) \longrightarrow C_2H_6(g)$$

8. Using standard entropy values, calculate the standard entropy change for a reaction forming one mole of $NH_3(g)$ from $N_2(g)$ and $H_2(g)$.

$$\tfrac{1}{2}\,N_2(g) + \tfrac{3}{2}\,H_2(g) \longrightarrow NH_3(g)$$

9. Calculate the standard molar entropy change for the formation of each of the following compounds from the elements at 25 °C.
   (a) $HCl(g)$ (b) $Ca(OH)_2(s)$

10. ■ Calculate the standard molar entropy change for the formation of each of the following compounds from the elements at 25 °C.
    (a) $H_2S(g)$ (b) $MgCO_3(s)$

11. ■ Calculate the standard molar entropy change for each of the following reactions at 25 °C. Comment on the sign of $\Delta S°$.
    (a) $2\,Al(s) + 3\,Cl_2(g) \longrightarrow 2\,AlCl_3(s)$
    (b) $2\,CH_3OH(\ell) + 3\,O_2(g) \longrightarrow 2\,CO_2(g) + 4\,H_2O(g)$

12. Calculate the standard molar entropy change for each of the following reactions at 25 °C. Comment on the sign of $\Delta S°$.
    (a) $2\,Na(s) + 2\,H_2O(\ell) \longrightarrow 2\,NaOH(aq) + H_2(g)$
    (b) $Na_2CO_3(s) + 2\,HCl(aq) \longrightarrow 2\,NaCl(aq) + H_2O(\ell) + CO_2(g)$

$\Delta S°_{univ}$ and Spontaneity

(See Example 19.3 and General ChemistryNow CD-ROM or website Screen 19.6.)

13. Is the reaction

$$Si(s) + 2\,Cl_2(g) \longrightarrow SiCl_4(g)$$

spontaneous? Answer this question by calculating $\Delta S°_{sys}$, $\Delta S°_{surr}$, and $\Delta S°_{univ}$. (The reactants and products are defined as the system.)

14. ■ Is the reaction

$$Si(s) + 2\,H_2(g) \longrightarrow SiH_4(g)$$

spontaneous? Answer this question by calculating $\Delta S°_{sys}$, $\Delta S°_{surr}$, and $\Delta S°_{univ}$. (The reactants and products are defined as the system and $T = 298$ K.)

15. Calculate the standard enthalpy and entropy changes for the decomposition of liquid water to form gaseous hydrogen and oxygen. Is this reaction spontaneous? Explain your answer briefly.

16. Calculate the standard enthalpy and entropy changes for the formation of HCl(g) from gaseous hydrogen and chlorine. Is this reaction spontaneous? Explain your answer briefly.

17. Classify each of the reactions according to one of the four reaction types summarized in Table 19.2.
    (a) $Fe_2O_3(s) + 2\,Al(s) \longrightarrow 2\,Fe(s) + Al_2O_3(s)$

$$\Delta H° = -851.5 \text{ kJ}; \qquad \Delta S° = -375.2 \text{ J/K}$$

    (b) $N_2(g) + 2\,O_2(g) \longrightarrow 2\,NO_2(g)$

$$\Delta H° = 66.2 \text{ kJ}; \qquad \Delta S° = -121.6 \text{ J/K}$$

18. ■ Classify each of the reactions according to one of the four reaction types summarized in Table 19.2.
    (a) $C_6H_{12}O_6(s) + 6\ O_2(g) \longrightarrow 6\ CO_2(g) + 6\ H_2O(\ell)$

    $\Delta H^\circ = -673\ kJ; \qquad \Delta S^\circ = 60.4\ J/K$

    (b) $MgO(s) + C(graphite) \longrightarrow Mg(s) + CO(g)$

    $\Delta H^\circ = 490.7\ kJ; \qquad \Delta S^\circ = 197.9\ J/K$

Effect of Temperature on Reactions

(See Example 19.4.)

19. Heating some metal carbonates, among them magnesium carbonate, leads to their decomposition.

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

    (a) Calculate ΔH° and ΔS° for the reaction.
    (b) Is the reaction spontaneous at 298 K?
    (c) Is the reaction predicted to be spontaneous at higher temperatures?

20. ■ Calculate ΔH° and ΔS° for the reaction of tin(IV) oxide with carbon.

$$SnO_2(s) + C(s) \longrightarrow Sn(s) + CO_2(g)$$

    (a) Is the reaction spontaneous at 298 K?
    (b) Is the reaction predicted to be spontaneous at higher temperatures?

Changes in Free Energy

(See Example 19.5; use $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$; see General ChemistryNow CD-ROM or website Screen 19.7.)

