Spontaneous Change: Entropy and Gibbs Energy

13

CONTENTS

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Thermodynamics originated in the early nineteenth century with attempts to improve the efficiency of steam engines. However, the laws of thermodynamics are widely useful throughout the field of chemistry and in biology and physics, as we discover in this chapter.

Our everyday experiences have conditioned us to accept that certain things happen naturally in one direction only. For example, a bouncing ball eventually comes to rest on the floor, but a ball at rest will not begin to bounce. An ice cube placed in hot water eventually melts, but a glass of water will not produce an ice cube and hot water. A shiny iron nail rusts in air, but a rusty nail will not naturally shed its rusty exterior to produce a shiny nail. In this chapter, we explore concepts needed to understand why change happens naturally in one direction only.

At the end of Chapter 7, we noted some chemical and physical processes that proceeded in a certain direction without external influence, that is,

LEARNING OBJECTIVES

13.1 Describe the concepts of microstate and entropy, and discuss how they are related. Identify situations in which entropy generally increases, and describe them in terms of the microstates involved.

13.2 Describe how Clausius's equation can be used to obtain equations for calculating entropy changes for simple physical changes, including phase changes, constant pressure heating/cooling, and isothermal expansion/compression. Apply the resulting equations to calculate entropy changes.

13.3 Explain how the standard molar entropy of a substance is obtained. Use the standard molar entropies of reactants and products to determine the entropy change for a chemical reaction.

13.4 State the second law of thermodynamics, and identify the relationship between Gibbs energy, enthalpy, and entropy.

13.5 Predict the direction of spontaneous chemical change by using values of the standard Gibbs energy of reaction ($\Delta_r G^\circ$) and the thermodynamic reaction quotient (Q).

13.6 Use the van't Hoff equation to calculate the equilibrium constant as a function of temperature.

13.7 Describe how the coupling of chemical reactions may make a nonspontaneous process become a spontaneous one.

13.8 Discuss the relationships among chemical potential activity and the Gibbs energy of a mixture.


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▲ The melting of an ice cube occurs spontaneously at temperatures above 0 °C.

spontaneously (Section 7-10). Among those examples, we saw situations in which the internal energy, U, of the system increased, decreased, or stayed the same. Clearly, the internal energy change, ΔU, is not a reliable criterion for deciding whether or not a particular change will occur spontaneously.

In 1850, Clausius introduced the concept of entropy to explain the direction of spontaneous change. Twenty-seven years later Ludwig Boltzmann proposed an alternative view of entropy based on probability theory. Not surprisingly, Clausius's and Boltzmann's definitions of entropy were eventually shown to be equivalent. So what is entropy and why is it important? Simply stated, entropy measures the dispersal of energy. It is an important concept because a great deal of experimental evidence supports the notion that energy spontaneously "spreads out" or "disperses" if it is not hindered from doing so. Entropy is the yardstick for measuring the dispersal of energy.

In this chapter, we will continue to interpret observations about macroscopic systems by using a microscopic point of view. We will develop a conceptual model for understanding entropy and learn how to evaluate entropy changes for a variety of physical and chemical processes. Most importantly, we will define the criterion for spontaneous change and discover that it considers not only the entropy change for the system but also that of the surroundings. Finally, we will also learn about another important thermodynamic quantity, called Gibbs energy, which can also be used for understanding the direction of spontaneous change.

13-1 Entropy: Boltzmann's View

We will soon see that the criterion for spontaneous change can be expressed in terms of a thermodynamic quantity called entropy. Let's first focus our attention on developing a conceptual model for understanding entropy. Then, we will be able to use entropy, more specifically entropy changes, to explain why certain processes are spontaneous and others are not.

