16 Spontaneity, Entropy, and Free Energy

Contents

Solid carbon dioxide (dry ice), when placed in water, causes violent bubbling as gaseous CO_2 is released. The "fog" is moisture condensed from the cold air.

The *first law of thermodynamics* is a statement of the law of conservation of energy: Energy can be neither created nor destroyed. In other words, *the energy of the universe is constant.* Although the total energy is constant, the various forms of energy can be interchanged in physical and chemical processes. For example, if you drop a book, some of the initial potential energy of the book is changed to kinetic energy, which is then transferred to the atoms in the air and the floor as random motion. The net effect of this process is to change a given quantity of potential energy to exactly the same quantity of thermal energy. Energy has been converted from one form to another, but the same quantity of energy exists before and after the process.

Now let's consider a chemical example. When methane is burned in excess oxygen, the major reaction is

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g) + \text{energy}$$

This reaction produces a quantity of energy, which is released as heat. This energy flow results from the lowering of the potential energy stored in the bonds of CH_4 and O_2 as they react to form CO_2 and H_2O. This is illustrated in Fig. 16.1. Potential energy has been converted to thermal energy, but the energy content of the universe has remained constant in accordance with the first law of thermodynamics.

The first law of thermodynamics is used mainly for energy bookkeeping, that is, to answer such questions as

How much energy is involved in the change?

Does energy flow into or out of the system?

What form does the energy finally assume?

The first law of thermodynamics: The energy of the universe is constant.

Although the first law of thermodynamics provides the means for accounting for energy, it gives no hint as to why a particular process occurs in a given direction. This is the main question to be considered in this chapter.

16.1 Spontaneous Processes and Entropy

Spontaneous does not mean fast.

A process is said to be *spontaneous* if it *occurs without outside intervention.* **Spontaneous processes** may be fast or slow. As we will see in this chapter, thermodynamics can tell us the *direction* in which a process will occur but can say nothing about the *speed* of the process. As we saw in Chapter 12, the rate of a reaction depends on many factors, such as activation energy, temperature, concentration, and catalysts, and we were able to explain these effects using a simple collision model. In describing a chemical reaction, the discipline of chemical kinetics focuses on the pathway between reactants and products; thermodynamics considers only the initial and final states and does not require knowledge of the pathway between reactants and products (see Fig. 16.2).

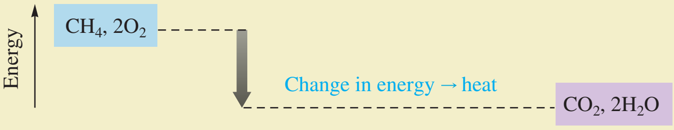


FIGURE 16.1
When methane and oxygen react to form carbon dioxide and water, the products have lower potential energy than the reactants. This change in potential energy results in energy flow (heat) to the surroundings.

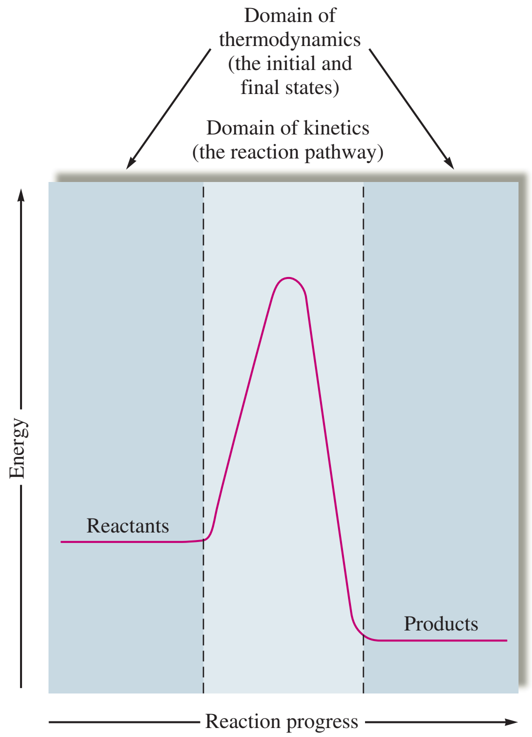


FIGURE 16.2
The rate of a reaction depends on the pathway from reactants to products; this is the domain of kinetics. Thermodynamics tells us whether a reaction is spontaneous based only on the properties of the reactants and products. The predictions of thermodynamics do not require knowledge of the pathway between reactants and products.

In summary, thermodynamics lets us predict whether a process will occur but gives no information about the amount of time required for the process. For example, according to the principles of thermodynamics, a diamond should change spontaneously to graphite. The fact that we do not observe this process does not mean the prediction is wrong; it simply means the process is very slow. Thus we need both thermodynamics and kinetics to describe reactions fully.

To explore the idea of spontaneity, consider the following physical and chemical processes:

A ball rolls down a hill but never spontaneously rolls back up the hill.

If exposed to air and moisture, steel rusts spontaneously. However, the iron oxide in rust does not spontaneously change back to iron metal and oxygen gas.

A gas fills its container uniformly. It never spontaneously collects at one end of the container.

Heat flow always occurs from a hot object to a cooler one. The reverse process never occurs spontaneously.

Wood burns spontaneously in an exothermic reaction to form carbon dioxide and water, but wood is not formed when carbon dioxide and water are heated together.

At temperatures below 0°C, water spontaneously freezes, and at temperatures above 0°C, ice spontaneously melts.

What thermodynamic principle will provide an explanation of why, under a given set of conditions, each of these diverse processes occurs in one direction and never in the reverse? In searching for an answer, we could explain the behavior of a ball on a hill in terms of gravity. But what does gravity have to do with the rusting of a nail or the freezing of water? Early developers of thermodynamics thought that exothermicity might be the key—that a process would be spontaneous if it were exothermic. Although this factor

Plant materials burn to form carbon dioxide and water.

does appear to be important, since many spontaneous processes are exothermic, it is not the total answer. For example, the melting of ice, which occurs spontaneously at temperatures greater than 0°C, is an endothermic process.

What common characteristic causes the processes listed above to be spontaneous in one direction only? After many years of observation, scientists have concluded that the characteristic common to all spontaneous processes is an increase in a property called **entropy,** denoted by the symbol S. *The driving force for a spontaneous process is an increase in the entropy of the universe.*

What is entropy? Although there is no simple definition that is completely accurate, *entropy can be viewed as a measure of molecular randomness or disorder.* The natural progression of things is from order to disorder, from lower entropy to higher entropy. To illustrate the natural tendency toward disorder, you only have to think about the condition of your room. Your room naturally tends to get messy (disordered), because an ordered room requires everything to be in its place. There are simply many more ways for things to be out of place than for them to be in their places.

A disordered pile of playing cards.

Probability refers to likelihood.

As another example, suppose you have a deck of playing cards ordered in some particular way. You throw these cards into the air and pick them all up at random. Looking at the new sequence of the cards, you would be very surprised to find that it matched the original order. Such an event would be possible, but *very improbable.* There are billions of ways for the deck to be disordered, but only one way to be ordered according to your definition. Thus the chances of picking the cards up out of order are much greater than the chance of picking them up in order. It is natural for disorder to increase.

Entropy is a thermodynamic function that describes the *number of arrangements* (positions and/or energy levels) that are *available to a system* existing in a given state. Entropy is closely associated with probability. The key concept is that the more ways a particular state can be achieved, the greater is the likelihood (probability) of finding that state. In other words, *nature spontaneously proceeds toward the states that have the highest probabilities of existing.* This conclusion is not surprising at all. The difficulty comes in connecting this concept to real-life processes. For example, what does the spontaneous rusting of steel have to do with probability? Understanding the connection between entropy and spontaneity will allow us to answer such questions. We will begin to explore this connection by considering a very simple process, the expansion of an ideal gas into

WWW Visualization: Entropy

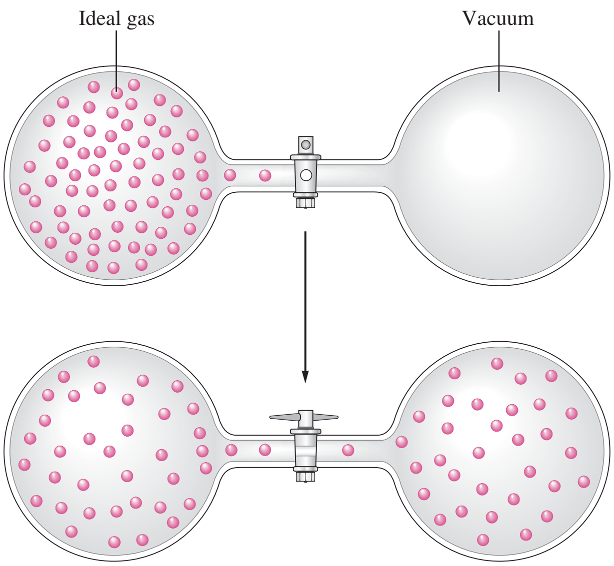
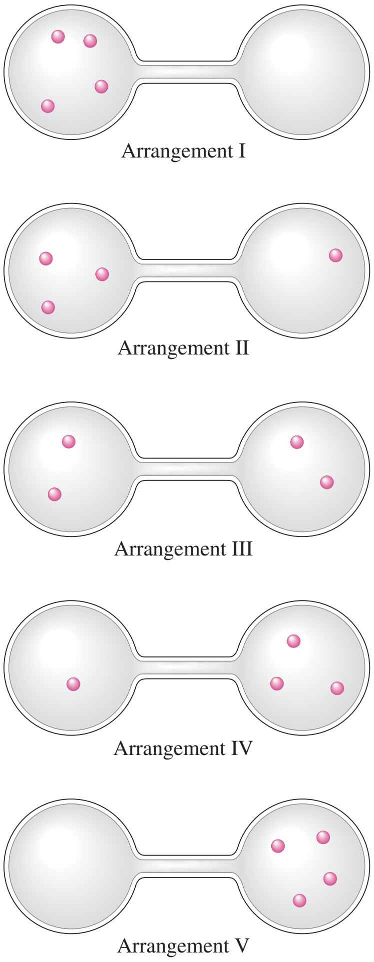


FIGURE 16.3
The expansion of an ideal gas into an evacuated bulb.


Arrangement I

Arrangement II

Arrangement III

Arrangement IV

Arrangement V

FIGURE 16.4
Possible arrangements (states) of four molecules in a two-bulbed flask.

a vacuum, as represented in Fig. 16.3. Why is this process spontaneous? The driving force is probability. Because there are more ways of having the gas evenly spread throughout the container than there are ways for it to be in any other possible state, the gas spontaneously attains the uniform distribution.

To understand this conclusion, we will greatly simplify the system and consider the possible arrangements of only four gas molecules in the two-bulbed container (Fig. 16.4). How many ways can each arrangement (state) be achieved? Arrangements I and V can be achieved in only one way—all the molecules must be in one end. Arrangements II and V can be achieved in four ways, as shown in Table 16.1. Each configuration that gives a particular arrangement is called a *microstate.* Arrangement I has one microstate, and arrangement II has four microstates. Arrangement III can be achieved in six ways (six microstates), as shown in Table 16.1. *Which arrangement is most likely to occur?* The one that can be achieved in the greatest number of ways. Thus arrangement III is most probable. The relative probabilities of arrangements III, II, and I are 6 : 4 : 1. We have discovered an important principle: The probability of occurrence of a particular arrangement (state) depends on the number of ways (microstates) in which that arrangement can be achieved.

The consequences of this principle are dramatic for large numbers of molecules. One gas molecule in the flask in Fig. 16.4 has one chance in two of being in the left bulb. We say that the probability of finding the molecule in the left bulb is $\frac{1}{2}$. For two molecules in the flask, there is one chance in two of finding each molecule in the left bulb, so there is one chance in four ($\frac{1}{2} \times \frac{1}{2} = \frac{1}{4}$) that *both* molecules will be in the left bulb. As the number of molecules increases, the relative probability of finding all of them in the left bulb decreases, as shown in Table 16.2. For 1 mole of gas, the probability of finding all the molecules in the left bulb is so small that this arrangement would "never" occur.

Thus a gas placed in one end of a container will spontaneously expand to fill the entire vessel evenly because, for a large number of gas molecules, there is a huge number of microstates in which equal numbers of molecules are in both ends. On the other hand, the opposite process,

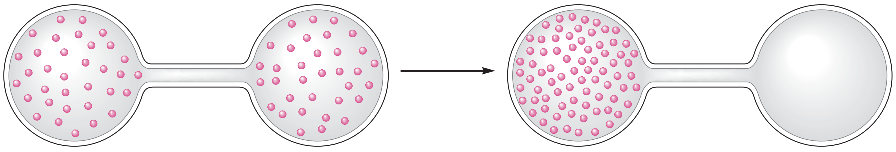


TABLE 16.1 The Microstates That Give a Particular Arrangement (State)

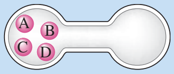
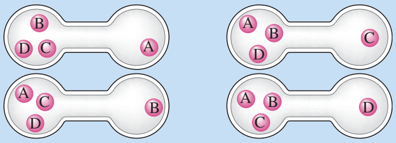
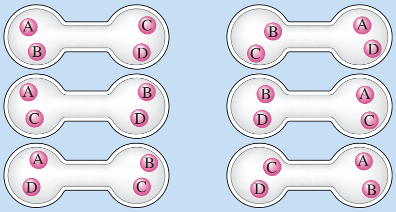
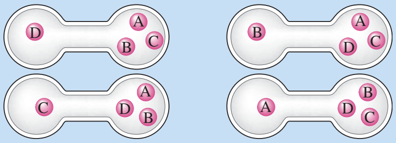
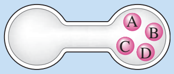
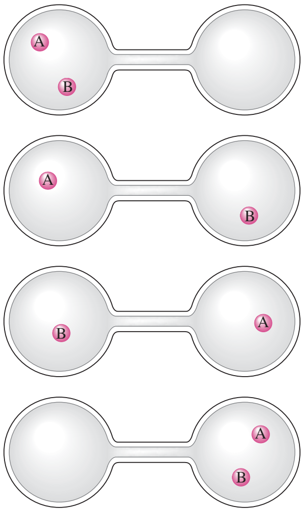
Arrangement	Microstates
I	
II	
III	
IV	
V	

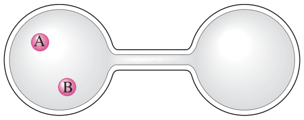
TABLE 16.2 Probability of Finding All the Molecules in the Left Bulb as a Function of the Total Number of Molecules

Number of Molecules	Relative Probability of Finding All Molecules in the Left Bulb
1	$\frac{1}{2}$
2	$\frac{1}{2}\times\frac{1}{2}=\frac{1}{2^2}=\frac{1}{4}$
3	$\frac{1}{2}\times\frac{1}{2}\times\frac{1}{2}=\frac{1}{2^3}=\frac{1}{8}$
5	$\frac{1}{2}\times\frac{1}{2}\times\frac{1}{2}\times\frac{1}{2}\times\frac{1}{2}=\frac{1}{2^5}=\frac{1}{32}$
10	$\frac{1}{2^{10}}=\frac{1}{1024}$
n	$\frac{1}{2^n}=\left(\frac{1}{2}\right)^n$
6×10^{23} (1 mole)	$\left(\frac{1}{2}\right)^{6\times10^{23}}\approx10^{-(2\times10^{23})}$

For two molecules in the flask, there are four possible microstates:



Thus there is one chance in four of finding



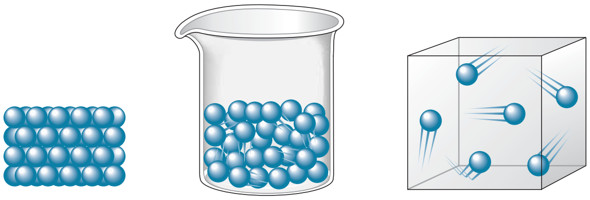
although not impossible, is *highly* improbable, since only one microstate leads to this arrangement. Therefore, this process does not occur spontaneously.

The type of probability we have been considering in this example is called **positional probability** because it depends on the number of configurations in space (positional microstates) that yield a particular state. A gas expands into a vacuum to give a uniform distribution because the expanded state has the highest positional probability, that is, the largest entropy, of the states available to the system.

Solid, liquid, and gaseous states were compared in Chapter 10.

Solids are more ordered than liquids or gases and thus have lower entropy.

Positional probability is also illustrated by changes of state. In general, positional entropy increases in going from solid to liquid to gas. A mole of a substance has a much smaller volume in the solid state than it does in the gaseous state. In the solid state, the molecules are close together, with relatively few positions available to them; in the gaseous state, the molecules are far apart, with many more positions available to them. The liquid state is closer to the solid state than it is to the gaseous state in these terms. We can summarize these comparisons as follows:



$$S_{\text{solid}} < S_{\text{liquid}} \ll S_{\text{gas}}$$

The tendency to mix is due to the increased volume available to the particles of each component of the mixture. For example, when two liquids are mixed, the molecules of each liquid have more available volume and thus more available positions.

Positional entropy is also very important in the formation of solutions. In Chapter 11 we saw that solution formation is favored by the natural tendency for substances to mix. We can now be more precise. The entropy change associated with the mixing of two pure substances is expected to be positive. An increase in entropy is expected because there are many more microstates for the mixed condition than for the separated condition. This effect is due principally to the increased volume available to a given "particle" after mixing occurs. For example, when two liquids are mixed to form a solution, the molecules of each liquid have more available volume and thus more available positions. Therefore, the increase in positional entropy associated with mixing favors the formation of solutions.

Sample Exercise 16.1 Positional Entropy

For each of the following pairs, choose the substance with the higher positional entropy (per mole) at a given temperature.

a. Solid CO_2 and gaseous CO_2
b. N_2 gas at 1 atm and N_2 gas at 1.0×10^{-2} atm

Solution

a. Since a mole of gaseous CO_2 has the greater volume by far, the molecules have many more available positions than in a mole of solid CO_2. Thus gaseous CO_2 has the higher positional entropy.
b. A mole of N_2 gas at 1×10^{-2} atm has a volume 100 times that (at a given temperature) of a mole of N_2 gas at 1 atm. Thus N_2 gas at 1×10^{-2} atm has the higher positional entropy.

See Exercise 16.23.

Sample Exercise 16.2

Predicting Entropy Changes

Predict the sign of the entropy change for each of the following processes.

a. Solid sugar is added to water to form a solution.
b. Iodine vapor condenses on a cold surface to form crystals.