21. Using values of ΔH_f° and S°, calculate ΔG°_{rxn} for each of the following reactions.
    (a) $2\ Pb(s) + O_2(g) \longrightarrow 2\ PbO(s)$
    (b) $NH_3(g) + HNO_3(aq) \longrightarrow NH_4NO_3(aq)$

    Which of these reactions is (are) predicted to be product-favored? Are the reactions enthalpy- or entropy-driven?

22. ■ Using values of ΔH_f° and S°, calculate ΔG°_{rxn} for each of the following reactions.
    (a) $Ca(s) + 2\ H_2O(\ell) \longrightarrow Ca(OH)_2(aq) + 2\ H_2(g)$
    (b) $6\ C(graphite) + 3\ H_2(g) \longrightarrow C_6H_6(\ell)$

    Which of these reactions is (are) predicted to be product-favored? Are the reactions enthalpy- or entropy-driven?

23. Using values of ΔH_f° and S°, calculate the standard molar free energy of formation, ΔG_f°, for each of the following compounds:
    (a) $CS_2(g)$
    (b) $NaOH(s)$
    (c) $ICl(g)$

    Compare your calculated values of ΔG_f° with those listed in Appendix L. Which compounds are predicted to be formed spontaneously?

24. ■ Using values of ΔH_f° and S°, calculate the standard molar free energy of formation, ΔG_f°, for each of the following:
    (a) $Ca(OH)_2(s)$
    (b) $Cl(g)$
    (c) $Na_2CO_3(s)$

    Compare your calculated values of ΔG_f° with those listed in Appendix L. Which compounds are predicted to be formed spontaneously?

Free Energy of Formation

(See Example 19.6; use $\Delta G^\circ_{rxn} = \Sigma\Delta G_f^\circ$ (products) $- \Sigma\Delta G_f^\circ$ (reactants); see General ChemistryNow CD-ROM or website Screen 19.7.)

25. Using values of ΔG_f°, calculate ΔG°_{rxn} for each of the following reactions. Which are product-favored?
    (a) $2\ K(s) + Cl_2(g) \longrightarrow KCl(s)$
    (b) $2\ CuO(s) \longrightarrow 2\ Cu(s) + O_2(g)$
    (c) $4\ NH_3(g) + 5\ O_2(g) \longrightarrow 4\ NO_2(g) + 6\ H_2O(g)$

26. ■ Using values of ΔG_f°, calculate ΔG°_{rxn} for each of the following reactions. Which are product-favored?
    (a) $HgS(s) + O_2(g) \longrightarrow Hg(\ell) + SO_2(g)$
    (b) $2\ H_2S(g) + 3\ O_2(g) \longrightarrow 2\ H_2O(g) + 2\ SO_2(g)$
    (c) $SiCl_4(g) + 2\ Mg(s) \longrightarrow 2\ MgCl_2(s) + Si(s)$

27. For the reaction $BaCO_3(s) \longrightarrow BaO(s) + CO_2(g)$, $\Delta G^\circ_{rxn} = +219.7\ kJ$. Using this value and other data available in Appendix L, calculate the value of ΔG_f° for $BaCO_3(s)$.

28. For the reaction $TiCl_2(s) + Cl_2(g) \longrightarrow TiCl_4(\ell)$, $\Delta G^\circ_{rxn} = -272.8\ kJ$. Using this value and other data available in Appendix L , calculate the value of ΔG_f° for $TiCl_2(s)$.

Effect of Temperature on ΔG

(See Example 19.7 and General ChemistryNow CD-ROM or website Screen 19.8.)

29. Determine whether each of the reactions listed below is entropy-favored or -disfavored under standard conditions. Predict how an increase in temperature will affect the value of ΔG°_{rxn}.
    (a) $N_2(g) + 2\ O_2(g) \longrightarrow 2\ NO_2(g)$
    (b) $2\ C(s) + O_2(g) \longrightarrow 2\ CO(g)$
    (c) $CaO(s) + CO_2(g) \longrightarrow CaCO_3(s)$
    (d) $2\ NaCl(s) \longrightarrow 2\ Na(s) + Cl_2(g)$

30. ■ Determine whether each of the reactions listed below is entropy-favored or -disfavored under standard conditions. Predict how an increase in temperature will affect the value of ΔG°_{rxn}.
    (a) $I_2(g) \longrightarrow 2\ I(g)$
    (b) $2\ SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$
    (c) $SiCl_4(g) + 2\ H_2O(\ell) \longrightarrow SiO_2(s) + 4\ HCl(g)$
    (d) $P_4(s, white) + 6\ H_2(g) \longrightarrow 4\ PH_3(g)$

31. Estimate the temperature required to decompose $HgS(s)$ into $Hg(\ell)$ and $S(g)$.

32. Estimate the temperature required to decompose $CaSO_4(s)$ into $CaO(s)$ and $SO_3(g)$.

Free Energy and Equilibrium Constants

(See Example 19.8; use $\Delta G^\circ = -RT \ln K$; see General ChemistryNow CD-ROM or website Screen 19.9.)