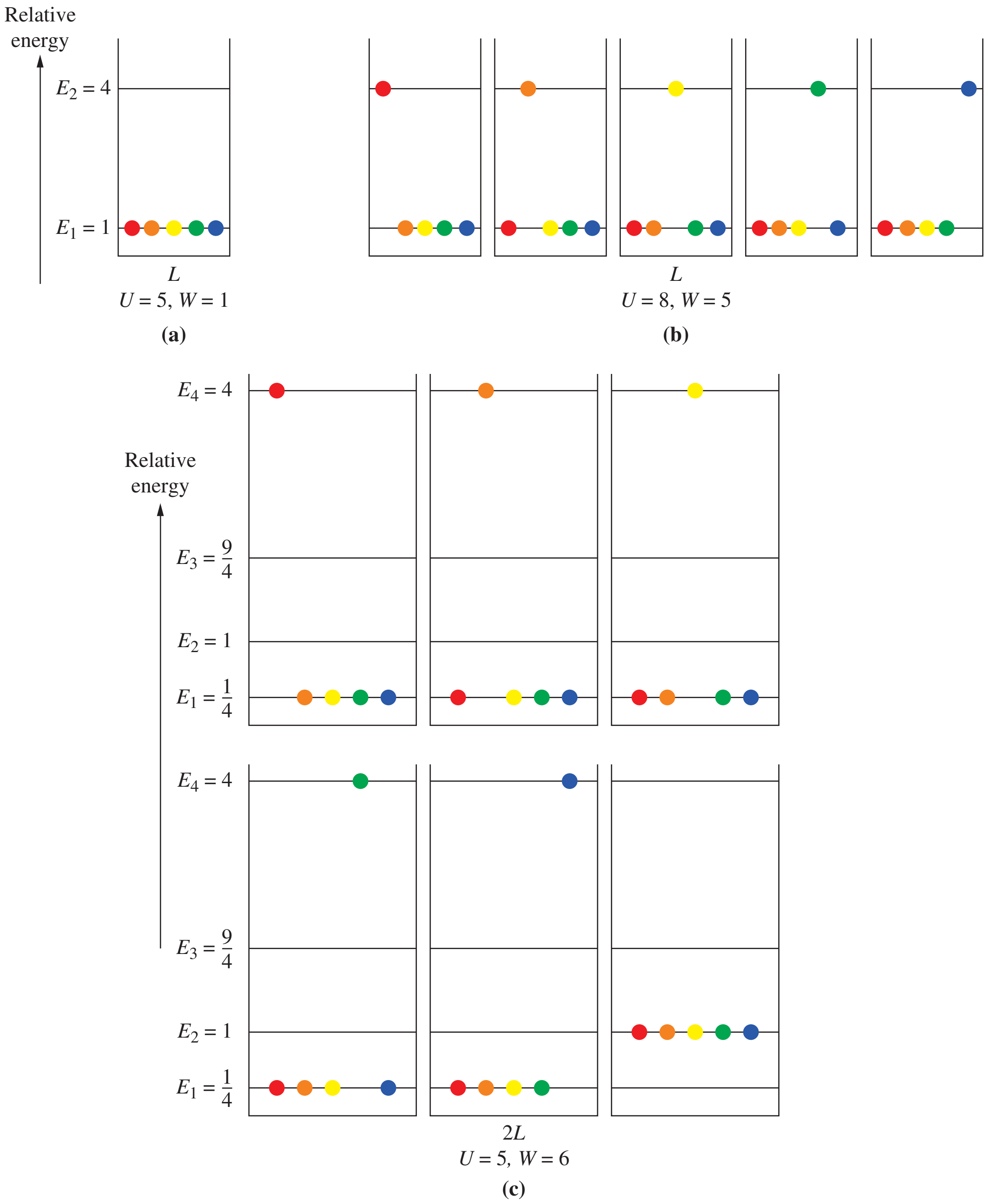
▶ Spontaneous: "proceeding from natural feeling or native tendency without external constraint . . . ; developing without apparent external influence, force, cause, or treatment" (*Merriam-Webster's Collegiate Dictionary*, online, 2000).

Microstates

The modern interpretation of entropy is firmly rooted in the idea that a macroscopic system is made up of many particles (often 10^{23} or more). Consider, for example, a fixed amount, n, of an ideal gas at temperature T in a container of volume V. The pressure of the gas is $P = nRT/V$. At the macroscopic level, the state of the gas is easily characterized by giving the values of n, T, V, and P. The state of the gas won't change without some external influence (e.g., by adding more gas, increasing the temperature, compressing the gas). However, on the microscopic level, the state of the system is not so easily characterized: The molecules are in continuous random motion, experiencing collisions with each other or the walls of the container. The positions, velocities, and energies of individual molecules change from one instant to the next. The main point is that for a given macroscopic state, characterized by n, T, P, and V, there are many possible microscopic configurations (or microstates), each of which might be characterized by giving the position, velocity, and energy of every molecule in the gas. Stated another way, the macroscopic properties of the gas, such as its temperature, pressure, and volume, could be described by any one of a very large number of microscopic configurations.

▶ A simple model for an ideal gas is obtained by treating the gas as a collection of noninteracting particles confined to a three-dimensional box. As we saw in Chapter 8, for a particle confined to a box, the kinetic energy (translational energy) is quantized. Each microstate corresponds to a particular way of distributing the molecules among the available translational energy levels.