Solution

a. The sugar molecules become randomly dispersed in the water when the solution forms and thus have access to a larger volume and a larger number of possible positions. The positional disorder is increased, and there will be an increase in entropy. ΔS is positive, since the final state has a larger entropy than the initial state, and $\Delta S = S_{\text{final}} - S_{\text{initial}}$.
b. Gaseous iodine is forming a solid. This process involves a change from a relatively large volume to a much smaller volume, which results in lower positional disorder. For this process ΔS is negative (the entropy decreases).

See Exercise 16.24.

16.2 Entropy and the Second Law of Thermodynamics

The total energy of the universe is constant, but the entropy is increasing.

We have seen that processes are spontaneous when they result in an increase in disorder. Nature always moves toward the most probable state available to it. We can state this principle in terms of entropy: *In any spontaneous process there is always an increase in the entropy of the universe.* This is the **second law of thermodynamics.** Contrast this with the first law of thermodynamics, which tells us that the energy of the universe is constant. Energy is conserved in the universe, but entropy is not. In fact, the second law can be paraphrased as follows: *The entropy of the universe is increasing.*

As in Chapter 6, we find it convenient to divide the universe into a system and the surroundings. Thus we can represent the change in the entropy of the universe as

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

where ΔS_{sys} and ΔS_{surr} represent the changes in entropy that occur in the system and surroundings, respectively.

To predict whether a given process will be spontaneous, we must know the sign of ΔS_{univ}. If ΔS_{univ} is positive, the entropy of the universe increases, and the process is spontaneous in the direction written. If ΔS_{univ} is negative, the process is spontaneous in the *opposite* direction. If ΔS_{univ} is zero, the process has no tendency to occur, and the system is at equilibrium. To predict whether a process is spontaneous, we must consider the entropy changes that occur both in the system and in the surroundings and then take their sum.

Sample Exercise 16.3

The Second Law

In a living cell, large molecules are assembled from simple ones. Is this process consistent with the second law of thermodynamics?

Solution

To reconcile the operation of an order-producing cell with the second law of thermodynamics, we must remember that ΔS_{univ}, not ΔS_{sys}, must be positive for a process to be spontaneous. A process for which ΔS_{sys} is negative can be spontaneous if the associated ΔS_{surr} is both larger and positive. The operation of a cell is such a process.

See Questions 16.7 and 16.8.

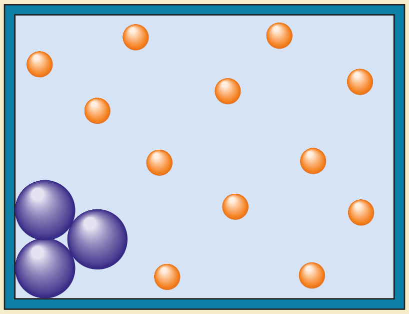
CHEMICAL IMPACT

Entropy: An Organizing Force?

In this text we have emphasized the meaning of the second law of thermodynamics—that the entropy of the universe is always increasing. Although the results of all our experiments support this conclusion, this does not mean that order cannot appear spontaneously in a given part of the universe. The best example of this phenomenon involves the assembly of cells in living organisms. Of course, when a process that creates an ordered system is examined in detail, it is found that other parts of the process involve an increase in disorder such that the sum of all the entropy changes is positive. In fact, scientists are now finding that the search for maximum entropy in one part of a system can be a powerful force for organization in another part of the system.

To understand how entropy can be an organizing force, look at the accompanying figure. In a system containing large and small "balls" as shown in the figure, the small balls can "herd" the large balls into clumps in the corners and near the walls. This clears out the maximum space for the small balls so that they can move more freely, thus maximizing the entropy of the system, as demanded by the second law of thermodynamics.

In essence, the ability to maximize entropy by sorting different-sized objects creates a kind of attractive force, called a *depletion,* or *excluded-volume, force.* These "entropic forces" operate for objects in the size range of approximately 10^{-8} to approximately 10^{-6} m. For entropy-induced ordering to occur, the particles must be constantly jostling each other and must be constantly agitated by solvent molecules, thus making gravity unimportant.



There is increasing evidence that entropic ordering is important in many biological systems. For example, this phenomenon seems to be responsible for the clumping of sickle-cell hemoglobin in the presence of much smaller proteins that act as the "smaller balls." Entropic forces also have been linked to the clustering of DNA in cells without nuclei, and Allen Minton of the National Institutes of Health in Bethesda, Maryland, is studying the role of entropic forces in the binding of proteins to cell membranes.

Entropic ordering also appears in nonbiological settings, especially in the ways polymer molecules clump together. For example, polymers added to paint to improve the flow characteristics of the paint actually caused it to coagulate because of depletion forces.

Thus, as you probably have concluded already, entropy is a complex issue. As entropy drives the universe to its ultimate death of maximum chaos, it provides some order along the way.

16.3 The Effect of Temperature on Spontaneity

To explore the interplay of ΔS_{sys} and ΔS_{surr} in determining the sign of ΔS_{univ}, we will first discuss the change of state for one mole of water from liquid to gas,

$$H_2O(l) \longrightarrow H_2O(g)$$

considering the water to be the system and everything else the surroundings.

What happens to the entropy of water in this process? A mole of liquid water (18 grams) has a volume of approximately 18 mL. A mole of gaseous water at 1 atmosphere and 100°C occupies a volume of approximately 31 liters. Clearly, there are many more positions available to the water molecules in a volume of 31 L than in 18 mL, and the vaporization of water is favored by this increase in positional probability. That is, for this process the entropy of the system increases; ΔS_{sys} has a positive sign.

What about the entropy change in the surroundings? Although we will not prove it here, entropy changes in the surroundings are determined primarily by the flow of energy into or out of the system as heat. To understand this, suppose an exothermic process transfers 50 J of energy as heat to the surroundings, where it becomes thermal energy, that is, kinetic energy associated with the random motions of atoms. Thus this flow of energy into the surroundings increases the random motions of atoms there and thereby increases the entropy of the surroundings. The sign of ΔS_{surr} is positive. When an endothermic process occurs in the system, it produces the opposite effect. Heat flows from the surroundings to the system, and the random motions of the atoms in the surroundings decrease, decreasing the entropy of the surroundings. The vaporization of water is an endothermic process. Thus, for this change of state, ΔS_{surr} is negative.

Boiling water to form steam increases its volume and thus its entropy.

In an endothermic process, heat flows from the surroundings into the system. In an exothermic process, heat flows into the surroundings from the system.

Remember it is the sign of ΔS_{univ} that tells us whether the vaporization of water is spontaneous. We have seen that ΔS_{sys} is positive and favors the process and that ΔS_{surr} is negative and unfavorable. Thus the components of ΔS_{univ} are in opposition. Which one controls the situation? The answer *depends on the temperature.* We know that at a pressure of 1 atmosphere, water changes spontaneously from liquid to gas at all temperatures above 100°C. Below 100°C, the opposite process (condensation) is spontaneous.

Since ΔS_{sys} and ΔS_{surr} are in opposition for the vaporization of water, the temperature must have an effect on the relative importance of these two terms. To understand why this is so, we must discuss in more detail the factors that control the entropy changes in the surroundings. The central idea is that *the entropy changes in the surroundings are primarily determined by heat flow.* An exothermic process in the system increases the entropy of the surroundings, because the resulting energy flow increases the random motions in the surroundings. This means that exothermicity is an important driving force for spontaneity. In earlier chapters we have seen that a system tends to undergo changes that lower its energy. We now understand the reason for this tendency. When a system at constant temperature moves to a lower energy, the energy it gives up is transferred to the surroundings, leading to an increase in entropy there.

The significance of exothermicity as a driving force *depends on the temperature at which the process occurs.* That is, the magnitude of ΔS_{surr} depends on the temperature at which the heat is transferred. We will not attempt to prove this fact here. Instead, we offer an analogy. Suppose that you have $50 to give away. Giving it to a millionaire would not create much of an impression—a millionaire has money to spare. However, to a poor college student, $50 would represent a significant sum and would be received with considerable joy. The same principle can be applied to energy transfer via the flow of heat. If 50 J of energy is transferred to the surroundings, the impact of that event depends greatly on the temperature. If the temperature of the surroundings is very high, the atoms there are in rapid motion. The 50 J of energy will not make a large percent change in these motions. On the other hand, if 50 J of energy is transferred to the surroundings at a very low temperature, where atomic motion is slow, the energy will cause a large percent change in these motions. *The impact of the transfer of a given quantity of energy as heat to or from the surroundings will be greater at lower temperatures.*

For our purposes, there are two important characteristics of the entropy changes that occur in the surroundings:

In a process occurring at constant temperature, the tendency for the system to lower its energy results from the positive value of ΔS_{surr}.

1. *The sign of ΔS_{surr} depends on the direction of the heat flow.* At constant temperature, an exothermic process in the system causes heat to flow into the surroundings, increasing the random motions and thus the entropy of the surroundings. For this case, ΔS_{surr} is positive. The opposite is true for an endothermic process in a system at constant temperature. Note that although the driving force described here really results from the change in entropy, it is often described in terms of energy: Nature tends to seek the lowest possible energy.
2. *The magnitude of ΔS_{surr} depends on the temperature.* The transfer of a given quantity of energy as heat produces a much greater percent change in the randomness of the surroundings at a low temperature than it does at a high temperature. Thus ΔS_{surr} depends directly on the quantity of heat transferred and inversely on temperature. In

other words, the tendency for the system to lower its energy becomes a more important driving force at lower temperatures.

$$\begin{array}{c}\text{Driving force}\\\text{provided by}\\\text{the energy flow}\\\text{(heat)}\end{array} = \begin{array}{c}\text{magnitude of the}\\\text{entropy change of}\\\text{the surroundings}\end{array} = \frac{\text{quantity of heat (J)}}{\text{temperature (K)}}$$

These ideas are summarized as follows:

Exothermic process: ΔS_{surr} = positive

Endothermic process: ΔS_{surr} = negative

$$\text{Exothermic process:} \qquad \Delta S_{\text{surr}} = +\frac{\text{quantity of heat (J)}}{\text{temperature (K)}}$$

$$\text{Endothermic process:} \qquad \Delta S_{\text{surr}} = -\frac{\text{quantity of heat (J)}}{\text{temperature (K)}}$$

We can express ΔS_{surr} in terms of the change in enthalpy ΔH for a process occurring at constant pressure, since

$$\text{Heat flow (constant } P\text{)} = \text{change in enthalpy} = \Delta H$$

When no subscript is present, the quantity (for example, ΔH) refers to the system.

Recall that ΔH consists of two parts: a sign and a number. The *sign* indicates the direction of flow, where a plus sign means into the system (endothermic) and a minus sign means out of the system (exothermic). The *number* indicates the quantity of energy.

Combining all these concepts produces the following definition of ΔS_{surr} for a reaction that takes place under conditions of constant temperature (in kelvins) and pressure:

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

The minus sign changes the point of view from the system to the surroundings.

The minus sign is necessary because the sign of ΔH is determined with respect to the reaction system, and this equation expresses a property of the surroundings. This means that if the reaction is exothermic, ΔH has a negative sign, but since heat flows into the surroundings, ΔS_{surr} is positive.

Sample Exercise 16.4

Determining ΔS_{surr}

In the metallurgy of antimony, the pure metal is recovered via different reactions, depending on the composition of the ore. For example, iron is used to reduce antimony in sulfide ores:

$$\mathrm{Sb_2S_3}(s) + 3\mathrm{Fe}(s) \longrightarrow 2\mathrm{Sb}(s) + 3\mathrm{FeS}(s) \qquad \Delta H = -125 \text{ kJ}$$

Carbon is used as the reducing agent for oxide ores:

$$\mathrm{Sb_4O_6}(s) + 6\mathrm{C}(s) \longrightarrow 4\mathrm{Sb}(s) + 6\mathrm{CO}(g) \qquad \Delta H = 778 \text{ kJ}$$

Calculate ΔS_{surr} for each of these reactions at 25°C and 1 atm.

Solution

We use

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

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

For the sulfide ore reaction,

$$\Delta S_{\text{surr}} = -\frac{-125 \text{ kJ}}{298 \text{ K}} = 0.419 \text{ kJ/K} = 419 \text{ J/K}$$

The mineral stibnite contains Sb_2S_3.

TABLE 16.3 Interplay of ΔS_{sys} and ΔS_{surr} in Determining the Sign of ΔS_{univ}

Signs of Entropy Changes			
ΔS_{sys}	ΔS_{surr}	ΔS_{univ}	*Process Spontaneous?*
+	+	+	Yes
−	−	−	No (reaction will occur in opposite direction)
+	−	?	Yes, if ΔS_{sys} has a larger magnitude than ΔS_{surr}
−	+	?	Yes, if ΔS_{surr} has a larger magnitude than ΔS_{sys}

Note that ΔS_{surr} is positive, as it should be, since this reaction is exothermic and heat flow occurs to the surroundings, increasing the randomness of the surroundings.

For the oxide ore reaction,

$$\Delta S_{surr} = -\frac{778 \text{ kJ}}{298} = -2.61 \text{ kJ/K} = -2.61 \times 10^3 \text{ J/K}$$

In this case ΔS_{surr} is negative because heat flow occurs from the surroundings to the system.

See Exercises 16.25 and 16.26.

We have seen that the spontaneity of a process is determined by the entropy change it produces in the universe. We also have seen that ΔS_{univ} has two components, ΔS_{sys} and ΔS_{surr}. If for some process both ΔS_{sys} and ΔS_{surr} are positive, then ΔS_{univ} is positive, and the process is spontaneous. If, on the other hand, both ΔS_{sys} and ΔS_{surr} are negative, the process does not occur in the direction indicated but is spontaneous in the opposite direction. Finally, if ΔS_{sys} and ΔS_{surr} have opposite signs, the spontaneity of the process depends on the sizes of the opposing terms. These cases are summarized in Table 16.3.

We can now understand why spontaneity is often dependent on temperature and thus why water spontaneously freezes below 0°C and melts above 0°C. The term ΔS_{surr} is temperature-dependent. Since

$$\Delta S_{surr} = -\frac{\Delta H}{T}$$

at constant pressure, the value of ΔS_{surr} changes markedly with temperature. The magnitude of ΔS_{surr} will be very small at high temperatures and will increase as the temperature decreases. That is, exothermicity is most important as a driving force at low temperatures.

16.4 Free Energy

The symbol G for free energy honors Josiah Willard Gibbs (1839–1903), who was professor of mathematical physics at Yale University from 1871 to 1903. He laid the foundations of many areas of thermodynamics, particularly as they apply to chemistry.

So far we have used ΔS_{univ} to predict the spontaneity of a process. However, another thermodynamic function is also related to spontaneity and is especially useful in dealing with the temperature dependence of spontaneity. This function is called the **free energy,** which is symbolized by G and defined by the relationship

$$G = H - TS$$

where H is the enthalpy, T is the Kelvin temperature, and S is the entropy.

Visualization: Spontaneous Reactions

For a process that occurs at constant temperature, the change in free energy (ΔG) is given by the equation

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

Note that all quantities here refer to the system. From this point on we will follow the usual convention that when no subscript is included, the quantity refers to the system.

To see how this equation relates to spontaneity, we divide both sides of the equation by $-T$ to produce

$$-\frac{\Delta G}{T} = -\frac{\Delta H}{T} + \Delta S$$

Remember that at constant temperature and pressure

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

So we can write

$$-\frac{\Delta G}{T} = -\frac{\Delta H}{T} + \Delta S = \Delta S_{\text{surr}} + \Delta S = \Delta S_{\text{univ}}$$

We have shown that

$$\Delta S_{\text{univ}} = -\frac{\Delta G}{T} \qquad \text{at constant } T \text{ and } P$$

This result is very important. It means that a process carried out at constant temperature and pressure will be spontaneous only if ΔG is negative. That is, *a process (at constant T and P) is spontaneous in the direction in which the free energy decreases* ($-\Delta G$ means $+\Delta S_{\text{univ}}$).

Now we have two functions that can be used to predict spontaneity: the entropy of the universe, which applies to all processes, and free energy, which can be used for processes carried out at constant temperature and pressure. Since so many chemical reactions occur under the latter conditions, free energy is the more useful to chemists.

Let's use the free energy equation to predict the spontaneity of the melting of ice:

$$H_2O(s) \longrightarrow H_2O(l)$$

for which $\Delta H° = 6.03 \times 10^3$ J/mol and $\Delta S° = 22.1$ J/K · mol

The superscript degree symbol (°) indicates all substances are in their standard states.

To review the definitions of standard states, see page 246.

Results of the calculations of ΔS_{univ} and $\Delta G°$ at -10°C, 0°C, and 10°C are shown in Table 16.4. These data predict that the process is spontaneous at 10°C; that is, ice melts at this temperature because ΔS_{univ} is positive and $\Delta G°$ is negative. The opposite is true at -10°C, where water freezes spontaneously.

Why is this so? The answer lies in the fact that ΔS_{sys} ($\Delta S°$) and ΔS_{surr} oppose each other. The term $\Delta S°$ favors the melting of ice because of the increase in positional entropy, and ΔS_{surr} favors the freezing of water because it is an exothermic process. At temperatures below

TABLE 16.4 Results of the Calculation of ΔS_{univ} and $\Delta G°$ for the Process $H_2O(s) \rightarrow H_2O(l)$ at -10°C, 0°C, and 10°C*

T (°C)	*T* (K)	$\Delta H°$ (J/mol)	$\Delta S°$ (J/K · mol)	$\Delta S_{\text{surr}} = -\frac{\Delta H°}{T}$ (J/K · mol)	$\Delta S_{\text{univ}} = \Delta S° + \Delta S_{\text{surr}}$ (J/K · mol)	$T\Delta S°$ (J/mol)	$\Delta G° = \Delta H° - T\Delta S°$ (J/mol)
-10	263	6.03×10^3	22.1	-22.9	-0.8	5.81×10^3	$+2.2 \times 10^2$
0	273	6.03×10^3	22.1	-22.1	0	6.03×10^3	0
10	283	6.03×10^3	22.1	-21.3	$+0.8$	6.25×10^3	-2.2×10^2

*Note that at 10°C, $\Delta S°$ (ΔS_{sys}) controls, and the process occurs even though it is endothermic. At -10°C, the magnitude of ΔS_{surr} is larger than that of $\Delta S°$, so the process is spontaneous in the opposite (exothermic) direction.