33. The formation of NO(g) from its elements

$$\tfrac{1}{2}\,\mathrm{N_2(g)} + \tfrac{1}{2}\,\mathrm{O_2(g)} \longrightarrow \mathrm{NO(g)}$$

has a standard free energy change, ΔG°, of +86.58 kJ/mol at 25 °C. Calculate K_p at this temperature. Comment on the connection between the sign of ΔG° and the magnitude of K_p.

34. The formation of O_3(g) from O_2(g) has a standard free energy change, ΔG°, of +163.2 kJ/mol at 25 °C. Calculate K_p at this temperature. Comment on the connection between the sign of ΔG° and the magnitude of K_p.

35. Calculate ΔG° and K_p at 25 °C for the reaction

$$\mathrm{C_2H_4(g)} + \mathrm{H_2(g)} \longrightarrow \mathrm{C_2H_6(g)}$$

Comment on the sign of ΔG° and the magnitude of K_p.

36. ■ Calculate ΔG° and K_p at 25 °C for the reaction

$$2\,\mathrm{HBr(g)} + \mathrm{Cl_2(g)} \longrightarrow 2\,\mathrm{HCl(g)} + \mathrm{Br_2}(\ell)$$

Is the reaction predicted to be product-favored under standard conditions? Comment on the sign of ΔG° and the magnitude of K_p.

General Questions

These questions are not designated as to type or location in the chapter. They may combine several concepts.

37. Calculate the standard molar entropy change, ΔS°, for each of the following reactions:
    1. $\mathrm{C(s)} + 2\,\mathrm{H_2(g)} \longrightarrow \mathrm{CH_4(g)}$
    2. $\mathrm{CH_4(g)} + \tfrac{1}{2}\,\mathrm{O_2(g)} \longrightarrow \mathrm{CH_3OH}(\ell)$
    3. $\mathrm{C(s)} + 2\,\mathrm{H_2(g)} + \tfrac{1}{2}\,\mathrm{O_2(g)} \longrightarrow \mathrm{CH_3OH}(\ell)$

    Verify that these values are related by the equation $\Delta S^\circ_1 + \Delta S^\circ_2 = \Delta S^\circ_3$. What general principle is illustrated here?

38. Hydrogenation, the addition of hydrogen to an organic compound, is a reaction of considerable industrial importance. Calculate ΔH°, ΔS°, and ΔG° at 25 °C for the hydrogenation of octene, C_8H_{16}, to give octane, C_8H_{18}. Is the reaction product- or reactant-favored under standard conditions?

$$\mathrm{C_8H_{16}(g)} + \mathrm{H_2(g)} \longrightarrow \mathrm{C_8H_{18}(g)}$$

The following information is required, in addition to data in Appendix L.

Compound	**ΔH_f° (kJ/mol)**	**S° (J/K · mol)**
Octene	−82.93	462.8
Octane	−208.45	463.639

39. Is the combustion of ethane, C_2H_6, a spontaneous reaction?

$$\mathrm{C_2H_6(g)} + \tfrac{7}{2}\,\mathrm{O_2(g)} \longrightarrow 2\,\mathrm{CO_2(g)} + 3\,\mathrm{H_2O(g)}$$

Answer the question by calculating the value of $\Delta S^\circ_{\text{univ}}$, using values of ΔH_f° and S° in Appendix L. Does your calculated answer agree with your preconceived idea of this reaction?

40. Write a balanced equation that depicts the formation of 1 mol of Fe_2O_3(s) from its elements. What is the standard free energy of formation of 1.00 mol of Fe_2O_3(s)? What is the value of $\Delta G^\circ_{\text{rxn}}$ when 454 g (1 lb) of Fe_2O_3(s) is formed from the elements?

41. When vapors from hydrochloric acid and aqueous ammonia come in contact, the following reaction takes place, producing a white "cloud" of solid NH_4Cl (Figure 19.11).

$$\mathrm{HCl(g)} + \mathrm{NH_3(g)} \longrightarrow \mathrm{NH_4Cl(s)}$$

Defining this as the system under study:

(a) Predict whether the signs of $\Delta S^\circ_{\text{sys}}$, $\Delta S^\circ_{\text{surr}}$, $\Delta S^\circ_{\text{univ}}$, ΔH°, and ΔG° are greater than zero, equal to zero, or less than zero, and explain your prediction. Verify your predictions by calculating values for each of these quantities.

(b) Calculate a value of K_p for this reaction at 298 K.

42. Calculate $\Delta S^\circ_{\text{sys}}$, $\Delta S^\circ_{\text{surr}}$, $\Delta S^\circ_{\text{univ}}$ for each of the following processes.

(a) $\mathrm{NaCl(s)} \longrightarrow \mathrm{NaCl(aq)}$

(b) $\mathrm{NaOH(s)} \longrightarrow \mathrm{NaOH(aq)}$

Comment on how these systems differ.

43. Methanol is now widely used as a fuel in race cars such as those that compete in the Indianapolis 500 race (see page 000). Consider the following reaction as a possible synthetic route to methanol.

$$\mathrm{C(graphite)} + \tfrac{1}{2}\,\mathrm{O_2(g)} + 2\,\mathrm{H_2(g)} \longrightarrow \mathrm{CH_3OH}(\ell)$$

Calculate K_p for the formation of methanol at 25 °C using this reaction. Would a different temperature be better suited to this reaction?

44. The enthalpy of vaporization of liquid diethyl ether, $(C_2H_5)_2O$, is 26.0 kJ/mol at the boiling point of 35.0 °C. Calculate ΔS° for (a) a liquid to vapor transformation and (b) a vapor to liquid transformation at 35.0 °C.

45. Calculate the entropy change, ΔS°, for the vaporization of ethanol, C_2H_5OH, at its normal boiling point, 78.0 °C. The enthalpy of vaporization of ethanol is 39.3 kJ/mol.

46. If gaseous hydrogen can be produced cheaply, it could be burned directly as a fuel or converted to another fuel, methane (CH_4), for example.

$$3\,\mathrm{H_2(g)} + \mathrm{CO(g)} \longrightarrow \mathrm{CH_4(g)} + \mathrm{H_2O(g)}$$

Calculate ΔG°, ΔS°, and ΔH° at 25 °C for the reaction. Is it predicted to be product- or reactant-favored under standard conditions?

47. Using thermodynamic data, estimate the normal boiling point of ethanol. (Recall that liquid and vapor are in equilibrium at 1.0 atm pressure at the normal boiling point.) The actual normal boiling point is 78 °C. How well does your calculated result agree with the actual value?

48. ■ ▲ Estimate the vapor pressure of ethanol at 37 °C using thermodynamic data. Express the result in millibars of mercury.

49. The following reaction is not spontaneous at room temperature.

$$COCl_2(g) \longrightarrow CO(g) + Cl_2(g)$$

Would you have to raise or lower the temperature to make it spontaneous?

50. ■ When calcium carbonate is heated strongly, CO_2 gas is evolved. The equilibrium pressure of the gas is 1.00 bar at 897 °C, and ΔH°_{rxn} at 298 K = 179.0 kJ.

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

Estimate the value of ΔS° at 897 °C for the reaction.

51. The reaction used by Joseph Priestley to prepare oxygen is

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

Defining this reaction as the system under study:

(a) Predict whether the signs of ΔS°_{sys}, ΔS°_{surr}, ΔS°_{univ}, ΔH°, and ΔG° are greater than zero, equal to zero, or less than zero, and explain your prediction. Using data from Appendix L, calculate the value of each of these quantities to verify your prediction.

(b) Calculate K_p at 298 K. Is the reaction product-favored?

52. ▲ Estimate the boiling point of water in Denver, Colorado (where the altitude is 1.60 km and the atmospheric pressure is 630 mm Hg).

53. Sodium reacts violently with water according to the equation

$$Na(s) + H_2O(\ell) \longrightarrow NaOH(aq) + \tfrac{1}{2}\ H_2(g)$$

Without doing calculations, predict the signs of ΔH° and ΔS° for the reaction. Verify your prediction with a calculation.

54. Yeast can produce ethanol by the fermentation of glucose ($C_6H_{12}O_6$), which is the basis for the production of most alcoholic beverages.

$$C_6H_{12}O_6(aq) \longrightarrow 2\ C_2H_5OH(\ell) + 2\ CO_2(g)$$

Calculate ΔH°, ΔS°, and ΔG° for the reaction. Is the reaction product- or reactant-favored? (In addition to the thermodynamic values in Appendix L, you will need the following data for $C_6H_{12}O_6(aq)$: $\Delta H^\circ_f = -1260.0$ kJ/mol; $S^\circ = 289$ J/K · mol; and $\Delta G^\circ_f = -918.8$ kJ/mol.)