0°C, the change of state occurs in the exothermic direction because ΔS_{surr} is larger in magnitude than ΔS_{sys}. But above 0°C the change occurs in the direction in which ΔS_{sys} is favorable, since in this case ΔS_{sys} is larger in magnitude than ΔS_{surr}. At 0°C the *opposing tendencies just balance,* and the two states coexist; there is no driving force in either direction. An equilibrium exists between the two states of water. Note that ΔS_{univ} is equal to 0 at 0°C.

We can reach the same conclusions by examining $\Delta G°$. At $-10°$, $\Delta G°$ is positive because the $\Delta H°$ term is larger than the $T\Delta S°$ term. The opposite is true at 10°C. At 0°C, $\Delta H°$ is equal to $T\Delta S°$ and $\Delta G°$ is equal to 0. This means that solid H_2O and liquid H_2O have the same free energy at 0°C ($\Delta G° = G_{\text{liquid}} - G_{\text{solid}}$), and the system is at equilibrium.

We can understand the temperature dependence of spontaneity by examining the behavior of ΔG. For a process occurring at constant temperature and pressure,

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

If ΔH and ΔS favor opposite processes, spontaneity will depend on temperature in such a way that the exothermic direction will be favored at low temperatures. For example, for the process

$$H_2O(s) \longrightarrow H_2O(l)$$

ΔH is positive and ΔS is positive. The natural tendency for this system to lower its energy is in opposition to its natural tendency to increase its positional randomness. At low temperatures, ΔH dominates, and at high temperatures, ΔS dominates. The various possible cases are summarized in Table 16.5.

Sample Exercise 16.5

Free Energy and Spontaneity

At what temperatures is the following process spontaneous at 1 atm?

$$Br_2(l) \longrightarrow Br_2(g)$$

$$\Delta H° = 31.0\text{ kJ/mol} \quad \text{and} \quad \Delta S° = 93.0\text{ J/K}\cdot\text{mol}$$

What is the normal boiling point of liquid Br_2?

Solution

The vaporization process will be spontaneous at all temperatures where $\Delta G°$ is negative. Note that $\Delta S°$ favors the vaporization process because of the increase in positional entropy, and $\Delta H°$ favors the *opposite* process, which is exothermic. These opposite tendencies will exactly balance at the boiling point of liquid Br_2, since at this temperature liquid and gaseous Br_2 are in equilibrium ($\Delta G° = 0$). We can find this temperature by setting $\Delta G° = 0$ in the equation

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

Note that although ΔH and ΔS are somewhat temperature-dependent, it is a good approximation to assume they are constant over a relatively small temperature range.

TABLE 16.5 Various Possible Combinations of ΔH and ΔS for a Process and the Resulting Dependence of Spontaneity on Temperature

Case	Result
ΔS positive, ΔH negative	Spontaneous at all temperatures
ΔS positive, ΔH positive	Spontaneous at high temperatures (where exothermicity is relatively unimportant)
ΔS negative, ΔH negative	Spontaneous at low temperatures (where exothermicity is dominant)
ΔS negative, ΔH positive	Process not spontaneous at *any* temperature (reverse process is spontaneous at *all* temperatures)

Then $$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{3.10 \times 10^4 \text{ J/mol}}{93.0 \text{ J/K} \cdot \text{mol}} = 333 \text{ K}$$

At temperatures above 333 K, $T\Delta S^\circ$ has a larger magnitude than ΔH°, and ΔG° (or $\Delta H^\circ - T\Delta S^\circ$) is negative. Above 333 K, the vaporization process is spontaneous; the opposite process occurs spontaneously below this temperature. At 333 K, liquid and gaseous Br_2 coexist in equilibrium. These observations can be summarized as follows (the pressure is 1 atm in each case):

1. $T > 333$ K. The term ΔS° controls. The increase in entropy when liquid Br_2 is vaporized is dominant.
2. $T < 333$ K. The process is spontaneous in the direction in which it is exothermic. The term ΔH° controls.
3. $T = 333$ K. The opposing driving forces are just balanced ($\Delta G^\circ = 0$), and the liquid and gaseous phases of bromine coexist. This is the normal boiling point.

See Exercises 16.29 through 16.31.

16.5 Entropy Changes in Chemical Reactions

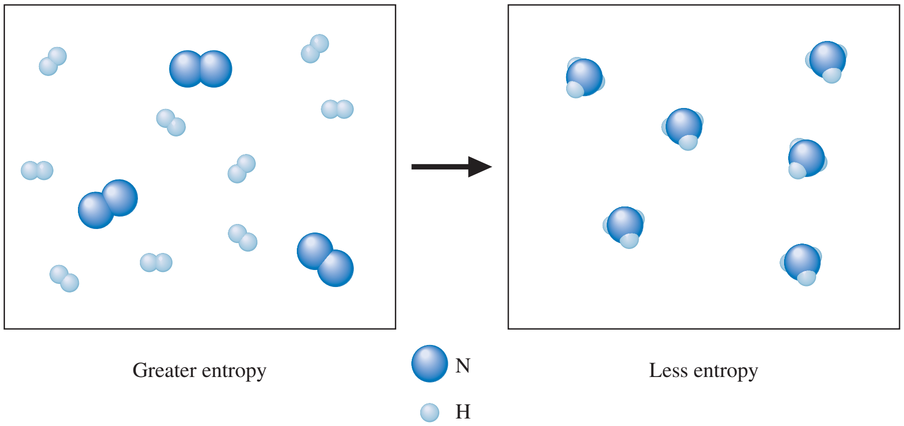
The second law of thermodynamics tells us that a process will be spontaneous if the entropy of the universe increases when the process occurs. We saw in Section 16.4 that for a process at constant temperature and pressure, we can use the change in free energy of the system to predict the sign of ΔS_{univ} and thus the direction in which it is spontaneous. So far we have applied these ideas only to physical processes, such as changes of state and the formation of solutions. However, the main business of chemistry is studying chemical reactions, and, therefore, we want to apply the second law to reactions.

First, we will consider the entropy changes accompanying chemical reactions that occur under conditions of constant temperature and pressure. As for the other types of processes we have considered, the entropy changes in the *surroundings* are determined by the heat flow that occurs as the reaction takes place. However, the entropy changes in the *system* (the reactants and products of the reaction) are determined by positional probability.

For example, in the ammonia synthesis reaction

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

four reactant molecules become two product molecules, lowering the number of independent units in the system, which leads to less positional disorder.



Fewer molecules mean fewer possible configurations. To help clarify this idea, consider a special container with a million compartments, each large enough to hold a hydrogen molecule. Thus there are a million ways one H_2 molecule can be placed in this container. But suppose we break the H—H bond and place the two independent H atoms in the same container. A little thought will convince you that there are *many* more than a million ways to place the two separate atoms. The number of arrangements possible for the two independent atoms is much greater than the number for the molecule. Thus for the process

$$H_2 \longrightarrow 2H$$

positional entropy increases.

Does positional entropy increase or decrease when the following reaction takes place?

$$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$$

In this case 9 gaseous molecules are changed to 10 gaseous molecules, and the positional entropy increases. There are more independent units as products than as reactants. In general, when a reaction involves gaseous molecules, *the change in positional entropy is dominated by the relative numbers of molecules of gaseous reactants and products.* If the number of molecules of the gaseous products is greater than the number of molecules of the gaseous reactants, positional entropy typically increases, and ΔS will be positive for the reaction.

Sample Exercise 16.6

Predicting the Sign of $\Delta S°$

Predict the sign of $\Delta S°$ for each of the following reactions.

a. The thermal decomposition of solid calcium carbonate:

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

b. The oxidation of SO_2 in air:

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

Solution

a. Since in this reaction a gas is produced from a solid reactant, the positional entropy increases, and $\Delta S°$ is positive.

b. Here three molecules of gaseous reactants become two molecules of gaseous products. Since the number of gas molecules decreases, positional entropy decreases, and $\Delta S°$ is negative.

See Exercises 16.33 and 16.34.

In thermodynamics it is the *change* in a certain function that is usually important. The change in enthalpy determines if a reaction is exothermic or endothermic at constant pressure. The change in free energy determines if a process is spontaneous at constant temperature and pressure. It is fortunate that changes in thermodynamic functions are sufficient for most purposes, since absolute values for many thermodynamic characteristics of a system, such as enthalpy or free energy, cannot be determined.

However, we can assign absolute entropy values. Consider a solid at 0 K, where molecular motion virtually ceases. If the substance is a perfect crystal, its internal arrangement is absolutely regular (see Fig. 16.5(a)). There is only *one way* to achieve this perfect order: Every particle must be in its place. For example, with N coins there is only one

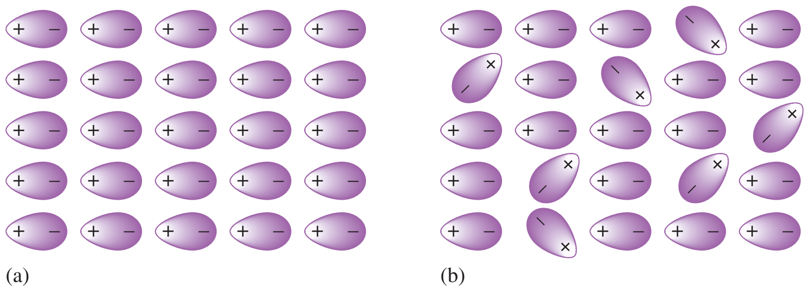


FIGURE 16.5
(a) A perfect crystal of hydrogen chloride at 0 K; the dipolar HCl molecules are represented by (+|−). The entropy is zero ($S = 0$) for this perfect crystal at 0 K.
(b) As the temperature rises above 0 K, lattice vibrations allow some dipoles to change their orientations, producing some disorder and an increase in entropy ($S > 0$).

A perfect crystal at 0 K is an unattainable ideal, taken as a standard but never actually observed.

way to achieve the state of all heads. Thus a perfect crystal represents the lowest possible entropy; that is, *the entropy of a perfect crystal at 0 K is zero.* This is a statement of the **third law of thermodynamics.**

As the temperature of a perfect crystal is increased, the random vibrational motions increase, and disorder increases within the crystal [see Fig. 16.5(b)]. Thus the entropy of a substance increases with temperature. Since S is zero for a perfect crystal at 0 K, the entropy value for a substance at a particular temperature can be calculated by knowing the temperature dependence of entropy. (We will not show such calculations here.)

The standard entropy values represent the increase in entropy that occurs when a substance is heated from 0 K to 298 K at 1 atm pressure.

The *standard entropy values* $S°$ of many common substances at 298 K and 1 atm are listed in Appendix 4. From these values you will see that the entropy of a substance does indeed increase in going from solid to liquid to gas. One especially interesting feature of this table is the very low $S°$ value for diamond. The structure of diamond is highly ordered, with each carbon strongly bound to a tetrahedral arrangement of four other carbon atoms (see Section 10.5, Fig. 10.22). This type of structure allows very little disorder and has a very low entropy, even at 298 K. Graphite has a slightly higher entropy because its layered structure allows for a little more disorder.

Because *entropy is a state function of the system* (it is not pathway-dependent), the entropy change for a given chemical reaction can be calculated by taking the difference between the standard entropy values of products and those of the reactants:

$$\Delta S°_{\text{reaction}} = \Sigma n_p S°_{\text{products}} - \Sigma n_r S°_{\text{reactants}}$$

where, as usual, Σ represents the sum of the terms. It is important to note that entropy is an extensive property (it depends on the amount of substance present). This means that the number of moles of a given reactant (n_r) or product (n_p) must be taken into account.

Sample Exercise 16.7

Calculating $\Delta S°$

Calculate $\Delta S°$ at 25°C for the reaction

$$2\text{NiS}(s) + 3\text{O}_2(g) \longrightarrow 2\text{SO}_2(g) + 2\text{NiO}(s)$$

given the following standard entropy values:

Substance	$S°$ (J/K · mol)
$\text{SO}_2(g)$	248
$\text{NiO}(s)$	38
$\text{O}_2(g)$	205
$\text{NiS}(s)$	53

Solution

Since

$$\begin{aligned}\Delta S^\circ &= \Sigma n_p S^\circ_{\text{products}} - \Sigma n_r S^\circ_{\text{reactants}}\\ &= 2S^\circ_{SO_2(g)} + 2S^\circ_{NiO(s)} - 2S^\circ_{NiS(s)} - 3S^\circ_{O_2(s)}\\ &= 2\text{ mol}\left(248\,\frac{\text{J}}{\text{K}\cdot\text{mol}}\right) + 2\text{ mol}\left(38\,\frac{\text{J}}{\text{K}\cdot\text{mol}}\right)\\ &\quad -2\text{ mol}\left(53\,\frac{\text{J}}{\text{K}\cdot\text{mol}}\right) - 3\text{ mol}\left(205\,\frac{\text{J}}{\text{K}\cdot\text{mol}}\right)\\ &= 496\text{ J/K} + 76\text{ J/K} - 106\text{ J/K} - 615\text{ J/K}\\ &= -149\text{ J/K}\end{aligned}$$

We would expect ΔS° to be negative because the number of gaseous molecules decreases in this reaction.

See Exercise 16.37.

Sample Exercise 16.8

Calculating ΔS°

Calculate ΔS° for the reduction of aluminum oxide by hydrogen gas:

$$Al_2O_3(s) + 3H_2(g) \longrightarrow 2Al(s) + 3H_2O(g)$$

Use the following standard entropy values:

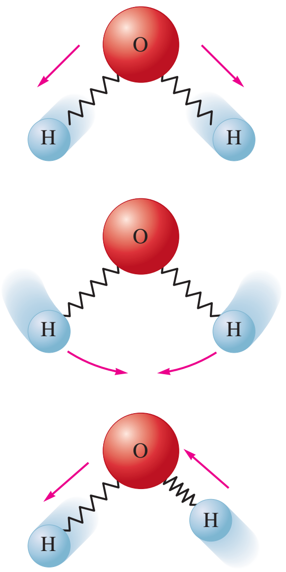
Substance	S° (J/K · mol)
$Al_2O_3(s)$	51
$H_2(g)$	131
$Al(s)$	28
$H_2O(g)$	189

Solution

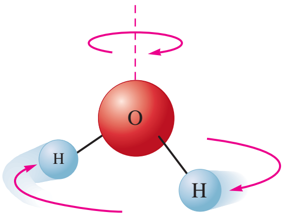
$$\begin{aligned}\Delta S^\circ &= \Sigma n_p S^\circ_{\text{products}} - \Sigma n_r S^\circ_{\text{reactants}}\\ &= 2S^\circ_{Al(s)} + 3S^\circ_{H_2O(g)} - 3S^\circ_{H_2(g)} - S^\circ_{Al_2O_3(s)}\\ &= 2\text{ mol}\left(28\,\frac{\text{J}}{\text{K}\cdot\text{mol}}\right) + 3\text{ mol}\left(189\,\frac{\text{J}}{\text{K}\cdot\text{mol}}\right)\\ &\quad -3\text{ mol}\left(131\,\frac{\text{J}}{\text{K}\cdot\text{mol}}\right) - 1\text{ mol}\left(51\,\frac{\text{J}}{\text{K}\cdot\text{mol}}\right)\\ &= 56\text{ J/K} + 567\text{ J/K} - 393\text{ J/K} - 51\text{ J/K}\\ &= 179\text{ J/K}\end{aligned}$$

See Exercises 16.38 through 16.40.

The reaction considered in Sample Exercise 16.8 involves 3 moles of hydrogen gas on the reactant side and 3 moles of water vapor on the product side. Would you expect ΔS to be large or small for such a case? We have assumed that ΔS depends on the relative numbers of molecules of gaseous reactants and products. Based on this assumption, ΔS should be near zero for this reaction. However, ΔS is large and positive. Why is this so? The large value for ΔS results from the difference in the entropy values for hydrogen gas and water vapor. The reason for this difference can be traced to the difference in molecular structure. Because it is a nonlinear, triatomic molecule, H_2O has more rotational and vibrational motions (see Fig. 16.6) than does the diatomic H_2 molecule. Thus the standard entropy value for $H_2O(g)$ is greater than that for $H_2(g)$. Generally, *the more complex the molecule, the higher the standard entropy value.*



Vibrations



Rotation

FIGURE 16.6
The H_2O molecule can vibrate and rotate in several ways, some of which are shown here. This freedom of motion leads to a higher entropy for water than for a substance like hydrogen, a simple diatomic molecule with fewer possible motions.

The value of ΔG° tells us nothing about the rate of a reaction, only its eventual equilibrium position.

16.6 Free Energy and Chemical Reactions

For chemical reactions we are often interested in the **standard free energy change** (ΔG°), *the change in free energy that will occur if the reactants in their standard states are converted to the products in their standard states.* For example, for the ammonia synthesis reaction at 25°C,

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta G^\circ = -33.3\ \text{kJ} \tag{16.1}$$

This ΔG° value represents the change in free energy when 1 mol nitrogen gas at 1 atm reacts with 3 mol hydrogen gas at 1 atm to produce 2 mol gaseous NH_3 at 1 atm.

It is important to recognize that the standard free energy change for a reaction is not measured directly. For example, we can measure heat flow in a calorimeter to determine ΔH°, but we cannot measure ΔG° this way. The value of ΔG° for the ammonia synthesis in Equation (16.1) was *not* obtained by mixing 1 mol N_2 and 3 mol H_2 in a flask and measuring the change in free energy as 2 mol NH_3 formed. For one thing, if we mixed 1 mol N_2 and 3 mol H_2 in a flask, the system would go to equilibrium rather than to completion. Also, we have no instrument that measures free energy. However, while we cannot directly measure ΔG° for a reaction, we can calculate it from other measured quantities, as we will see later in this section.

Why is it useful to know ΔG° for a reaction? As we will see in more detail later in this chapter, knowing the ΔG° values for several reactions allows us to compare the relative tendency of these reactions to occur. The more negative the value of ΔG°, the further a reaction will go to the right to reach equilibrium. We must use standard-state free energies to make this comparison because free energy varies with pressure or concentration. Thus, to get an accurate comparison of reaction tendencies, we must compare all reactions under the same pressure or concentration conditions. We will have more to say about the significance of ΔG° later.