55. ■ Elemental boron, in the form of thin fibers, can be made by reducing a boron halide with H_2.

$$BCl_3(g) + \tfrac{3}{2}\ H_2(g) \longrightarrow B(s) + 3\ HCl(g)$$

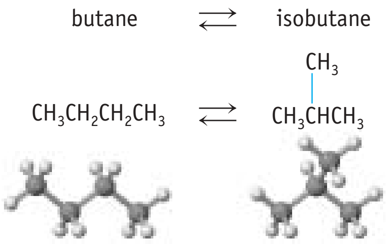
Calculate ΔH°, ΔS°, and ΔG° at 25 °C for this reaction. Is the reaction predicted to be spontaneous under standard conditions? If spontaneous, is it enthalpy-driven or entropy-driven? [S° for B(s) is 5.86 J/K · mol.]

56. The equilibrium constant, K_p, for $N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$ is 0.14 at 25 °C. Calculate ΔG° from this constant, and compare your calculated value with that determined from the ΔG°_f values in Appendix L.

57. Most metal oxides can be reduced with hydrogen to the pure metal. (Although such reactions work well, this expensive method is not used often for large-scale preparations.) The equilibrium constant for the reduction of iron(II) oxide is 0.422 at 700 °C. Estimate ΔG°_{rxn}.

$$FeO(s) + H_2(g) \longrightarrow Fe(s) + H_2O(g)$$

58. The equilibrium constant for the butane $\rightleftharpoons$ isobutane equilibrium at 25 °C is 2.50.



$$\text{butane} \rightleftharpoons \text{isobutane}$$

$$CH_3CH_2CH_2CH_3 \rightleftharpoons CH_3\overset{\displaystyle CH_3}{\overset{|}{C}}HCH_3$$

$$K_c = \frac{[\text{isobutane}]}{[\text{butane}]} = 2.50 \text{ at } 298\text{ K}$$

Calculate ΔG°_{rxn} at this temperature in units of kJ/mol.

59. Almost 5 billion kilograms of benzene, C_6H_6, are made each year. Benzene is used as a starting material for many other compounds and as a solvent (although it is also a carcinogen, and its use is restricted). One compound that can be made from benzene is cyclohexane, C_6H_{12}.

$$C_6H_6(\ell) + 3\ H_2(g) \longrightarrow C_6H_{12}(\ell)$$

$$\Delta H^\circ_{rxn} = -206.7\text{ kJ}; \quad \Delta S^\circ_{rxn} = -361.5\text{ J/K}$$

Is this reaction predicted to be spontaneous under standard conditions at 25 °C? Is the reaction enthalpy- or entropy-driven?

60. A crucial reaction for the production of synthetic fuels is the conversion of coal to H_2 with steam. The chemical reaction is

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

(a) Calculate ΔG°_{rxn} for this reaction at 25 °C assuming C(s) is graphite.

(b) Calculate K_p for the reaction at 25 °C.

(c) Is the reaction predicted to be spontaneous under standard conditions? If not, at what temperature will it become so?

61. Calculate ΔG°_{rxn} for the decomposition of sulfur trioxide to sulfur dioxide and oxygen.

$$2\ SO_3(g) \longrightarrow 2\ SO_2(g) + O_2(g)$$

(a) Is the reaction spontaneous under standard conditions at 25 °C?

(b) If the reaction is not spontaneous at 25 °C, is there a temperature at which it will become so? Estimate this temperature.

(c) What is the equilibrium constant for the reaction at 1500 °C?

62. Methanol is relatively inexpensive to produce. Much consideration has been given to using it as a precursor to other fuels such as methane, which could be obtained by the decomposition of the alcohol.

$$CH_3OH(\ell) \longrightarrow CH_4(g) + \tfrac{1}{2}\,O_2(g)$$

   (a) What are the sign and magnitude of the entropy change for the reaction? Does the sign of $\Delta S°$ agree with your expectation? Explain briefly.
   (b) Is the reaction spontaneous under standard conditions at 25 °C? Use thermodynamic values to prove your answer.
   (c) If it is not spontaneous at 25 °C, at what temperature does the reaction become spontaneous?

63. A cave in Mexico was recently discovered to have some interesting chemistry (see Chapter 21). Hydrogen sulfide, H_2S, reacts with oxygen in the cave to give sulfuric acid, which drips from the ceiling in droplets with a pH less than 1. If the reaction occurring is

$$H_2S(g) + 2\,O_2(g) \longrightarrow H_2SO_4(\ell)$$

calculate $\Delta H°$, $\Delta S°$, and $\Delta G°$. Is the reaction spontaneous? Is it enthalpy- or entropy-driven?

64. Wet limestone is used to scrub SO_2 gas from the exhaust gases of power plants. One possible reaction gives hydrated calcium sulfite:

$$CaCO_3(s) + SO_2(g) + \tfrac{1}{2}\,H_2O(\ell) \rightleftharpoons CaSO_3 \cdot \tfrac{1}{2}\,H_2O(s) + CO_2(g)$$

Another reaction gives hydrated calcium sulfate:

$$CaCO_3(s) + SO_2(g) + \tfrac{1}{2}\,H_2O(\ell) + \tfrac{1}{2}\,O_2(g) \rightleftharpoons CaSO_4 \cdot \tfrac{1}{2}\,H_2O(s) + CO_2(g)$$

Which is the more product-favored reaction? Use the data in the table below and any other needed in Appendix L.

	$CaSO_3 \cdot \frac{1}{2}\,H_2O(s)$	$CaSO_4 \cdot \frac{1}{2}\,H_2O(s)$
$\Delta H_f°$ (kJ/mol)	−1311.7	−1574.65
$S°$(J/K mol)	121.3	134.8

65. Sulfur undergoes a phase transition between between 80 and 100 °C.

$$S_8(\text{rhombic}) \longrightarrow S_8(\text{monoclinic})$$
$$\Delta H°_{rxn} = 3.213\ \text{kJ/mol} \qquad \Delta S°_{rxn} = 8.7\ \text{J/K}$$

   (a) Estimate $\Delta G°$ for the transition at 80.0 °C and 110.0 °C. What do these results tell you about the stability of the two forms of sulfur at each of these temperatures?
   (b) Calculate the temperature at which $\Delta G° = 0$. What is the significance of this temperature?

66. Copper(II) oxide, CuO, can be reduced to copper metal with hydrogen at higher temperatures.

$$CuO(s) + H_2(g) \longrightarrow Cu(s) + H_2O(g)$$

Is this reaction product- or reactant-favored under standard conditions at 298 K?

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If copper metal is heated in air, a black film of CuO forms on the surface. In this photo the heated bar, covered with a black CuO film, has been bathed in hydrogen gas. Black, solid CuO is reduced rapidly to copper at higher temperatures.

67. ▲ Consider the formation of NO(g) from its elements.

$$N_2(g) + O_2(g) \longrightarrow 2\,NO(g)$$

   (a) Calculate K_p at 25 °C. Is the reaction product-favored at this temperature?
   (b) Assuming $\Delta H°_{rxn}$ and $\Delta S°_{rxn}$ are nearly constant with temperature, calculate $\Delta G°_{rxn}$ at 700 °C. Estimate K_p from the new value of $\Delta G°_{rxn}$ at 700 °C. Is the reaction product-favored at 700 °C?
   (c) Using K_p at 700 °C, calculate the equilibrium partial pressures of the three gases if you mix 1.00 bar each of N_2 and O_2.

68. ▲ Silver(I) oxide can be formed by the reaction of silver metal and oxygen.

$$4\,Ag(s) + O_2(g) \longrightarrow 2\,Ag_2O(s)$$

   (a) Calculate $\Delta H°_{rxn}$, $\Delta S°_{rxn}$, and $\Delta G°_{rxn}$ for the reaction.
   (b) What is the pressure of O_2 in equilibrium with Ag and Ag_2O at 25 °C?
   (c) At what temperature would the pressure of O_2 in equilibrium with Ag and Ag_2O become equal to 1.00 bar?

69. Calculate $\Delta G_f°$ for HI(g) at 350 °C, given the following equilibrium partial pressures: $P(H_2) = 0.132$ bar, $P(I_2) = 0.295$ bar, and $P(HI) = 1.61$ bar. At 350 °C and 1 bar, I_2 is a gas.

$$\tfrac{1}{2}\,H_2(g) + \tfrac{1}{2}\,I_2(g) \rightleftharpoons HI(g)$$

70. Calculate the entropy change for dissolving HCl gas in water. Is the sign of $\Delta S°$ what you expected? Why or why not?

71. ▲ Mercury vapor is dangerous because it can be breathed into the lungs. We wish to estimate the vapor pressure of mercury at two different temperatures from the following data:

	ΔH_f° (kJ/mol)	S° (J/K · mol)	ΔG_f° (kJ/mol)
Hg(ℓ)	0	76.02	0
Hg(g)	61.38	174.97	31.88

Estimate the temperature at which K_p for the process $Hg(\ell) \longrightarrow Hg(g)$ is equal to (a) 1.00 and (b) 1/760. What is the vapor pressure at each of these temperatures? (Experimental vapor pressures are 1.00 mm Hg at 126.2 °C and 1.00 bar at 356.6 °C.) (Note: The temperature at which $P = 1.00$ bar can be calculated from thermodynamic data. To find the other temperature, you will need to use the temperature for $P = 1.00$ bar and the Clausius-Clapeyron equation on page 612.)

72. ■ Some metal oxides can be decomposed to the metal and oxygen under reasonable conditions. Is the decomposition of silver(I) oxide product-favored at 25 °C?

$$2\ Ag_2O(s) \longrightarrow 4\ Ag(s) + O_2(g)$$

If not, can it become so if the temperature is raised? At what temperature is the reaction product-favored?