There are several ways to calculate ΔG°. One common method uses the equation

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

which applies to a reaction carried out at constant temperature. For example, for the reaction

$$C(s) + O_2(g) \longrightarrow CO_2(g)$$

the values of ΔH° and ΔS° are known to be −393.5 kJ and 3.05 J/K, respectively, and ΔG° can be calculated at 298 K as follows:

$$\begin{aligned}
\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\
&= -3.935 \times 10^5\ \text{J} - (298\ \text{K})(3.05\ \text{J/K}) \\
&= -3.944 \times 10^5\ \text{J} \\
&= -394.4\ \text{kJ (per mole of } CO_2)
\end{aligned}$$

Sample Exercise 16.9 Calculating $\Delta H°$, $\Delta S°$, and $\Delta G°$

Consider the reaction

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

carried out at 25°C and 1 atm. Calculate $\Delta H°$, $\Delta S°$, and $\Delta G°$ using the following data:

Substance	ΔH_f° (kJ/mol)	$S°$ (J/K · mol)
$SO_2(g)$	−297	248
$SO_3(g)$	−396	257
$O_2(g)$	0	205

Solution

The value of $\Delta H°$ can be calculated from the enthalpies of formation using the equation we discussed in Section 6.4:

$$\Delta H° = \Sigma n_p \Delta H^\circ_{f\,(\text{products})} - \Sigma n_r \Delta H^\circ_{f\,(\text{reactants})}$$

Then

$$\begin{aligned}\Delta H° &= 2\Delta H^\circ_{f\,(SO_3(g))} - 2\Delta H^\circ_{f\,(SO_2(g))} - \Delta H^\circ_{f\,(O_2(g))}\\ &= 2\text{ mol}(-396\text{ kJ/mol}) - 2\text{ mol}(-297\text{ kJ/mol}) - 0\\ &= -792\text{ kJ} + 594\text{ kJ}\\ &= -198\text{ kJ}\end{aligned}$$

The value of $\Delta S°$ can be calculated using the standard entropy values and the equation discussed in Section 16.5:

$$\Delta S° = \Sigma n_p S^\circ_{\text{products}} - \Sigma n_r S^\circ_{\text{reactants}}$$

Thus

$$\begin{aligned}\Delta S° &= 2S^\circ_{SO_3(g)} - 2S^\circ_{SO_2(g)} - S^\circ_{O_2(g)}\\ &= 2\text{ mol}(257\text{ J/K}\cdot\text{mol}) - 2\text{ mol}(248\text{ J/K}\cdot\text{mol}) - 1\text{ mol}(205\text{ J/K}\cdot\text{mol})\\ &= 514\text{ J/K} - 496\text{ J/K} - 205\text{ J/K}\\ &= -187\text{ J/K}\end{aligned}$$

We would expect $\Delta S°$ to be negative because three molecules of gaseous reactants give two molecules of gaseous products.

The value of $\Delta G°$ can now be calculated from the equation

$$\begin{aligned}\Delta G° &= \Delta H° - T\Delta S°\\ &= -198\text{ kJ} - (298\text{ K})\left(-187\,\frac{\text{J}}{\text{K}}\right)\left(\frac{1\text{ kJ}}{1000\text{ J}}\right)\\ &= -198\text{ kJ} + 55.7\text{ kJ} = -142\text{ kJ}\end{aligned}$$

See Exercises 16.45 through 16.47.

A second method for calculating ΔG for a reaction takes advantage of the fact that, like enthalpy, *free energy is a state function.* Therefore, we can use procedures for finding ΔG that are similar to those for finding ΔH using Hess's law.

To illustrate this method for calculating the free energy change, we will obtain $\Delta G°$ for the reaction

$$2\text{CO}(g) + \text{O}_2(g) \longrightarrow 2\text{CO}_2(g) \qquad (16.2)$$

from the following data:

$$2\text{CH}_4(g) + 3\text{O}_2(g) \longrightarrow 2\text{CO}(g) + 4\text{H}_2\text{O}(g) \qquad \Delta G° = -1088 \text{ kJ} \qquad (16.3)$$

$$\text{CH}_4(g) + 2\text{O}_2(g) \longrightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g) \qquad \Delta G° = -801 \text{ kJ} \qquad (16.4)$$

Note that CO(g) is a reactant in Equation (16.2). This means that Equation (16.3) must be reversed, since CO(g) is a product in that reaction as written. When a reaction is reversed, the sign of $\Delta G°$ is also reversed. In Equation (16.4), $\text{CO}_2(g)$ is a product, as it is in Equation (16.2), but only one molecule of CO_2 is formed. Thus Equation (16.4) must be multiplied by 2, which means the $\Delta G°$ value for Equation (16.4) also must be multiplied by 2. Free energy is an extensive property, since it is defined by two extensive properties, H and S.

Reversed Equation (16.3)

$$2\text{CO}(g) + 4\text{H}_2\text{O}(g) \longrightarrow 2\text{CH}_4(g) + 3\text{O}_2(g) \qquad \Delta G° = -(-1088 \text{ kJ})$$

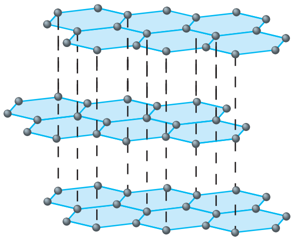
2 × Equation (16.4)

$$2\text{CH}_4(g) + 4\text{O}_2(g) \longrightarrow 2\text{CO}_2(g) + 4\text{H}_2\text{O}(g) \qquad \Delta G° = 2(-801 \text{ kJ})$$

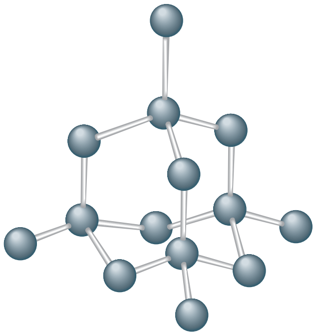
$$\begin{aligned} 2\text{CO}(g) + \text{O}_2(g) \longrightarrow 2\text{CO}_2(g) \qquad \Delta G° &= -(-1088 \text{ kJ}) \\ &\quad + 2(-801 \text{ kJ}) \\ &= -514 \text{ kJ} \end{aligned}$$

This example shows that the ΔG values for reactions are manipulated in exactly the same way as the ΔH values.

Sample Exercise 16.10 Calculating $\Delta G°$



Graphite



Diamond

Using the following data (at 25°C)

$$\text{C}_{\text{diamond}}(s) + \text{O}_2(g) \longrightarrow \text{CO}_2(g) \qquad \Delta G° = -397 \text{ kJ} \qquad (16.5)$$

$$\text{C}_{\text{graphite}}(s) + \text{O}_2(g) \longrightarrow \text{CO}_2(g) \qquad \Delta G° = -394 \text{ kJ} \qquad (16.6)$$

calculate $\Delta G°$ for the reaction

$$\text{C}_{\text{diamond}}(s) \longrightarrow \text{C}_{\text{graphite}}(s)$$

Solution

We reverse Equation (16.6) to make graphite a product, as required, and then add the new equation to Equation (16.5):

$$\text{C}_{\text{diamond}}(s) + \text{O}_2(g) \longrightarrow \text{CO}_2(g) \qquad \Delta G° = -397 \text{ kJ}$$

Reversed Equation (16.6)

$$\text{CO}_2(g) \longrightarrow \text{C}_{\text{graphite}}(s) + \text{O}_2(g) \qquad \Delta G° = -(-394 \text{ kJ})$$

$$\begin{aligned} \text{C}_{\text{diamond}}(s) \longrightarrow \text{C}_{\text{graphite}}(s) \qquad \Delta G° &= -397 \text{ kJ} + 394 \text{ kJ} \\ &= -3 \text{ kJ} \end{aligned}$$

Since $\Delta G°$ is negative for this process, diamond should spontaneously change to graphite at 25°C and 1 atm. However, the reaction is so slow under these conditions that we do not observe the process. This is another example of kinetic rather than thermodynamic control of a reaction. We can say that diamond is kinetically stable with respect to graphite even though it is thermodynamically unstable.

See Exercises 16.51 and 16.52.

In Sample Exercise 16.10 we saw that the process

$$C_{\text{diamond}}(s) \longrightarrow C_{\text{graphite}}(s)$$

is spontaneous but very slow at 25°C and 1 atm. The reverse process can be made to occur at high temperatures and pressures. Diamond has a more compact structure and thus a higher density than graphite, so exerting very high pressure causes it to become thermodynamically favored. If high temperatures are also used to make the process fast enough to be feasible, diamonds can be made from graphite. The conditions typically used involve temperatures greater than 1000°C and pressures of about 10^5 atm. About half of all industrial diamonds are made this way.

A third method for calculating the free energy change for a reaction uses standard free energies of formation. The **standard free energy of formation** (ΔG_f°) of a substance is defined as the *change in free energy that accompanies the formation of 1 mole of that substance from its constituent elements with all reactants and products in their standard states.* For the formation of glucose ($C_6H_{12}O_6$), the appropriate reaction is

The standard state of an element is its most stable state of 25°C and 1 atm.

$$6C(s) + 6H_2(g) + 3O_2(g) \longrightarrow C_6H_{12}O_6(s)$$

The standard free energy associated with this process is called the *free energy of formation of glucose.* Values of the standard free energy of formation are useful in calculating ΔG° for specific chemical reactions using the equation

$$\Delta G^\circ = \Sigma n_p \Delta G^\circ_{f\,(\text{products})} - \Sigma n_r \Delta G^\circ_{f\,(\text{reactants})}$$

Calculating ΔG° is very similar to calculating ΔH°, as shown in Section 6.4.

Values of ΔG_f° for many common substances are listed in Appendix 4. Note that, analogous to the enthalpy of formation, *the standard free energy of formation of an element in its standard state is zero.* Also note that the number of moles of each reactant (n_r) and product (n_p) must be used when calculating ΔG° for a reaction.

Sample Exercise 16.11

Calculating ΔG°

Methanol is a high-octane fuel used in high-performance racing engines. Calculate ΔG° for the reaction

$$2CH_3OH(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 4H_2O(g)$$

given the following free energies of formation:

Substance	ΔG_f° (kJ/mol)
$CH_3OH(g)$	−163
$O_2(g)$	0
$CO_2(g)$	−394
$H_2O(g)$	−229

Solution

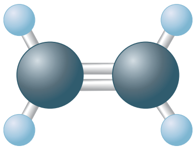
We use the equation

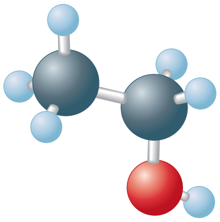
$$\begin{aligned}
\Delta G^\circ &= \Sigma n_p \Delta G^\circ_{f\,(\text{products})} - \Sigma n_r \Delta G^\circ_{f\,(\text{reactants})} \\
&= 2\Delta G^\circ_{f\,(CO_2(g))} + 4\Delta G^\circ_{f\,(H_2O(g))} - 3\Delta G^\circ_{f\,(O_2(g))} - 2\Delta G^\circ_{f\,(CH_3OH(g))} \\
&= 2\text{ mol}(-394\text{ kJ/mol}) + 4\text{ mol}(-229\text{ kJ/mol}) - 3(0) \\
&\quad -2\text{ mol}(-163\text{ kJ/mol}) \\
&= -1378\text{ kJ}
\end{aligned}$$

The large magnitude and the negative sign of $\Delta G°$ indicate that this reaction is very favorable thermodynamically.

See Exercises 16.53 through 16.55.

Sample Exercise 16.12 Free Energy and Spontaneity


Ethylene


Ethanol

A chemical engineer wants to determine the feasibility of making ethanol (C_2H_5OH) by reacting water with ethylene (C_2H_4) according to the equation

$$C_2H_4(g) + H_2O(l) \longrightarrow C_2H_5OH(l)$$

Is this reaction spontaneous under standard conditions?

Solution

To determine the spontaneity of this reaction under standard conditions, we must determine $\Delta G°$ for the reaction. We can do this using standard free energies of formation at 25° from Appendix 4:

$$\Delta G°_{f\ (C_2H_5OH(l))} = -175 \text{ kJ/mol}$$
$$\Delta G°_{f\ (H_2O(l))} = -237 \text{ kJ/mol}$$
$$\Delta G°_{f\ (C_2H_4(g))} = 68 \text{ kJ/mol}$$

Then
$$\begin{aligned}\Delta G° &= \Delta G°_{f\ (C_2H_5OH(l))} - \Delta G°_{f\ (H_2O(l))} - \Delta G°_{f\ (C_2H_4(g))} \\ &= -175 \text{ kJ} - (-237 \text{ kJ}) - 68 \text{ kJ} \\ &= -6 \text{ kJ}\end{aligned}$$

Thus the process is spontaneous under standard conditions at 25°C.

See Exercise 16.56.

Although the reaction considered in Sample Exercise 16.12 is spontaneous, other features of the reaction must be studied to see if the process is feasible. For example, the chemical engineer will need to study the kinetics of the reaction to determine whether it is fast enough to be useful and, if it is not, whether a catalyst can be found to enhance the rate. In doing these studies, the engineer must remember that $\Delta G°$ depends on temperature:

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

Thus, if the process must be carried out at high temperatures to be fast enough to be feasible, $\Delta G°$ must be recalculated at that temperature from the $\Delta H°$ and $\Delta S°$ values for the reaction.

16.7 The Dependence of Free Energy on Pressure

In this chapter we have seen that a system at constant temperature and pressure will proceed spontaneously in the direction that lowers its free energy. This is why reactions proceed until they reach equilibrium. As we will see later in this section, *the equilibrium position represents the lowest free energy value available to a particular reaction system.* The free energy of a reaction system changes as the reaction proceeds, because free energy is dependent on the pressure of a gas or on the concentration of species in solution. We will deal only with the pressure dependence of the free energy of an ideal gas. The dependence of free energy on concentration can be developed using similar reasoning.

To understand the pressure dependence of free energy, we need to know how pressure affects the thermodynamic functions that comprise free energy, that is, enthalpy and entropy (recall that $G = H - TS$). For an ideal gas, enthalpy is not pressure-dependent. However, entropy *does* depend on pressure because of its dependence on volume. Consider 1 mole of an ideal gas at a given temperature. At a volume of 10.0 L, the gas has many more positions available for its molecules than if its volume is 1.0 L. The positional entropy is greater in the larger volume. In summary, at a given temperature for 1 mole of ideal gas

$$S_{\text{large volume}} > S_{\text{small volume}}$$

or, since pressure and volume are inversely related,

$$S_{\text{low pressure}} > S_{\text{high pressure}}$$

We have shown qualitatively that the entropy and therefore the free energy of an ideal gas depend on its pressure. Using a more detailed argument, which we will not consider here, it can be shown that

$$G = G^\circ + RT\ln(P)$$

where G° is the free energy of the gas at a pressure of 1 atm, G is the free energy of the gas at a pressure of P atm, R is the universal gas constant, and T is the Kelvin temperature.

To see how the change in free energy for a reaction depends on pressure, we will consider the ammonia synthesis reaction

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

In general, $\Delta G = \Sigma n_p G_{\text{products}} - \Sigma n_r G_{\text{reactants}}$

For this reaction $\Delta G = 2G_{NH_3} - G_{N_2} - 3G_{H_2}$

See Appendix 1.2 to review logarithms.

where

$$G_{NH_3} = G^\circ_{NH_3} + RT\ln(P_{NH_3})$$
$$G_{N_2} = G^\circ_{N_2} + RT\ln(P_{N_2})$$
$$G_{H_2} = G^\circ_{H_2} + RT\ln(P_{H_2})$$

Substituting these values into the equation gives

$$\begin{aligned}\Delta G &= 2[G^\circ_{NH_3} + RT\ln(P_{NH_3})] - [G^\circ_{N_2} + RT\ln(P_{N_2})] - 3[G^\circ_{H_2} + RT\ln(P_{H_2})]\\ &= 2G^\circ_{NH_3} - G^\circ_{N_2} - 3G^\circ_{H_2} + 2RT\ln(P_{NH_3}) - RT\ln(P_{N_2}) - 3RT\ln(P_{H_2})\\ &= \underbrace{(2G^\circ_{NH_3} - G^\circ_{N_2} - 3G^\circ_{H_2})}_{\Delta G^\circ\text{ reaction}} + RT[2\ln(P_{NH_3}) - \ln(P_{N_2}) - 3\ln(P_{H_2})]\end{aligned}$$

The first term (in parentheses) is ΔG° for the reaction. Thus we have

$$\Delta G = \Delta G^\circ_{\text{reaction}} + RT[2\ln(P_{NH_3}) - \ln(P_{N_2}) - 3\ln(P_{H_2})]$$

and since

$$2\ln(P_{NH_3}) = \ln(P_{NH_3}{}^2)$$
$$-\ln(P_{N_2}) = \ln\left(\frac{1}{P_{N_2}}\right)$$
$$-3\ln(P_{H_2}) = \ln\left(\frac{1}{P_{H_2}{}^3}\right)$$

the equation becomes

$$\Delta G = \Delta G^\circ + RT\ln\left(\frac{P_{NH_3}{}^2}{(P_{N_2})(P_{H_2}{}^3)}\right)$$

But the term $$\frac{P_{NH_3}{}^2}{(P_{N_2})(P_{H_2}{}^3)}$$

is the reaction quotient Q discussed in Section 13.5. Therefore, we have

$$\Delta G = \Delta G° + RT \ln(Q)$$

where Q is the reaction quotient (from the law of mass action), T is the temperature (K), R is the gas law constant and is equal to 8.3145 J/K · mol, $\Delta G°$ is the free energy change for the reaction with all reactants and products at a pressure of 1 atm, and ΔG is the free energy change for the reaction for the specified pressures of reactants and products.

Sample Exercise 16.13

Calculating $\Delta G°$

One method for synthesizing methanol (CH_3OH) involves reacting carbon monoxide and hydrogen gases:

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

Calculate ΔG at 25°C for this reaction where carbon monoxide gas at 5.0 atm and hydrogen gas at 3.0 atm are converted to liquid methanol.

Solution

To calculate ΔG for this process, we use the equation

$$\Delta G = \Delta G° + RT \ln(Q)$$

We must first compute $\Delta G°$ from standard free energies of formation (see Appendix 4). Since

$$\Delta G°_{f\ (CH_3OH(l))} = -166 \text{ kJ}$$
$$\Delta G°_{f\ (H_2(g))} = 0$$
$$\Delta G°_{f\ (CO(g))} = -137 \text{ kJ}$$
$$\Delta G° = -166 \text{ kJ} - (-137 \text{ kJ}) - 0 = -29 \text{ kJ} = -2.9 \times 10^4 \text{ J}$$

Note that this is the value of $\Delta G°$ for the reaction of 1 mol CO with 2 mol H_2 to produce 1 mol CH_3OH. We might call this the value of $\Delta G°$ for one "round" of the reaction or for one mole of the reaction. Thus the $\Delta G°$ value might better be written as -2.9×10^4 J/mol of reaction, or -2.9×10^4 J/mol rxn.