Summary and Conceptual Questions

The following questions may use concepts from the preceding chapters.

73. Based on your experience and common sense, which of the following processes would you describe as product-favored and which as reactant-favored under standard conditions?
   (a) $Hg(\ell) \longrightarrow Hg(s)$
   (b) $H_2O(g) \longrightarrow H_2O(\ell)$
   (c) $2\ HgO(s) \longrightarrow Hg(\ell) + O_2(g)$
   (d) $C(s) + O_2(g) \longrightarrow CO_2(g)$
   (e) $NaCl(s) \longrightarrow NaCl(aq)$
   (f) $CaCO_3(s) \longrightarrow Ca^{2+}(aq) + CO_3^{2-}(aq)$

74. Explain why each of the following statements is incorrect.
   (a) Entropy increases in all spontaneous reactions.
   (b) Reactions with a negative free energy change ($\Delta G^\circ_{rxn} < 0$) are product-favored and occur with rapid transformation of reactants to products.
   (c) All spontaneous processes are exothermic.
   (d) Endothermic processes are never spontaneous.

75. Decide whether each of the following statements is true or false. If false, rewrite it to make it true.
   (a) The entropy of a substance increases on going from the liquid to the vapor state at any temperature.
   (b) An exothermic reaction will always be spontaneous.
   (c) Reactions with a positive ΔH°_{rxn} and a positive ΔS°_{rxn} can never be product-favored.
   (d) If ΔG°_{rxn} for a reaction is negative, the reaction will have an equilibrium constant greater than 1.

76. Under what conditions is the entropy of a pure substance 0 J/K · mol? Could a substance at standard conditions have a value of 0 J/K · mol? A negative entropy value? Are there any conditions under which a substance will have negative entropy? Explain your answer.

77. In Chapter 14 you learned that entropy, as well as enthalpy, plays a role in the solution process. If ΔH° for the solution process is zero, explain how the process can be driven by entropy.

78. Draw a diagram like that in Figure 19.13 for a reactant-favored process.

79. Write a chemical equation for the oxidation of $C_2H_6(g)$ by $O_2(g)$ to form $CO_2(g)$ and $H_2O(g)$. Defining this as the system:
   (a) Predict whether the signs of ΔS°_{sys}, ΔS°_{surr}, and ΔS°_{univ} will be greater than zero, equal to zero, or less than zero. Explain your prediction.
   (b) Predict the signs of ΔH° and ΔG°. Explain how you made this prediction.
   (c) Will the value of K_p be very large, very small, or near 1? Will the equilibrium constant, K_p, for this system be larger or smaller at temperatures greater than 298 K? Explain how you made this prediction.

80. The normal melting point of benzene, C_6H_6, is 5.5 °C. For the process of melting, what is the sign of each of the following?
   (a) ΔH°
   (b) ΔS°
   (c) ΔG° at 5.5 °C
   (d) ΔG° at 0.0 °C
   (e) ΔG° at 25.0°C

81. Explain why the entropy of the system increases on dissolving solid NaCl in water {$S^\circ[NaCl(s)] = 72.1$ J/K · mol and $S^\circ[NaCl(aq)] = 115.5$ J/K · mol}.

82. For each of the following processes, give the algebraic sign of ΔH°, ΔS°, and ΔG°. No calculations are necessary; use your common sense.
   (a) The decomposition of liquid water to give gaseous oxygen and hydrogen, a process that requires a considerable amount of energy.
   (b) Dynamite is a mixture of nitroglycerin, $C_3H_5N_3O_9$, and diatomaceous earth. The explosive decomposition of nitroglycerin gives gaseous products such as water, CO_2, and others; much heat is evolved.
   (c) The combustion of gasoline in the engine of your car, as exemplified by the combustion of octane.

$$2\ C_8H_{18}(g) + 25\ O_2(g) \longrightarrow 16\ CO_2(g) + 18\ H_2O(g)$$

83. Iodine, I_2, dissolves readily in carbon tetrachloride. For this process, $\Delta H^\circ = 0$ kJ/mol.

$$I_2(s) \longrightarrow I_2\ (\text{in } CCl_4 \text{ solution})$$

What is the sign of ΔG°_{rxn}? Is the dissolving process entropy-driven or enthalpy-driven? Explain briefly.

84. The *Desert Refrigerator* was described on page 232 as an example of the validity of the second law of thermodynamics. Example how the second law applies to this simple but useful device.

85. “Heater Meals” are food packages that contain their own heat source. Just pour water into the heater unit, wait a few minutes, and voila! You have a hot meal.