We can now calculate ΔG using

Note in this case that ΔG is defined for "one mole of the reaction," that is, for 1 mol $CO(g)$ reacting with 2 mol $H_2(g)$ to form 1 mol $CH_3OH(l)$. Thus ΔG, $\Delta G°$, and $RT \ln(Q)$ all have units of J/mol of reaction. In this case the units of R are actually J/K · mol of reaction, although they are usually not written this way.

$$\Delta G° = -2.9 \times 10^4 \text{ J/mol rxn}$$
$$R = 8.3145 \text{ J/K} \cdot \text{mol}$$
$$T = 273 + 25 = 298 \text{ K}$$
$$Q = \frac{1}{(P_{CO})(P_{H_2}{}^2)} = \frac{1}{(5.0)(3.0)^2} = 2.2 \times 10^{-2}$$

Note that the pure liquid methanol is not included in the calculation of Q. Then

$$\begin{aligned}\Delta G &= \Delta G° + RT \ln(Q)\\ &= (-2.9 \times 10^4 \text{ J/mol rxn}) + (8.3145 \text{ J/K} \cdot \text{mol rxn})(298 \text{ K}) \ln(2.2 \times 10^{-2})\\ &= (-2.9 \times 10^4 \text{ J/mol rxn}) - (9.4 \times 10^3 \text{ J/mol rxn}) = -3.8 \times 10^4 \text{ J/mol rxn}\\ &= -38 \text{ kJ/mol rxn}\end{aligned}$$

Note that ΔG is significantly more negative than $\Delta G°$, implying that the reaction is more spontaneous at reactant pressures greater than 1 atm. We might expect this result from Le Châtelier's principle.

See Exercises 16.57 and 16.58.

The Meaning of ΔG for a Chemical Reaction

In this section we have learned to calculate ΔG for chemical reactions under various conditions. For example, in Sample Exercise 16.13 the calculations show that the formation of $CH_3OH(l)$ from $CO(g)$ at 5.0 atm reacting with $H_2(g)$ at 3.0 atm is spontaneous. What does this result mean? Does it mean that if we mixed 1.0 mol $CO(g)$ and 2.0 mol $H_2(g)$ together at pressures of 5.0 and 3.0 atm, respectively, that 1.0 mol $CH_3OH(l)$ would form in the reaction flask? The answer is no. This answer may surprise you in view of what has been said in this section. It is true that 1.0 mol $CH_3OH(l)$ has a lower free energy than 1.0 mol $CO(g)$ at 5.0 atm plus 2.0 mol $H_2(g)$ at 3.0 atm. However, when $CO(g)$ and $H_2(g)$ are mixed under these conditions, there is *an even lower free energy available to this system than 1.0 mol pure $CH_3OH(l)$*. For reasons we will discuss shortly, *the system can achieve the lowest possible free energy by going to equilibrium, not by going to completion.* At the equilibrium position, some of the $CO(g)$ and $H_2(g)$ will remain in the reaction flask. So even though 1.0 mol pure $CH_3OH(l)$ is at a lower free energy than 1.0 mol $CO(g)$ and 2.0 mol $H_2(g)$ at 5.0 and 3.0 atm, respectively, the reaction system will stop short of forming 1.0 mol $CH_3OH(l)$. The reaction stops short of completion because the equilibrium mixture of $CH_3OH(l)$, $CO(g)$, and $H_2(g)$ exists at the lowest possible free energy available to the system.

To illustrate this point, we will explore a mechanical example. Consider balls rolling down the two hills shown in Fig. 16.7. Note that in both cases point *B* has a lower potential energy than point *A*.

In Fig. 16.7(a) the ball will roll to point *B*. This diagram is analogous to a phase change. For example, at 25°C ice will spontaneously change completely to liquid water, because the latter has the lowest free energy. In this case liquid water is the only choice. There is no intermediate mixture of ice and water with lower free energy.

The situation is different for a chemical reaction system, as illustrated in Fig. 16.7(b). In Fig. 16.7(b) the ball will not get to point *B* because there is a lower potential energy at point *C*. Like the ball, a chemical system will seek the *lowest possible* free energy, which, for reasons we will discuss below, is the equilibrium position.

Therefore, although the value of ΔG for a given reaction system tells us whether the products or reactants are favored under a given set of conditions, it does not mean that the system will proceed to pure products (if ΔG is negative) or remain at pure reactants (if ΔG is positive). Instead, the system will spontaneously go to the equilibrium position,

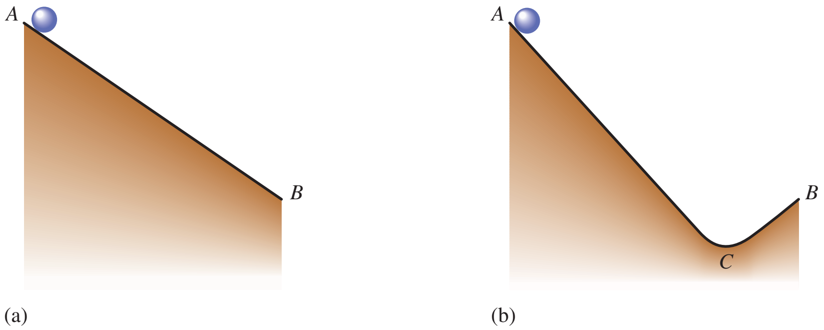


FIGURE 16.7
Schematic representations of balls rolling down two types of hills.

the lowest possible free energy available to it. In the next section we will see that the value of ΔG° for a particular reaction tells us exactly where this position will be.

16.8 Free Energy and Equilibrium

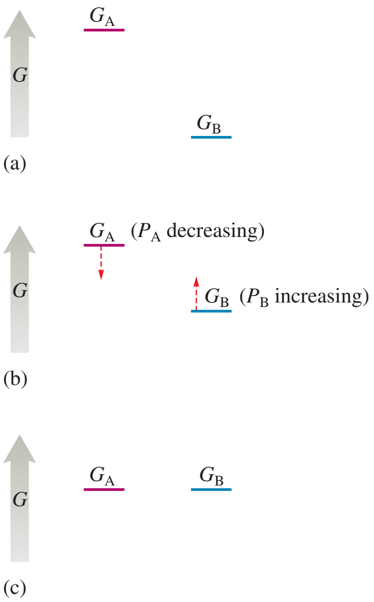


FIGURE 16.8
(a) The initial free energies of A and B. (b) As A(g) changes to B(g), the free energy of A decreases and that of B increases. (c) Eventually, pressures of A and B are achieved such that $G_A = G_B$, the equilibrium position.

When the components of a given chemical reaction are mixed, they will proceed, rapidly or slowly depending on the kinetics of the process, to the equilibrium position. In Chapter 13 we defined the equilibrium position as the point at which the forward and reverse reaction rates are equal. In this chapter we look at equilibrium from a thermodynamic point of view, and we find that the **equilibrium point** *occurs at the lowest value of free energy available to the reaction system.* As it turns out, the two definitions give the same equilibrium state, which must be the case for both the kinetic and thermodynamic models to be valid.

To understand the relationship of free energy to equilibrium, let's consider the following simple hypothetical reaction:

$$\mathrm{A}(g) \rightleftharpoons \mathrm{B}(g)$$

where 1.0 mole of gaseous A is initially placed in a reaction vessel at a pressure of 2.0 atm. The free energies for A and B are diagramed as shown in Fig. 16.8(a). As A reacts to form B, the total free energy of the system changes, yielding the following results:

$$\text{Free energy of A} = G_A = G_A^\circ + RT\ln(P_A)$$

$$\text{Free energy of B} = G_B = G_B^\circ + RT\ln(P_B)$$

$$\text{Total free energy of system} = G = G_A + G_B$$

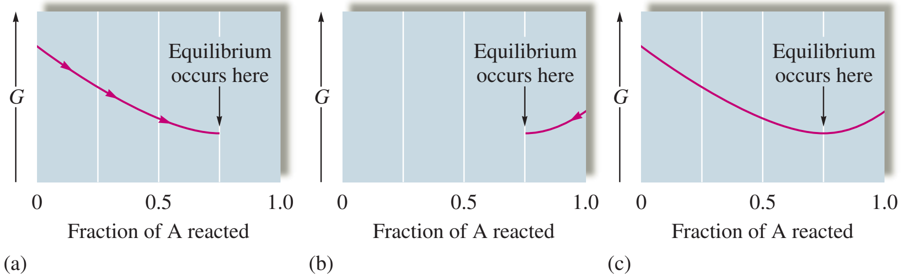
As A changes to B, G_A will decrease because P_A is decreasing [Fig. 16.8(b)]. In contrast, G_B will increase because P_B is increasing. The reaction will proceed to the right as long as the total free energy of the system decreases (as long as G_B is less than G_A). At some point the pressures of A and B reach the values P_A^e and P_B^e that make G_A equal to G_B. *The system has reached equilibrium* [Fig. 16.8(c)]. Since A at pressure P_A^e and B at pressure P_B^e have the same free energy (G_A equals G_B), ΔG is zero for A at pressure P_A^e changing to B at pressure P_B^e. *The system has reached minimum free energy.* There is no longer any driving force to change A to B or B to A, so the system remains at this position (the pressures of A and B remain constant).

Suppose that for the experiment described above the plot of free energy versus the mole fraction of A reacted is defined as shown in Fig. 16.9(a). In this experiment, minimum free energy is reached when 75% of A has been changed to B. At this point, the pressure of A is 0.25 times the original pressure, or

$$(0.25)(2.0\ \text{atm}) = 0.50\ \text{atm}$$

The pressure of B is

$$(0.75)(2.0\ \text{atm}) = 1.5\ \text{atm}$$



(a) (b) (c)

FIGURE 16.9
(a) The change in free energy to reach equilibrium, beginning with 1.0 mol A(g) at $P_A = 2.0$ atm. (b) The change in free energy to reach equilibrium, beginning with 1.0 mol B(g) at $P_B = 2.0$ atm. (c) The free energy profile for $\mathrm{A}(g) \rightleftharpoons \mathrm{B}(g)$ in a system containing 1.0 mol (A plus B) at $P_{\text{TOTAL}} = 2.0$ atm. Each point on the curve corresponds to the total free energy of the system for a given combination of A and B.

Since this is the equilibrium position, we can use the equilibrium pressures to calculate a value for K for the reaction in which A is converted to B at this temperature:

$$K = \frac{P_B^e}{P_A^e} = \frac{1.5 \text{ atm}}{0.50 \text{ atm}} = 3.0$$

For the reaction $A(g) \rightleftharpoons B(g)$, the pressure is constant during the reaction, since the same number of gas molecules is always present.

Exactly the same equilibrium point would be achieved if we placed 1.0 mol pure $B(g)$ in the flask at a pressure of 2.0 atm. In this case B would change to A until equilibrium ($G_B = G_A$) is reached. This is shown in Fig. 16.9(b).

The overall free energy curve for this system is shown in Fig. 16.9(c). Note that any mixture of $A(g)$ and $B(g)$ containing 1.0 mol (A plus B) at a total pressure of 2.0 atm will react until it reaches the minimum in the curve.

In summary, when substances undergo a chemical reaction, the reaction proceeds to the minimum free energy (equilibrium), which corresponds to the point where

$$G_{\text{products}} = G_{\text{reactants}} \quad \text{or} \quad \Delta G = G_{\text{products}} - G_{\text{reactants}} = 0$$

We can now establish a quantitative relationship between free energy and the value of the equilibrium constant. We have seen that

$$\Delta G = \Delta G^\circ + RT \ln(Q)$$

and at equilibrium ΔG equals 0 and Q equals K.

So $$\Delta G = 0 = \Delta G^\circ + RT \ln(K)$$

or $$\Delta G^\circ = -RT \ln(K)$$

We must note the following characteristics of this very important equation.

Case 1: $\Delta G^\circ = 0$. When ΔG° equals zero for a particular reaction, the free energies of the reactants and products are equal when all components are in the standard states (1 atm for gases). The system is at equilibrium when the pressures of all reactants and products are 1 atm, which means that K equals 1.

Case 2: $\Delta G^\circ < 0$. In this case ΔG° ($G^\circ_{\text{products}} - G^\circ_{\text{reactants}}$) is negative, which means that

$$G^\circ_{\text{products}} < G^\circ_{\text{reactants}}$$

If a flask contains the reactants and products, all at 1 atm, the system will *not* be at equilibrium. Since $G^\circ_{\text{products}}$ is less than $G^\circ_{\text{reactants}}$, the system will adjust to the right to reach equilibrium. In this case K will be *greater than 1,* since the pressures of the products at equilibrium will be greater than 1 atm and the pressures of the reactants at equilibrium will be less than 1 atm.

Case 3: $\Delta G^\circ > 0$. Since ΔG° ($G^\circ_{\text{products}} - G^\circ_{\text{reactants}}$) is positive,

$$G^\circ_{\text{reactants}} < G^\circ_{\text{products}}$$

If a flask contains the reactants and products, all at 1 atm, the system will *not* be at equilibrium. In this case the system will adjust to the left (toward the reactants, which have a lower free energy) to reach equilibrium. The value of K will be *less than 1,* since at equilibrium the pressures of the reactants will be greater than 1 atm and the pressures of the products will be less than 1 atm.

These results are summarized in Table 16.6. The value of K for a specific reaction can be calculated from the equation

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

as is shown in Sample Exercises 16.14 and 16.15.

TABLE 16.6 Qualitative Relationship Between the Change in Standard Free Energy and the Equilibrium Constant for a Given Reaction

ΔG°	K
$\Delta G^\circ = 0$	$K = 1$
$\Delta G^\circ < 0$	$K > 1$
$\Delta G^\circ > 0$	$K < 1$

Sample Exercise 16.14 Free Energy and Equilibrium I

Consider the ammonia synthesis reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

where $\Delta G^\circ = -33.3$ kJ per mole of N_2 consumed at 25°C. For each of the following mixtures of reactants and products at 25°C, predict the direction in which the system will shift to reach equilibrium.

a. $P_{NH_3} = 1.00$ atm, $P_{N_2} = 1.47$ atm, $P_{H_2} = 1.00 \times 10^{-2}$ atm
b. $P_{NH_3} = 1.00$ atm, $P_{N_2} = 1.00$ atm, $P_{H_2} = 1.00$ atm

Solution

The units of ΔG, ΔG°, and $RT \ln(Q)$ all refer to the balanced reaction with all amounts expressed in moles. We might say that the units are joules per "mole of reaction," although only the "per mole" is indicated for R (as is customary).

a. We can predict the direction of reaction to equilibrium by calculating the value of ΔG using the equation

$$\Delta G = \Delta G^\circ + RT\ln(Q)$$

where

$$Q = \frac{P_{NH_3}{}^2}{(P_{N_2})(P_{H_2}{}^3)} = \frac{(1.00)^2}{(1.47)(1.00 \times 10^{-2})^3} = 6.80 \times 10^5$$

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

$$R = 8.3145 \text{ J/K} \cdot \text{mol}$$

and

$$\Delta G^\circ = -33.3 \text{ kJ/mol} = -3.33 \times 10^4 \text{ J/mol}$$

Then

$$\begin{aligned}\Delta G &= (-3.33 \times 10^4 \text{ J/mol}) + (8.3145 \text{ J/K} \cdot \text{mol})(298 \text{ K})\ln(6.8 \times 10^5)\\ &= (-3.33 \times 10^4 \text{ J/mol}) + (3.33 \times 10^4 \text{ J/mol}) = 0\end{aligned}$$

Since $\Delta G = 0$, the reactants and products have the same free energies at these partial pressures. The system is already at equilibrium, and no shift will occur.

b. The partial pressures given here are all 1.00 atm, which means that the system is in the standard state. That is,

$$\begin{aligned}\Delta G &= \Delta G^\circ + RT\ln(Q) = \Delta G^\circ + RT\ln\frac{(1.00)^2}{(1.00)(1.00)^3}\\ &= \Delta G^\circ + RT\ln(1.00) = \Delta G^\circ + 0 = \Delta G^\circ\end{aligned}$$

For this reaction at 25°C,

$$\Delta G^\circ = -33.3 \text{ kJ/mol}$$

The negative value for ΔG° means that in their standard states the products have a lower free energy than the reactants. Thus the system will move to the right to reach equilibrium. That is, K is greater than 1.

See Exercise 16.59.

Sample Exercise 16.15 Free Energy and Equilibrium II

The overall reaction for the corrosion (rusting) of iron by oxygen is

$$4Fe(s) + 3O_2(g) \rightleftharpoons 2Fe_2O_3(s)$$

Using the following data, calculate the equilibrium constant for this reaction at 25°C.

Substance	ΔH_f° (kJ/mol)	S° (J/K · mol)
$Fe_2O_3(s)$	−826	90
$Fe(s)$	0	27
$O_2(g)$	0	205

Solution

To calculate K for this reaction, we will use the equation

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

We must first calculate ΔG° from

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

where

$$\begin{aligned}\Delta H^\circ &= 2\Delta H^\circ_{\mathrm{f}\,(Fe_2O_3(s))} - 3\Delta H^\circ_{\mathrm{f}\,(O_2(g))} - 4\Delta H^\circ_{\mathrm{f}\,(Fe(s))}\\ &= 2\text{ mol}(-826\text{ kJ/mol}) - 0 - 0\\ &= -1652\text{ kJ} = -1.652 \times 10^6\text{ J}\\ \Delta S^\circ &= 2S^\circ_{Fe_2O_3} - 3S^\circ_{O_2} - 4S^\circ_{Fe}\\ &= 2\text{ mol}(90\text{ J/K}\cdot\text{mol}) - 3\text{ mol}(205\text{ J/K}\cdot\text{mol}) - 4\text{ mol}(27\text{ J/K}\cdot\text{mol})\\ &= -543\text{ J/K}\end{aligned}$$

Formation of rust on bare steel is a spontaneous process.

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

Then $$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ = (-1.652 \times 10^6\text{ J}) - (298\text{ K})(-543\text{ J/K})\\ &= -1.490 \times 10^6\text{ J}\end{aligned}$$

and

$$\Delta G^\circ = -RT\ln(K) = -1.490 \times 10^6\text{ J} = -(8.3145\text{ J/K}\cdot\text{mol})(298\text{ K})\ln(K)$$

Thus $$\ln(K) = \frac{1.490 \times 10^6}{2.48 \times 10^3} = 601$$

and $$K = e^{601}$$

This is a very large equilibrium constant. The rusting of iron is clearly very favorable from a thermodynamic point of view.

See Exercise 16.62.

The Temperature Dependence of *K*

In Chapter 13 we used Le Châtelier's principle to predict qualitatively how the value of K for a given reaction would change with a change in temperature. Now we can specify the quantitative dependence of the equilibrium constant on temperature from the relationship

$$\Delta G^\circ = -RT\ln(K) = \Delta H^\circ - T\Delta S^\circ$$

We can rearrange this equation to give

$$\ln(K) = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^\circ}{R}$$

Note that this is a linear equation of the form $y = mx + b$, where $y = \ln(K)$, $m = -\Delta H°/R =$ slope, $x = 1/T$, and $b = \Delta S°/R =$ intercept. This means that if values of K for a given reaction are determined at various temperatures, a plot of $\ln(K)$ versus $1/T$ will be linear, with slope $-\Delta H°/R$ and intercept $\Delta S°/R$. This result assumes that both $\Delta H°$ and $\Delta S°$ are independent of temperature over the temperature range considered. This assumption is a good approximation over a relatively small temperature range.

16.9 Free Energy and Work

One of the main reasons we are interested in physical and chemical processes is that we want to use them to do work for us, and we want this work done as efficiently and economically as possible. We have already seen that at constant temperature and pressure, the sign of the change in free energy tells us whether a given process is spontaneous. This is very useful information because it prevents us from wasting effort on a process that has no inherent tendency to occur. Although a thermodynamically favorable chemical reaction may not occur to any appreciable extent because it is too slow, it makes sense in this case to try to find a catalyst to speed up the reaction. On the other hand, if the reaction is prevented from occurring by its thermodynamic characteristics, we would be wasting our time looking for a catalyst.

In addition to its qualitative usefulness (telling us whether a process is spontaneous), the change in free energy is important quantitatively because it can tell us how much work can be done with a given process. In fact, the *maximum possible useful work obtainable from a process at constant temperature and pressure is equal to the change in free energy:*

$$w_{\max} = \Delta G$$

This relationship explains why this function is called the *free* energy. Under certain conditions, ΔG for a spontaneous process represents the energy that is *free to do useful work.* On the other hand, for a process that is not spontaneous, the value of ΔG tells us the minimum amount of work that must be *expended* to make the process occur.

Note that "*PV* work" is not counted as useful work here.

Knowing the value of ΔG for a process thus gives us valuable information about how close the process is to 100% efficiency. For example, when gasoline is burned in a car's engine, the work produced is about 20% of the maximum work available.

For reasons we will only briefly introduce in this book, the amount of work we actually obtain from a spontaneous process is *always* less than the maximum possible amount.

To explore this idea more fully, let's consider an electric current flowing through the starter motor of a car. The current is generated from a chemical change in a battery, and we can calculate ΔG for the battery reaction and so determine the energy available to do work. Can we use all this energy to do work? No, because a current flowing through a wire causes frictional heating, and the greater the current, the greater the heat. This heat represents wasted energy—it is not useful for running the starter motor. We can minimize this energy waste by running very low currents through the motor circuit. However, zero current flow would be necessary to eliminate frictional heating entirely, and we cannot derive any work from the motor if no current flows. This represents the difficulty in which nature places us. Using a process to do work requires that some of the energy be wasted, and usually the faster we run the process, the more energy we waste.

Achieving the maximum work available from a spontaneous process can occur only via a hypothetical pathway. Any real pathway wastes energy. If we could discharge the battery infinitely slowly by an infinitesimal current flow, we would achieve the maximum useful work. Also, if we could then recharge the battery using an infinitesimally small

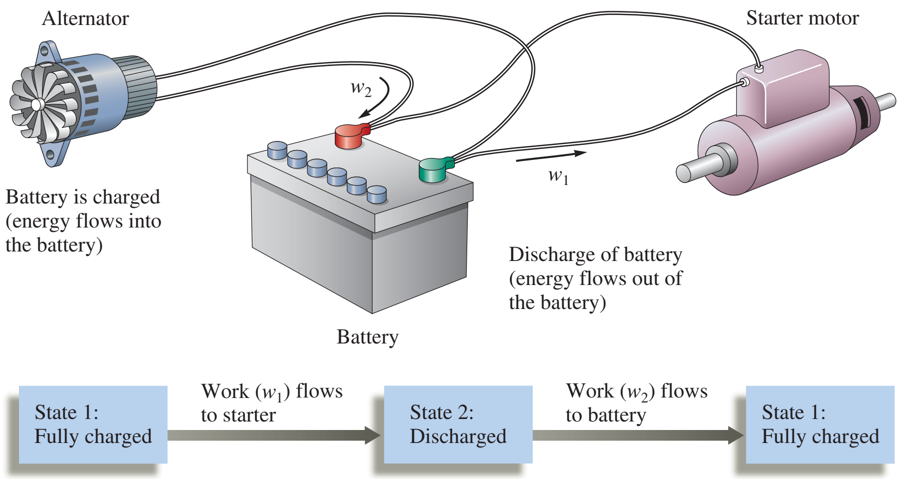


FIGURE 16.10
A battery can do work by sending current to a starter motor. The battery can then be recharged by forcing current through it in the opposite direction. If the current flow in both processes is infinitesimally small, $w_1 = w_2$. This is a *reversible process.* But if the current flow is finite, as it would be in any real case, $w_2 > w_1$. This is an *irreversible process* (the *universe is different* after the cyclic process occurs). All real processes are irreversible.

current, exactly the same amount of energy would be used to return the battery to its original state. After we cycle the battery in this way, the universe (the system and surroundings) is exactly the same as it was before the cyclic process. This is a **reversible process** (see Fig. 16.10).

However, if the battery is discharged to run the starter motor and then recharged using a *finite* current flow, as is the case in reality, *more* work will always be required to recharge the battery than the battery produces as it discharges. This means that even though the battery (the system) has returned to its original state, the surroundings have not, because the surroundings had to furnish a net amount of work as the battery was cycled. The *universe is different* after this cyclic process is performed, and this function is called an **irreversible process.** *All real processes are irreversible.*

In general, after any real cyclic process is carried out in a system, the surroundings have less ability to do work and contain more thermal energy. In other words, *in any real cyclic process in the system, work is changed to heat in the surroundings, and the entropy of the universe increases.* This is another way of stating the second law of thermodynamics.

Thus thermodynamics tells us the work potential of a process and then tells us that we can never achieve this potential. In this spirit, thermodynamicist Henry Bent has paraphrased the first two laws of thermodynamics as follows:

First law: You can't win, you can only break even.

Second law: You can't break even.

When energy is used to do work, it becomes less organized and less concentrated and thus less useful.

The ideas we have discussed in this section are applicable to the energy crisis that will probably increase in severity over the next 25 years. The crisis is obviously not one of supply; the first law tells us that the universe contains a constant supply of energy. The problem is the availability of *useful* energy. *As we use energy, we degrade its usefulness.* For example, when gasoline reacts with oxygen in the combustion reaction, the change in potential energy results in heat flow. Thus the energy concentrated in the bonds of the gasoline and oxygen molecules ends up *spread* over the surroundings as thermal energy, where it is much more difficult to harness for useful work. This is a way in which the entropy of the universe increases: Concentrated energy becomes spread out—more disordered and less useful. Thus the crux of the energy problem is that we are rapidly consuming the concentrated energy found in fossil fuels. It took millions of years to concentrate the sun's energy in these fuels, and we will consume these same fuels in a few hundred years. Thus we must use these energy sources as wisely as possible.

Key Terms

Section 16.1

spontaneous process
entropy
positional probability

Section 16.2

second law of thermodynamics

Section 16.4

free energy

Section 16.5

third law of thermodynamics

Section 16.6

standard free energy change
standard free energy of formation

Section 16.8

equilibrium point (thermodynamic definition)

Section 16.9

reversible process
irreversible process

For Review

First law of thermodynamics

- States that the energy of the universe is constant
- Provides a way to keep track of energy as it changes form
- Gives no information about why a particular process occurs in a given direction

Second law of thermodynamics

- States that for any spontaneous process there is always an increase in the entropy of the universe
- Entropy(S) is a thermodynamic function that describes the number of arrangements (positions and/or energy levels) available to a system existing in a given state
  - Nature spontaneously proceeds toward states that have the highest probability of occurring
  - Using entropy, thermodynamics can predict the direction in which a process will occur spontaneously

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

  - For a spontaneous process, ΔS_{univ} must be positive
  - For a process at constant temperature and pressure:
    - ΔS_{sys} is dominated by "positional" entropy
      For a chemical reaction, ΔS_{sys} is dominated by changes in the number of gaseous molecules
    - ΔS_{surr} is determined by heat:

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

      ΔS_{surr} is positive for an exothermic process (ΔH is negative)
      Because ΔS_{surr} depends inversely on T, exothermicity becomes a more important driving force at low temperatures
- Thermodynamics cannot predict the rate at which a system will spontaneously change; the principles of kinetics are necessary to do this

Third law of thermodynamics

- States that the entropy of a perfect crystal at 0 K is zero

Free energy (*G*)

- Free energy is a state function:

$$G = H - TS$$

- A process occurring at constant temperature and pressure is spontaneous in the direction in which its free energy decreases ($\Delta G < 0$)
- For a reaction the standard free energy change ($\Delta G°$) is the change in free energy that occurs when reactants in their standard states are converted to products in their standard states
- The standard free energy change for a reaction can be determined from the standard free energies of formation ($\Delta G_f°$) of the reactants and products:

$$\Delta G° = \Sigma n_p \Delta G_f°(\text{products}) - \Sigma n_r \Delta G_f°(\text{reactants})$$

- Free energy depends on temperature and pressure:

$$G = G° + RT \ln P$$

- This relationship can be used to derive the relationship between ΔG° for a reaction and the value of its equilibrium constant K:

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

  - For $\Delta G^\circ = 0, K = 1$
  - For $\Delta G^\circ < 0, K > 1$
  - For $\Delta G^\circ > 0, K < 1$

- The maximum possible useful work obtainable from a process at constant temperature and pressure is equal to the change in free energy:

$$w_{\text{max}} = \Delta G$$

- In any real process, $w < w_{\text{max}}$
- When energy is used to do work in a real process, the energy of the universe remains constant but the usefulness of the energy decreases
  - Concentrated energy is spread out in the surroundings as thermal energy

REVIEW QUESTIONS

1. Define the following:
   a. spontaneous process
   b. entropy
   c. positional probability
   d. system
   e. surroundings
   f. universe
2. What is the second law of thermodynamics? For any process, there are four possible sign combinations for ΔS_{sys} and ΔS_{surr}. Which sign combination(s) always give a spontaneous process? Which sign combination(s) always give a nonspontaneous process? Which sign combination(s) may or may not give a spontaneous process?
3. What determines ΔS_{surr} for a process? To calculate ΔS_{surr} at constant pressure and temperature, we use the following equation: $\Delta S_{\text{surr}} = -\Delta H/T$. Why does a minus sign appear in the equation, and why is ΔS_{surr} inversely proportional to temperature?
4. The free energy change, ΔG, for a process at constant temperature and pressure is related to ΔS_{univ} and reflects the spontaneity of the process. How is ΔG related to ΔS_{univ}? When is a process spontaneous? Nonspontaneous? At equilibrium? ΔG is a composite term composed of ΔH, T, and ΔS. What is the ΔG equation? Give the four possible sign combinations for ΔH and ΔS. What temperatures are required for each sign combination to yield a spontaneous process? If ΔG is positive, what does it say about the reverse process? How does the $\Delta G = \Delta H - T\Delta S$ equation reduce when at the melting-point temperature of a solid-to-liquid phase change or at the boiling-point temperature of a liquid-to-gas phase change? What is the sign of ΔG for the solid-to-liquid phase change at temperatures above the freezing point? What is the sign of ΔG for the liquid-to-gas phase change at temperatures below the boiling point?
5. What is the third law of thermodynamics? What are standard entropy values, S°, and how are these S° values (listed in Appendix 4) used to calculate ΔS° for a reaction? How would you use Hess's law to calculate ΔS° for a reaction? What does the superscript ° indicate?

   Predicting the sign of ΔS° for a reaction is an important skill to master. For a gas-phase reaction, what do you concentrate on to predict the sign of ΔS°? For a phase change, what do you concentrate on to predict the sign of ΔS°?

That is, how are S°_{solid}, S°_{liquid}, and S°_{gas} related to one another? When a solute dissolves in water, what is usually the sign of ΔS° for this process?

6. What is the standard free energy change, ΔG°, for a reaction? What is the standard free energy of formation, ΔG°_f, for a substance? How are ΔG°_f values used to calculate $\Delta G^\circ_{\text{rxn}}$? How can you use Hess's law to calculate $\Delta G^\circ_{\text{rxn}}$? How can you use ΔH° and ΔS° values to calculate $\Delta G^\circ_{\text{rxn}}$? Of the functions ΔH°, ΔS°, and ΔG°, which depends most strongly on temperature? When ΔG° is calculated at temperatures other than 25°C, what assumptions are generally made concerning ΔH° and ΔS°?
7. If you calculate a value for ΔG° for a reaction using the values of ΔG°_f in Appendix 4 and get a negative number, is it correct to say that the reaction is always spontaneous? Why or why not? Free energy changes also depend on concentration. For gases, how is G related to the pressure of the gas? What are standard pressures for gases and standard concentrations for solutes? How do you calculate ΔG for a reaction at nonstandard conditions? The equation to determine ΔG at nonstandard conditions has Q in it: What is Q? A reaction is spontaneous as long as ΔG is negative; that is, reactions always proceed as long as the products have a lower free energy than the reactants. What is so special about equilibrium? Why don't reactions move away from equilibrium?
8. Consider the equation $\Delta G = \Delta G^\circ + RT\ln(Q)$. What is the value of ΔG for a reaction at equilibrium? What does Q equal at equilibrium? At equilibrium, the previous equation reduces to $\Delta G^\circ = -RT\ln(K)$. When $\Delta G^\circ > 0$, what does it indicate about K? When $\Delta G^\circ < 0$, what does it indicate about K? When $\Delta G^\circ = 0$, what does it indicate about K? ΔG predicts spontaneity for a reaction, whereas ΔG° predicts the equilibrium position. Explain what this statement means. Under what conditions can you use ΔG° to determine the spontaneity of a reaction?
9. Even if ΔG is negative, the reaction may not occur. Explain the interplay between the thermodynamics and the kinetics of a reaction. High temperatures are favorable to a reaction kinetically but may be unfavorable to a reaction thermodynamically. Explain.
10. Discuss the relationship between w_{max} and the magnitude and sign of the free energy change for a reaction. Also discuss w_{max} for real processes. What is a reversible process?

Active Learning Questions

These questions are designed to be used by groups of students in class. The questions allow students to explore their understanding of concepts through discussion and peer teaching. The real value of these questions is the learning that occurs while students talk to each other about chemical concepts.

1. For the process $A(l) \longrightarrow A(g)$, which direction is favored by changes in energy probability? Positional probability? Explain your answers. If you wanted to favor the process as written, would you raise or lower the temperature of the system? Explain.

2. For a liquid, which would you expect to be larger, ΔS_{fusion} or $\Delta S_{\text{evaporation}}$? Why?

3. Gas A_2 reacts with gas B_2 to form gas AB at a constant temperature. The bond energy of AB is much greater than that of either reactant. What can be said about the sign of ΔH? ΔS_{surr}? ΔS? Explain how potential energy changes for this process. Explain how random kinetic energy changes during the process.

4. What types of experiments can be carried out to determine whether a reaction is spontaneous? Does spontaneity have any relationship to the final equilibrium position of a reaction? Explain.

5. A friend tells you, "Free energy G and pressure P are related by the equation $G = G^\circ + RT\ln(P)$. Also, G is related to the equilibrium constant K in that when $G_{\text{products}} = G_{\text{reactants}}$, the system is at equilibrium. Therefore, it must be true that a system is at equilibrium when all the pressures are equal." Do you agree with this friend? Explain.

6. You remember that ΔG° is related to $RT\ln(K)$ but cannot remember if it's $RT\ln(K)$ or $-RT\ln(K)$. Realizing what ΔG° and K mean, how can you figure out the correct sign?

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide*.

Questions

7. The synthesis of glucose directly from CO_2 and H_2O and the synthesis of proteins directly from amino acids are both nonspontaneous processes under standard conditions. Yet it is necessary for these to occur for life to exist. In light of the second law of thermodynamics, how can life exist?

8. When the environment is contaminated by a toxic or potentially toxic substance (for example, from a chemical spill or the use of insecticides), the substance tends to disperse. How is this consistent with the second law of thermodynamics? In terms of the second law, which requires the least work: cleaning the environment after it has been contaminated or trying to prevent the contamination before it occurs? Explain.

9. A green plant synthesizes glucose by photosynthesis, as shown in the reaction

$$6CO_2(g) + 6H_2O(l) \longrightarrow C_6H_{12}O_6(s) + 6O_2(g)$$

Animals use glucose as a source of energy:

$$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l)$$

If we were to assume that both these processes occur to the same extent in a cyclic process, what thermodynamic property must have a nonzero value?

10. Human DNA contains almost twice as much information as is needed to code for all the substances produced in the body. Likewise, the digital data sent from *Voyager II* contained one redundant bit out of every two bits of information. The Hubble space telescope transmits three redundant bits for every bit of information. How is entropy related to the transmission of information? What do you think is accomplished by having so many redundant bits of information in both DNA and the space probes?

11. Entropy has been described as "time's arrow." Interpret this view of entropy.

12. A mixture of hydrogen gas and chlorine gas remains unreacted until it is exposed to ultraviolet light from a burning magnesium strip. Then the following reaction occurs very rapidly:

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

Explain.

13. Table 16.1 shows the possible arrangements of four molecules in a two-bulbed flask. What are the possible arrangements if there is one molecule in this two-bulbed flask or two molecules or three molecules? For each, what arrangement is most likely?

14. ΔS_{surr} is sometime called the energy disorder term. Explain.

15. The third law of thermodynamics states that the entropy of a perfect crystal at 0 K is zero. In Appendix 4, $F^-(aq)$, $OH^-(aq)$, and $S^{2-}(aq)$ all have negative standard entropy values. How can $S°$ values be less than zero?

16. The deciding factor on why HF is a weak acid and not a strong acid like the other hydrogen halides is entropy. What occurs when HF dissociates in water as compared to the other hydrogen halides?