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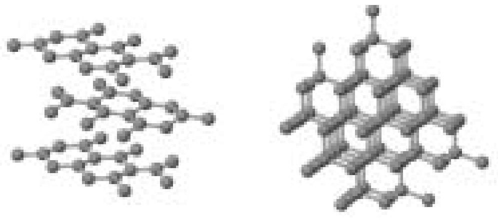
The heat for the heater unit is developed by the reaction of magnesium with water.

$$Mg(s) + 2\ H_2O(\ell) \longrightarrow Mg(OH)_2(s) + H_2(g)$$

(a) Confirm that this is a spontaneous reaction.

(b) What mass of magnesium is required to produce sufficient energy to heat 225 mL of water (density = 0.995 g/mL) from 25 °C to the boiling point?

86. The formation of diamond from graphite is a process of considerable importance.



(a) Using data in Appendix L, calculate ΔS°_{univ}, ΔH°, and ΔG° for this process.

(b) The calculations will suggest that this process is not possible under any conditions. However, the synthesis of diamonds by this reaction is a commercial process. How can this contradiction be rationalized? (Note: In the synthesis, high pressures and temperatures are used.)

87. Oxygen dissolved in water can cause corrosion in hot-water heating systems. To remove oxygen, hydrazine (N_2H_4) is often added. Hydrazine reacts with dissolved O_2 to form water and N_2.

(a) Write a balanced chemical equation for the reaction of hydrazine and oxygen. Identify the oxidizing and reducing agents in this redox reaction.

(b) Calculate ΔH°, ΔS°, and ΔG° for this reaction.

(c) Because this is an exothermic reaction, heat is evolved. What temperature change is expected in a heating system containing 5.5×10^4 L of water? (Assume no heat is lost to the surroundings.)

(d) The mass of a hot-water heating system is 5.5×10^4 Kg. What amount of O_2 (in moles) would be present in this system if it is filled with water saturated with O_2? (The solubility of O_2 in water at 25 °C is 0.000434 g per 100 g of water.)

(e) Assume hydrazine is available as a 5.0% solution in water. What mass of this solution should be added to totally consume the dissolved O_2 (described in part d)?

(f) Assuming the N_2 escapes as a gas, calculate the volume of $N_2(g)$ (measured at standard conditions) that will be produced.

88. If gaseous H_2 and O_2 are carefully mixed and left alone, they can remain intact for millions of years. Is this “stability” a function of thermodynamics or of kinetics? (You may wish to review the General ChemistryNow CD-ROM or website Screen 6.3.)

89. Use the simulation on the General ChemistryNow CD-ROM or website Screen 19.6 to answer the following questions regarding the reaction of NO and Cl_2 to produce NOCl.

(a) What is ΔS°_{sys} at 400 K for this reaction?

(b) Does ΔS°_{sys} change with temperature?

(c) Does ΔS°_{surr} change with temperature?

(d) Does ΔS°_{surr} always change with an increase in temperature?

(e) Do exothermic reactions always lead to positive values of ΔS°_{surr}?

(f) Is the NO + Cl_2 reaction spontaneous at 400 K? At 700 K?

90. Use the simulation on the General ChemistryNow CD-ROM or website Screen 19.6 to answer the following questions.

(a) Does the spontaneity of the decomposition of CH_3OH change as the temperature increases?

(b) Is there a temperature between 400 K and 1000 K at which the decomposition is spontaneous?

91. Use the simulation on the General ChemistryNow CD-ROM or website Screen 19.8 to answer the following questions.

(a) Consider the reaction of Fe_2O_3 and C. How does ΔG°_{rxn} vary with temperature? Is there a temperature at which the reaction is spontaneous?

(b) Consider the reaction of HCl and Na_2CO_3. Is there a temperature at which the reaction is no longer spontaneous?

(c) Why is the spontaneity of a reaction dependent or independent of temperature?

92. The General ChemistryNow CD-ROM or website Screen 19.9 considers the relationships among thermodynamics, the equilibrium constant, and kinetics. Use the simulation to consider the outcome of the reaction sequence

$$A \rightleftharpoons B \quad \text{and} \quad B \rightleftharpoons C$$

(a) Set up the activation energy diagram with $\Delta E_a(1) = 18$ kJ, $\Delta G^\circ(1) = 7$ kJ, $\Delta E_a(2) = 13$ kJ, and $\Delta G^\circ(2) = -22$ kJ. (Energies need only be approximate.) When the system reaches equilibrium, will there be an appreciable concentration of B? Which species predominates? Explain the results.

(b) Leave the activation energy values the same as in (a) but make $\Delta G^\circ(1) = 10$ kJ and $\Delta G^\circ(2) = -10$ kJ. When equilibrium is attained, what are the relative amounts of A, B, and C? Explain the results.