17. List three different ways to calculate the standard free energy change, $\Delta G°$, for a reaction at 25°C? How is $\Delta G°$ estimated at temperatures other than 25°C? What assumptions are made?

18. What information can be determined from ΔG for a reaction? Does one get the same information from $\Delta G°$, the standard free energy change? $\Delta G°$ allows determination of the equilibrium constant K for a reaction. How? How can one estimate the value of K at temperatures other than 25°C for a reaction? How can one estimate the temperature where $K = 1$ for a reaction? Do all reactions have a specific temperature where $K = 1$?

Exercises

In this section similar exercises are paired.

Spontaneity, Entropy, and the Second Law of Thermodynamics: Free Energy

19. Which of the following processes are spontaneous?

a. Salt dissolves in H_2O.
b. A clear solution becomes a uniform color after a few drops of dye are added.
c. Iron rusts.
d. You clean your bedroom.

20. Which of the following processes are spontaneous?

a. A house is built.
b. A satellite is launched into orbit.
c. A satellite falls back to earth.
d. The kitchen gets cluttered.

21. Consider the following energy levels, each capable of holding two objects:

$E = 2$ kJ ____
$E = 1$ kJ ____
$E = 0$ XX

Draw all the possible arrangements of the two identical particles (represented by X) in the three energy levels. What total energy is most likely, that is, occurs the greatest number of times? Assume that the particles are indistinguishable from each other.

22. Redo Exercise 21 with two particles A and B, which can be distinguished from each other.

23. Choose the compound with the greatest positional probability in each case.

a. 1 mol H_2 (at STP) or 1 mol H_2 (at 100°C, 0.5 atm)
b. 1 mol N_2 (at STP) or 1 mol N_2 (at 100 K, 2.0 atm)
c. 1 mol $H_2O(s)$ (at 0°C) or 1 mol $H_2O(l)$ (at 20°C)

24. Which of the following involve an increase in the entropy of the system?

a. melting of a solid
b. sublimation
c. freezing
d. mixing
e. separation
f. boiling

25. Predict the sign of ΔS_{surr} for the following processes.

a. $H_2O(l) \longrightarrow H_2O(g)$
b. $CO_2(g) \longrightarrow CO_2(s)$

26. Calculate ΔS_{surr} for the following reactions at 25°C and 1 atm.

a. $C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$ $\Delta H° = -2221$ kJ

b. $2NO_2(g) \longrightarrow 2NO(g) + O_2(g)$ $\Delta H° = 112$ kJ

27. Given the values of ΔH and ΔS, which of the following changes will be spontaneous at constant T and P?

a. $\Delta H = +25$ kJ, $\Delta S = +5.0$ J/K, $T = 300.$ K

b. $\Delta H = +25$ kJ, $\Delta S = +100.$ J/K, $T = 300.$ K

c. $\Delta H = -10.$ kJ, $\Delta S = +5.0$ J/K, $T = 298$ K

d. $\Delta H = -10.$ kJ, $\Delta S = -40.$ J/K, $T = 200.$ K

28. At what temperatures will the following processes be spontaneous?

a. $\Delta H = -18$ kJ and $\Delta S = -60.$ J/K

b. $\Delta H = +18$ kJ and $\Delta S = +60.$ J/K

c. $\Delta H = +18$ kJ and $\Delta S = -60.$ J/K

d. $\Delta H = -18$ kJ and $\Delta S = +60.$ J/K

29. Ethanethiol (C_2H_5SH; also called ethyl mercaptan) is commonly added to natural gas to provide the "rotten egg" smell of a gas leak. The boiling point of ethanethiol is 35°C and its heat of vaporization is 27.5 kJ/mol. What is the entropy of vaporization for this substance?

30. For mercury, the enthalpy of vaporization is 58.51 kJ/mol and the entropy of vaporization is 92.92 J/K · mol. What is the normal boiling point of mercury?

31. For ammonia (NH_3), the enthalpy of fusion is 5.65 kJ/mol and the entropy of fusion is 28.9 J/K · mol.

a. Will $NH_3(s)$ spontaneously melt at 200. K?

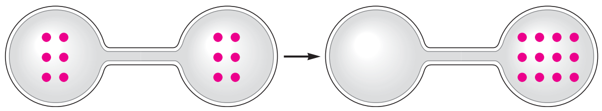
b. What is the approximate melting point of ammonia?

32. The enthalpy of vaporization of ethanol is 38.7 kJ/mol at its boiling point (78°C). Determine ΔS_{sys}, ΔS_{surr}, and ΔS_{univ} when 1.00 mol of ethanol is vaporized at 78°C and 1.00 atm.

Chemical Reactions: Entropy Changes and Free Energy

33. Predict the sign of $\Delta S°$ for each of the following changes.

a.



b. $AgCl(s) \longrightarrow Ag^+(aq) + Cl^-(aq)$

c. $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

d. $H_2O(l) \longrightarrow H_2O(g)$

34. Predict the sign of $\Delta S°$ for each of the following changes.

a. $Na(s) + \frac{1}{2}Cl_2(g) \longrightarrow NaCl(s)$

b. $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

c. $NaCl(s) \longrightarrow Na^+(aq) + Cl^-(aq)$

d. $NaCl(s) \longrightarrow NaCl(l)$

35. For each of the following pairs of substances, which substance has the greater value of $S°$?

a. $C_{\text{graphite}}(s)$ or $C_{\text{diamond}}(s)$

b. $C_2H_5OH(l)$ or $C_2H_5OH(g)$

c. $CO_2(s)$ or $CO_2(g)$

36. For each of the following pairs, which substance has the greater value of S?

a. N_2O (at 0 K) or He (at 10 K)

b. $N_2O(g)$ (at 1 atm, 25°C) or $He(g)$ (at 1 atm, 25°C)

c. $H_2O(s)$ (at 0°C) or $H_2O(l)$ (at 0°C)

37. Predict the sign of $\Delta S°$ and then calculate $\Delta S°$ for each of the following reactions.

a. $2H_2S(g) + SO_2(g) \longrightarrow 3S_{\text{rhombic}}(s) + 2H_2O(g)$

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

c. $Fe_2O_3(s) + 3H_2(g) \longrightarrow 2Fe(s) + 3H_2O(g)$

38. Predict the sign of $\Delta S°$ and then calculate $\Delta S°$ for each of the following reactions.

a. $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$

b. $2CH_3OH(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 4H_2O(g)$

c. $HCl(g) \longrightarrow H^+(aq) + Cl^-(aq)$

39. For the reaction

$$C_2H_2(g) + 4F_2(g) \longrightarrow 2CF_4(g) + H_2(g)$$

$\Delta S°$ is equal to -358 J/K. Use this value and data from Appendix 4 to calculate the value of $S°$ for $CF_4(g)$.

40. For the reaction

$$2Al(s) + 3Br_2(l) \longrightarrow 2AlBr_3(s)$$

$\Delta S°$ is equal to -144 J/K. Use this value and data from Appendix 4 to calculate the value of $S°$ for solid aluminum bromide.

41. It is quite common for a solid to change from one structure to another at a temperature below its melting point. For example, sulfur undergoes a phase change from the rhombic crystal structure to the monoclinic crystal form at temperatures above 95°C.

a. Predict the signs of ΔH and ΔS for the process $S_{\text{rhombic}} \longrightarrow S_{\text{monoclinic}}$.

b. Which form of sulfur has the more ordered crystalline structure?

42. When most biologic enzymes are heated they lose their catalytic activity. The change

$$\text{original enzyme} \longrightarrow \text{new form}$$

that occurs on heating is endothermic and spontaneous. Is the structure of the original enzyme or its new form more ordered? Explain.

43. Consider the reaction

$$2O(g) \longrightarrow O_2(g)$$

a. Predict the signs of ΔH and ΔS.

b. Would the reaction be more spontaneous at high or low temperatures?

44. Hydrogen cyanide is produced industrially by the following exothermic reaction:

$$2NH_3(g) + 3O_2(g) + 2CH_4(g) \xrightarrow[\text{Pt-Rh}]{1000°\text{C}} 2HCN(g) + 6H_2O(g)$$

Is the high temperature needed for thermodynamic or kinetic reasons?

45. From data in Appendix 4, calculate $\Delta H°$, $\Delta S°$, and $\Delta G°$ for each of the following reactions at 25°C.

a. $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$
b. $6CO_2(g) + 6H_2O(l) \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6(s)} + 6O_2(g)$
c. $P_4O_{10}(s) + 6H_2O(l) \longrightarrow 4H_3PO_4(s)$
d. $HCl(g) + NH_3(g) \longrightarrow NH_4Cl(s)$

46. The decomposition of ammonium dichromate $[(NH_4)_2Cr_2O_7]$ is called the "volcano" demonstration for its fiery display. The decomposition reaction involves breaking down ammonium dichromate into nitrogen gas, water vapor, and solid chromium(III) oxide. From the data in Appendix 4 and given $\Delta H_f^\circ = -23$ kJ/mol and $\Delta S^\circ = 114$ J/K · mol for $(NH_4)_2Cr_2O_7$, calculate ΔG° for the "volcano" reaction and calculate ΔG_f° for ammonium dichromate.

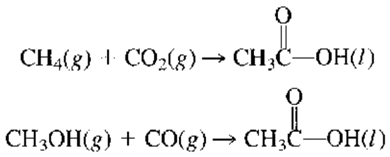
47. For the reaction at 298 K,

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

the values of ΔH° and ΔS° are -58.03 kJ and -176.6 J/K, respectively. What is the value of ΔG° at 298 K? Assuming that ΔH° and ΔS° do not depend on temperature, at what temperature is $\Delta G^\circ = 0$? Is ΔG° negative above or below this temperature?

48. At 100.°C and 1.00 atm, $\Delta H^\circ = 40.6$ kJ/mol for the vaporization of water. Estimate ΔG° for the vaporization of water at 90.°C and 110.°C. Assume ΔH° and ΔS° at 100.°C and 1.00 atm do not depend on temperature.

49. Using data from Appendix 4, calculate ΔH°, ΔS°, and ΔG° for the following reactions that produce acetic acid:



$$CH_4(g) + CO_2(g) \rightarrow CH_3\overset{\overset{\large O}{\|}}{C}—OH(l)$$

$$CH_3OH(g) + CO(g) \rightarrow CH_3\overset{\overset{\large O}{\|}}{C}—OH(l)$$

Which reaction would you choose as a commercial method for producing acetic acid (CH_3CO_2H) at standard conditions? What temperature conditions would you choose for the reaction? Assume ΔH° and ΔS° do not depend on temperature.

50. Consider two reactions for the production of ethanol:

$$C_2H_4(g) + H_2O(g) \longrightarrow CH_3CH_2OH(l)$$
$$C_2H_6(g) + H_2O(g) \longrightarrow CH_3CH_2OH(l) + H_2(g)$$

Which would be the more thermodynamically feasible at standard conditions? Why?

51. Given the following data:

$$\begin{array}{rll} 2H_2(g) + C(s) \longrightarrow CH_4(g) & & \Delta G^\circ = -51 \text{ kJ} \\ 2H_2(g) + O_2(g) \longrightarrow 2H_2O(l) & & \Delta G^\circ = -474 \text{ kJ} \\ C(s) + O_2(g) \longrightarrow CO_2(g) & & \Delta G^\circ = -394 \text{ kJ} \end{array}$$

Calculate ΔG° for $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$.

52. Given the following data:

$$\begin{array}{ll} 2C_6H_6(l) + 15O_2(g) \longrightarrow 12CO_2(g) + 6H_2O(l) & \\ & \Delta G^\circ = -6399 \text{ kJ} \\ C(s) + O_2(g) \longrightarrow CO_2(g) & \Delta G^\circ = -394 \text{ kJ} \\ H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) & \Delta G^\circ = -237 \text{ kJ} \end{array}$$

calculate ΔG° for the reaction

$$6C(s) + 3H_2(g) \longrightarrow C_6H_6(l)$$

53. For the reaction

$$SF_4(g) + F_2(g) \longrightarrow SF_6(g)$$

the value of ΔG° is -374 kJ. Use this value and data from Appendix 4 to calculate the value of ΔG_f° for $SF_4(g)$.

54. The value of ΔG° for the reaction

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

is $-5490.$ kJ. Use this value and data from Appendix 4 to calculate the standard free energy of formation for $C_4H_{10}(g)$.

55. Assuming standard conditions, can the following reaction take place at room temperature?

$$3Cl_2(g) + 2CH_4(g) \longrightarrow CH_3Cl(g) + CH_2Cl_2(g) + 3HCl(g)$$

$\Delta G^\circ\ (CH_4) = -50.72$ kJ/mol $\Delta G^\circ\ (CH_3Cl) = -57.37$ kJ/mol
$\Delta G^\circ\ (CH_2Cl_2) = -68.85$ kJ/mol $\Delta G^\circ\ (HCl) = -95.30$ kJ/mol

56. Consider the reaction

$$2POCl_3(g) \longrightarrow 2PCl_3(g) + O_2(g)$$

a. Calculate ΔG° for this reaction. The ΔG_f° values for $POCl_3(g)$ and $PCl_3(g)$ are -502 kJ/mol and $-270.$ kJ/mol, respectively.
b. Is this reaction spontaneous under standard conditions at 298 K?
c. The value of ΔS° for this reaction is 179 J/K. At what temperatures is this reaction spontaneous at standard conditions? Assume that ΔH° and ΔS° do not depend on temperature.

Free Energy: Pressure Dependence and Equilibrium

57. Using data from Appendix 4, calculate ΔG for the reaction

$$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$$

for these conditions:

$T = 298$ K
$P_{NO} = 1.00 \times 10^{-6}$ atm, $P_{O_3} = 2.00 \times 10^{-6}$ atm
$P_{NO_2} = 1.00 \times 10^{-7}$ atm, $P_{O_2} = 1.00 \times 10^{-3}$ atm

58. Using data from Appendix 4, calculate ΔG for the reaction

$$2H_2S(g) + SO_2(g) \rightleftharpoons 3S_{\text{rhombic}}(s) + 2H_2O(g)$$

for the following conditions at 25°C:

$P_{H_2S} = 1.0 \times 10^{-4}$ atm
$P_{SO_2} = 1.0 \times 10^{-2}$ atm
$P_{H_2O} = 3.0 \times 10^{-2}$ atm

59. Consider the reaction

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

For each of the following mixtures of reactants and products at 25°C, predict the direction in which the reaction will shift to reach equilibrium.

a. $P_{NO_2} = P_{N_2O_4} = 1.0$ atm
b. $P_{NO_2} = 0.21$ atm, $P_{N_2O_4} = 0.50$ atm
c. $P_{NO_2} = 0.29$ atm, $P_{N_2O_4} = 1.6$ atm

60. Consider the following reaction:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Calculate ΔG for this reaction under the following conditions (assume an uncertainty of ±1 in all quantities):

a. $T = 298$ K, $P_{N_2} = P_{H_2} = 200$ atm, $P_{NH_3} = 50$ atm

b. $T = 298$ K, $P_{N_2} = 200$ atm, $P_{H_2} = 600$ atm, $P_{NH_3} = 200$ atm

61. Consider the following reaction at 25.0°C:

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

The values of $\Delta H°$ and $\Delta S°$ are -58.03 kJ/mol and -176.6 J/K · mol, respectively. Calculate the value of K at 25.0°C. Assuming $\Delta H°$ and $\Delta S°$ are temperature independent, estimate the value of K at 100.0°C.

62. Consider the reaction

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

a. Calculate $\Delta H°$, $\Delta S°$, $\Delta G°$, and K (at 298 K) using data in Appendix 4.

b. If $H_2(g)$, $Cl_2(g)$, and $HCl(g)$ are placed in a flask such that the pressure of each gas is 1 atm, in which direction will the system shift to reach equilibrium at 25°C?

63. Calculate $\Delta G°$ for $H_2O(g) + \frac{1}{2}O_2(g) \rightleftharpoons H_2O_2(g)$ at 600. K, using the following data:

$$H_2(g) + O_2(g) \rightleftharpoons H_2O_2(g) \qquad K = 2.3 \times 10^6 \text{ at 600. K}$$
$$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g) \qquad K = 1.8 \times 10^{37} \text{ at 600. K}$$

64. The Ostwald process for the commercial production of nitric acid involves three steps:

$$4NH_3(g) + 5O_2(g) \xrightarrow[825°C]{Pt} 4NO(g) + 6H_2O(g)$$
$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$
$$3NO_2(g) + H_2O(l) \longrightarrow 2HNO_3(l) + NO(g)$$

a. Calculate $\Delta H°$, $\Delta S°$, $\Delta G°$, and K (at 298 K) for each of the three steps in the Ostwald process (see Appendix 4).

b. Calculate the equilibrium constant for the first step at 825°C, assuming $\Delta H°$ and $\Delta S°$ do not depend on temperature.

c. Is there a thermodynamic reason for the high temperature in the first step assuming standard conditions?

65. Consider the following reaction at 800. K:

$$N_2(g) + 3F_2(g) \longrightarrow 2NF_3(g)$$

An equilibrium mixture contains the following partial pressures: $P_{N_2} = 0.021$ atm, $P_{F_2} = 0.063$ atm, $P_{NF_3} = 0.48$ atm. Calculate $\Delta G°$ for the reaction at 800. K.

66. Consider the following reaction at 298 K:

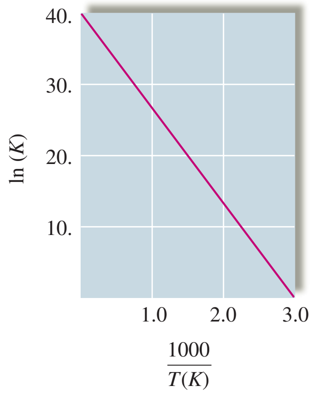
$$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$$

An equilibrium mixture contains $O_2(g)$ and $SO_3(g)$ at partial pressures of 0.50 atm and 2.0 atm, respectively. Using data from Appendix 4, determine the equilibrium partial pressure of SO_2 in the mixture. Will this reaction be most favored at a high or a low temperature, assuming standard conditions?

67. Consider the relationship:

$$\ln(K) = \frac{-\Delta H°}{RT} + \frac{\Delta S°}{R}$$

The equilibrium constant for some hypothetical process was determined as a function of temperature (in Kelvin) with the results plotted below.



From the plot, determine the values of $\Delta H°$ and $\Delta S°$ for this process. What would be the major difference in the ln(K) versus $1/T$ plot for an endothermic process as compared to an exothermic process?

68. The equilibrium constant K for the reaction

$$2Cl(g) \rightleftharpoons Cl_2(g)$$

was measured as a function of temperature (Kelvin). A graph of ln K versus $1/T$ for this reaction gives a straight line with a slope of 1.352×10^4 K and a y-intercept of -14.51. Determine the values of $\Delta H°$ and $\Delta S°$ for this reaction. Reference Exercise 67.

Additional Exercises

69. Using Appendix 4 and the following data, determine $S°$ for $Fe(CO)_5(g)$.

$$Fe(s) + 5CO(g) \longrightarrow Fe(CO)_5(g) \qquad \Delta S° = ?$$
$$Fe(CO)_5(l) \longrightarrow Fe(CO)_5(g) \qquad \Delta S° = 107 \text{ J/K}$$
$$Fe(s) + 5CO(g) \longrightarrow Fe(CO)_5(l) \qquad \Delta S° = -677 \text{ J/K}$$

70. Some water is placed in a coffee-cup calorimeter. When 1.0 g of an ionic solid is added, the temperature of the solution increases from 21.5°C to 24.2°C as the solid dissolves. For the dissolving process, what are the signs for ΔS_{sys}, ΔS_{surr}, and ΔS_{univ}?

71. Consider the following system at equilibrium at 25°C:

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g) \qquad \Delta G° = -92.50 \text{ kJ}$$

What will happen to the ratio of partial pressure of PCl_5 to partial pressure of PCl_3 if the temperature is raised? Explain completely.

72. Calculate the entropy change for the vaporization of liquid methane and liquid hexane using the following data.

	Boiling Point (1 atm)	**ΔH_{vap}**
Methane	112 K	8.20 kJ/mol
Hexane	342 K	28.9 kJ/mol

Compare the molar volume of gaseous methane at 112 K with that of gaseous hexane at 342 K. How do the differences in molar volume affect the values of ΔS_{vap} for these liquids?

73. As $O_2(l)$ is cooled at 1 atm, it freezes at 54.5 K to form solid I. At a lower temperature, solid I rearranges to solid II, which has a different crystal structure. Thermal measurements show that ΔH for the I → II phase transition is -743.1 J/mol, and ΔS for the same transition is -17.0 J/K · mol. At what temperature are solids I and II in equilibrium?

74. Consider the following reaction:

$$H_2O(g) + Cl_2O(g) \rightleftharpoons 2HOCl(g) \qquad K_{298} = 0.090$$

For $Cl_2O(g)$,

$$\Delta G_f^\circ = 97.9 \text{ kJ/mol}$$
$$\Delta H_f^\circ = 80.3 \text{ kJ/mol}$$
$$S^\circ = 266.1 \text{ J/K} \cdot \text{mol}$$

a. Calculate ΔG° for the reaction using the equation $\Delta G^\circ = -RT \ln(K)$.

b. Use bond energy values (Table 8.4) to estimate ΔH° for the reaction.

c. Use the results from parts a and b to estimate ΔS° for the reaction.

d. Estimate ΔH_f° and S° for $HOCl(g)$.

e. Estimate the value of K at 500. K.

f. Calculate ΔG at 25°C when $P_{H_2O} = 18$ torr, $P_{Cl_2O} = 2.0$ torr, and $P_{HOCl} = 0.10$ torr.

75. Carbon monoxide is toxic because it bonds much more strongly to the iron in hemoglobin (Hgb) than does O_2. Consider the following reactions and approximate standard free energy changes:

$$Hgb + O_2 \longrightarrow HgbO_2 \qquad \Delta G^\circ = -70 \text{ kJ}$$
$$Hgb + CO \longrightarrow HgbCO \qquad \Delta G^\circ = -80 \text{ kJ}$$

Using these data, estimate the equilibrium constant value at 25°C for the following reaction:

$$HgbO_2 + CO \rightleftharpoons HgbCO + O_2$$

76. Using the following data, calculate the value of K_{sp} for $Ba(NO_3)_2$, one of the *least* soluble of the common nitrate salts.

Species	**ΔG_f°**
$Ba^{2+}(aq)$	-561 kJ/mol
$NO_3^-(aq)$	-109 kJ/mol
$Ba(NO_3)_2(s)$	-797 kJ/mol

77. In the text the equation

$$\Delta G = \Delta G^\circ + RT \ln(Q)$$

was derived for gaseous reactions where the quantities in Q were expressed in units of pressure. We also can use units of mol/L for the quantities in Q, specifically for aqueous reactions. With this in mind, consider the reaction

$$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$$

for which $K_a = 7.2 \times 10^{-4}$ at 25°C. Calculate ΔG for the reaction under the following conditions at 25°C.

a. $[HF] = [H^+] = [F^-] = 1.0\ M$

b. $[HF] = 0.98\ M$, $[H^+] = [F^-] = 2.7 \times 10^{-2}\ M$

c. $[HF] = [H^+] = [F^-] = 1.0 \times 10^{-5}\ M$

d. $[HF] = [F^-] = 0.27\ M$, $[H^+] = 7.2 \times 10^{-4}\ M$

e. $[HF] = 0.52\ M$, $[F^-] = 0.67\ M$, $[H^+] = 1.0 \times 10^{-3}\ M$

Based on the calculated ΔG values, in what direction will the reaction shift to reach equilibrium for each of the five sets of conditions?

78. Many biochemical reactions that occur in cells require relatively high concentrations of potassium ion (K^+). The concentration of K^+ in muscle cells is about 0.15 *M*. The concentration of K^+ in blood plasma is about 0.0050 *M*. The high internal concentration in cells is maintained by pumping K^+ from the plasma. How much work must be done to transport 1.0 mol K^+ from the blood to the inside of a muscle cell at 37°C, normal body temperature? When 1.0 mol K^+ is transferred from blood to the cells, do any other ions have to be transported? Why or why not?

79. Cells use the hydrolysis of adenosine triphosphate, abbreviated as ATP, as a source of energy. Symbolically, this reaction can be written as

$$ATP(aq) + H_2O(l) \longrightarrow ADP(aq) + H_2PO_4^-(aq)$$

where ADP represents adenosine diphosphate. For this reaction, $\Delta G^\circ = -30.5$ kJ/mol.

a. Calculate K at 25°C.

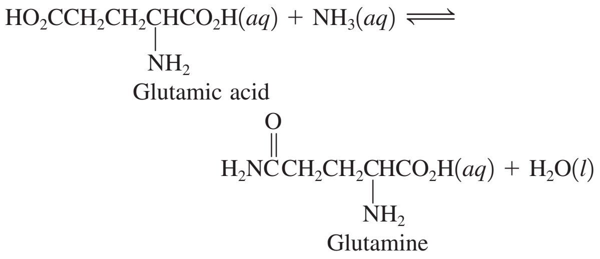
b. If all the free energy from the metabolism of glucose

$$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l)$$

goes into forming ATP from ADP, how many ATP molecules can be produced for every molecule of glucose?

c. Much of the ATP formed from metabolic processes is used to provide energy for transport of cellular components. What amount (mol) of ATP must be hydrolyzed to provide the energy for the transport of 1.0 mol of K^+ from the blood to the inside of a muscle cell at 37°C as described in Exercise 78?

80. One reaction that occurs in human metabolism is



$$HO_2CCH_2CH_2CH(NH_2)CO_2H(aq) + NH_3(aq) \rightleftharpoons H_2NC(=O)CH_2CH_2CH(NH_2)CO_2H(aq) + H_2O(l)$$

Glutamic acid

Glutamine

For this reaction $\Delta G^\circ = 14$ kJ at 25°C.

a. Calculate K for this reaction at 25°C.

b. In a living cell this reaction is coupled with the hydrolysis of ATP. (See Exercise 79.) Calculate ΔG° and K at 25°C for the following reaction:

$$\text{Glutamic acid}(aq) + \text{ATP}(aq) + \text{NH}_3(aq) \rightleftharpoons \text{Glutamine}(aq) + \text{ADP}(aq) + \text{H}_2\text{PO}_4^-(aq)$$

81. Consider the reactions

$$\text{Ni}^{2+}(aq) + 6\text{NH}_3(aq) \longrightarrow \text{Ni(NH}_3)_6{}^{2+}(aq) \qquad (1)$$
$$\text{Ni}^{2+}(aq) + 3\text{en}(aq) \longrightarrow \text{Ni(en)}_3{}^{2+}(aq) \qquad (2)$$

where

$$\text{en} = \text{H}_2\text{N—CH}_2\text{—CH}_2\text{—NH}_2$$

The ΔH values for the two reactions are quite similar, yet $K_{\text{reaction 2}} > K_{\text{reaction 1}}$. Explain.

82. Use the equation in Exercise 67 to determine ΔH° and ΔS° for the autoionization of water:

$$\text{H}_2\text{O}(l) \rightleftharpoons \text{H}^+(aq) + \text{OH}^-(aq)$$

***T*(°C)**	**K_w**
0	1.14×10^{-15}
25	1.00×10^{-14}
35	2.09×10^{-14}
40.	2.92×10^{-14}
50.	5.47×10^{-14}

83. Consider the reaction

$$\text{Fe}_2\text{O}_3(s) + 3\text{H}_2(g) \longrightarrow 2\text{Fe}(s) + 3\text{H}_2\text{O}(g)$$

Assuming ΔH° and ΔS° do not depend on temperature, calculate the temperature where $K = 1.00$ for this reaction.

Challenge Problems

84. Liquid water at 25°C is introduced into an evacuated, insulated vessel. Identify the signs of the following thermodynamic functions for the process that occurs: ΔH, ΔS, ΔT_{water}, ΔS_{surr}, ΔS_{univ}.

85. Using data from Appendix 4, calculate ΔH°, ΔG°, and K (at 298 K) for the production of ozone from oxygen:

$$3\text{O}_2(g) \rightleftharpoons 2\text{O}_3(g)$$

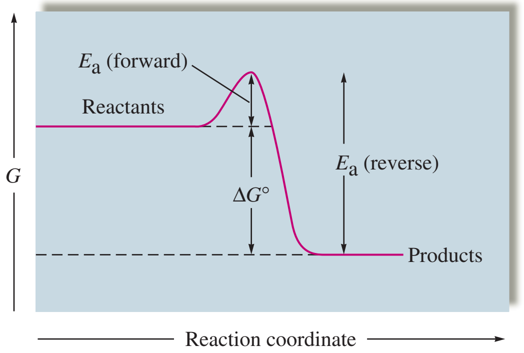
At 30 km above the surface of the earth, the temperature is about 230. K and the partial pressure of oxygen is about 1.0×10^{-3} atm. Estimate the partial pressure of ozone in equilibrium with oxygen at 30 km above the earth's surface. Is it reasonable to assume that the equilibrium between oxygen and ozone is maintained under these conditions? Explain.

86. Entropy can be calculated by a relationship proposed by Ludwig Boltzmann:

$$S = k \ln(W)$$

where $k = 1.38 \times 10^{-23}$ J/K and W is the number of ways a particular state can be obtained. (This equation is engraved on Boltzmann's tombstone.) Calculate S for the three arrangements of particles in Table 16.1.

87. **a.** Using the free energy profile for a simple one-step reaction, show that at equilibrium $K = k_f/k_r$, where k_f and k_r are the rate constants for the forward and reverse reactions. *Hint:* Use the relationship $\Delta G^\circ = -RT \ln(K)$ and represent k_f and k_r using the Arrhenius equation ($k = Ae^{-E_a/RT}$).



b. Why is the following statement false? "A catalyst can increase the rate of a forward reaction but not the rate of the reverse reaction."

88. Consider the reaction

$$\text{H}_2(g) + \text{Br}_2(g) \rightleftharpoons 2\text{HBr}(g)$$

where $\Delta H^\circ = -103.8$ kJ/mol. In a particular experiment, equal moles of $\text{H}_2(g)$ at 1.00 atm and $\text{Br}_2(g)$ at 1.00 atm were mixed in a 1.00-L flask at 25°C and allowed to reach equilibrium. Then the molecules of H_2 at equilibrium were counted using a very sensitive technique, and 1.10×10^{13} molecules were found. For this reaction, calculate the values of K, ΔG°, and ΔS°.

89. Consider the system

$$\text{A}(g) \longrightarrow \text{B}(g)$$

at 25°C.

a. Assuming that $G^\circ_{\text{A}} = 8996$ J/mol and $G^\circ_{\text{B}} = 11{,}718$ J/mol, calculate the value of the equilibrium constant for this reaction.

b. Calculate the equilibrium pressures that result if 1.00 mol A(g) at 1.00 atm and 1.00 mol B(g) at 1.00 atm are mixed at 25°C.

c. Show by calculations that $\Delta G = 0$ at equilibrium.

90. The equilibrium constant for a certain reaction decreases from 8.84 to 3.25×10^{-2} when the temperature increases from 25°C to 75°C. Estimate the temperature where $K = 1.00$ for this reaction. Estimate the value of ΔS° for this reaction. *Hint:* Manipulate the equation in Exercise 67.

91. If wet silver carbonate is dried in a stream of hot air, the air must have a certain concentration level of carbon dioxide to prevent silver carbonate from decomposing by the reaction

$$\text{Ag}_2\text{CO}_3(s) \rightleftharpoons \text{Ag}_2\text{O}(s) + \text{CO}_2(g)$$

ΔH° for this reaction is 79.14 kJ/mol in the temperature range of 25 to 125°C. Given that the partial pressure of carbon dioxide in equilibrium with pure solid silver carbonate is 6.23×10^{-3} torr at 25°C, calculate the partial pressure of CO_2 necessary to prevent decomposition of Ag_2CO_3 at 110.°C. *Hint:* Manipulate the equation in Exercise 67.

92. Carbon tetrachloride (CCl_4) and benzene (C_6H_6) form ideal solutions. Consider an equimolar solution of CCl_4 and C_6H_6 at 25°C. The vapor above the solution is collected and condensed. Using the following data, determine the composition in mole fraction of the condensed vapor.

Substance	ΔG°_f
$C_6H_6(l)$	124.50 kJ/mol
$C_6H_6(g)$	129.66 kJ/mol
$CCl_4(l)$	−65.21 kJ/mol
$CCl_4(g)$	−60.59 kJ/mol

93. Some nonelectrolyte solute (molar mass = 142 g/mol) was dissolved in 150. mL of a solvent (density = 0.879 g/cm^3). The elevated boiling point of the solution was 355.4 K. What mass of solute was dissolved in the solvent? For the solvent, the enthalpy of vaporization is 33.90 kJ/mol, the entropy of vaporization is 95.95 J/K · mol, and the boiling-point elevation constant is 2.5 K · kg/mol.

94. You have a 1.00-L sample of hot water (90.0°C) sitting open in a 25.0°C room. Eventually the water cools to 250°C while the temperature of the room remains unchanged. Calculate ΔS_{surr} for this process. Assume the density of water is 1.00 g/cm^3 over this temperature range, and the heat capacity of water is constant over this temperature range and equal to 75.4 J/K · mol.

95. Consider a weak acid, HX. If a 0.10 *M* solution of HX has a pH of 5.83 at 25°C, what is ΔG° for the acid's dissociation reaction at 25°C?

96. Sodium chloride is added to water (at 25°C) until it is saturated. Calculate the Cl^- concentration in such a solution.

Species	ΔG° (kJ/mol)
$NaCl(s)$	−384
$Na^+(aq)$	−262
$Cl^-(aq)$	−131

Integrative Problems

These problems require the integration of multiple concepts to find the solutions.

97. For the equilibrium

$$A(g) + 2B(g) \rightleftharpoons C(g)$$

the initial concentrations are [A] = [B] = [C] = 0.100 atm. Once equilibrium has been established, it is found that [C] = 0.040 atm. What is ΔG° for this reaction at 25°C?

98. What is the pH of a 0.125 *M* solution of the weak base B if $\Delta H^\circ = -28.0$ kJ and $\Delta S^\circ = -175$ J/K for the following equilibrium reaction at 25°C?

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

Marathon Problem

This problem is designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

99. Impure nickel, refined by smelting sulfide ores in a blast furnace, can be converted into metal from 99.90% to 99.99% purity by the Mond process. The primary reaction involved in the Mond process is

$$Ni(s) + 4CO(g) \rightleftharpoons Ni(CO)_4(g)$$

a. Without referring to Appendix 4, predict the sign of ΔS° for the above reaction. Explain.

b. The spontaneity of the above reaction is temperature dependent. Predict the sign of ΔS_{surr} for this reaction. Explain.

c. For $Ni(CO)_4(g)$, $\Delta H^\circ_f = -607$ kJ/mol and $S^\circ = 417$ J/K · mol at 298 K. Using these values and data in Appendix 4, calculate ΔH° and ΔS° for the above reaction.

d. Calculate the temperature at which $\Delta G^\circ = 0$ ($K = 1$) for the above reaction, assuming that ΔH° and ΔS° do not depend on temperature.

e. The first step of the Mond process involves equilibrating impure nickel with $CO(g)$ and $Ni(CO)_4(g)$ at about 50°C. The purpose of this step is to convert as much nickel as possible into the gas phase. Calculate the equilibrium constant for the above reaction at 50.°C.

f. In the second step of the Mond process, the gaseous $Ni(CO)_4$ is isolated and heated to 227°C. The purpose of this step is to deposit as much nickel as possible as pure solid (the reverse of the above reaction). Calculate the equilibrium constant for the above reaction at 227°C.

g. Why is temperature increased for the second step of the Mond process?

h. The Mond process relies on the volatility of $Ni(CO)_4$ for its success. Only pressures and temperatures at which $Ni(CO)_4$ is a gas are useful. A recently developed variation of the Mond process carries out the first step at higher pressures and a temperature of 152°C. Estimate the maximum pressure of $Ni(CO)_4(g)$ that can be attained before the gas will liquefy at 152°C. The boiling point for $Ni(CO)_4$ is 42°C and the enthalpy of vaporization is 29.0 kJ/mol.

[*Hint:* The phase change reaction and the corresponding equilibrium expression are

$$Ni(CO)_4(l) \rightleftharpoons Ni(CO)_4(g) \qquad K = P_{Ni(CO)_4}$$

$Ni(CO)_4(g)$ will liquefy when the pressure of $Ni(CO)_4$ is greater than the *K* value.]

Get help understanding core concepts and visualizing molecular-level interactions, and practice problem solving, by visiting the Online Study Center at **college.hmco.com/PIC/zumdahl7e.**