In this discussion, we suggested that the microstate of an ideal gas could be described by giving the position, velocity, and energy of every molecule in the gas. However, such a description is not consistent with quantum mechanics because, according to the Heisenberg uncertainty principle (page 323), exact values for the position and velocity (or momentum) of a particle cannot be simultaneously specified. To be consistent with quantum mechanics, a microstate is characterized by specifying the quantum state (quantum numbers and energy) of every particle or by specifying how the particles are distributed among the quantized energy levels. Thus, according to quantum mechanics, a



▲ FIGURE 13-1
Enumeration of microstates
The distribution of five different particles among among the particle-in-a-box energy levels. The energies are expressed as multiples of $h^2/8mL^2$. The height of the pink shaded region represents the total internal energy of the system. **(a)** For a box of length L, there is only one possible microstate when $U = 5 \times (h^2/8mL^2)$. **(b)** When the internal energy is increased to $8 \times (h^2/8mL^2)$, the number of microstates increases to five because more energy levels are accessible. **(c)** When length of the box is increased to $2L$, the number of microstates for $U = 5 \times (h^2/8mL^2)$ increases to six. More energy levels are accessible because the energy levels are shifted to lower values and are more closely spaced.

microstate is a specific microscopic configuration describing how the particles of a system are distributed among the available energy levels.

Let's explore the concept of a microstate by considering a system of five particles confined to a one-dimensional box of length L. (We discussed the model of a particle in a box on page 326.) To start, we use the energy level expression $E_n = n^2h^2/8mL^2$ to calculate a few energy levels. Representative energy levels, expressed as multiples of $h^2/8mL^2$, are shown in the diagrams in Figure 13-1. Let's place the five particles among these energy levels with the constraint that the total energy, U, of the system must be $5 \times (h^2/8mL^2)$. The only possible arrangement (Fig. 13-1a) has all the particles in the $n = 1$ level. The total energy of this microstate is obtained by adding the particle energies:

$$U = (1 + 1 + 1 + 1 + 1) \times (h^2/8mL^2) = 5 \times (h^2/8mL^2)$$

Notice that, for the situation just discussed, the state of the system can be described in two ways. At the macroscopic level, the state of the system is described by specifying the total energy, U, and the length, L, of the box. At the molecular level, the state of the system is described in terms of a microstate having all particles in the $n = 1$ level. If we use the symbol W to represent the number of microstates, we have for this case $W = 1$. Notice that for this total energy, one energy level is accessible to the particles, namely, the $n = 1$ level.

Let's suppose we increase the total energy of the system to $8 \times (h^2/8mL^2)$ without changing the length of the box. Such an increase in U can be achieved, for example, by raising the temperature of the system. Figure 13.1(b) shows that, for $U = 8 \times (h^2/8mL^2)$, there are five possible microstates ($W = 5$) and an increase in the number of energy levels that are accessible to the particles. We see that as the total energy (or temperature) of a system increases, so too do the number of microstates and the number of accessible energy levels.

Now suppose we increase the length of the box from L to $2L$ but keep the total energy fixed at a value of $5 \times (h^2/8mL^2)$. The increase in L may be considered an "expansion" of the system. Figure 13-1(c) shows that, for this total energy, there are six possible microstates ($W = 6$) and a greater number of energy levels are accessible to the particles. We observe that, for a fixed total energy, the number of microstates increases as the box length increases, that is, as the system expands. The number of microstates increases when the box length increases because, for the larger box, the various levels are not only lower in energy but also more closely spaced. Thus, the number of energy levels that are accessible by the particles increases.

The point of this discussion was to illustrate not only the enumeration of microstates through the distribution of particles among the available energy levels but also that W, the number of microstates, increases with both the total energy and total space available to the particles of the system. The number of accessible energy levels also increases with the total energy and total space available. Now we make the connection between the number of microstates, W, and entropy.

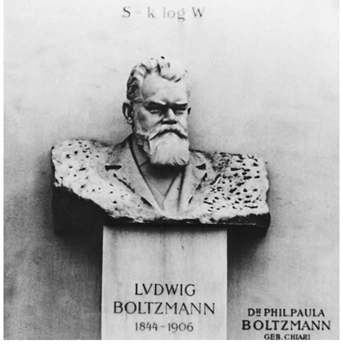
The Boltzmann Equation for Entropy

Entropy, S, is a thermodynamic property that is related to the way in which the energy of a system is distributed among the available energy levels. Ludwig Boltzmann made this important conceptual breakthrough when he associated the number of energy levels in the system with the number of ways of arranging the particles (atoms, ions, or molecules) in these energy levels. Boltzmann derived the relationship

$$S = k_B \ln W \tag{13.1}$$

where S is the entropy, k_B is the Boltzmann constant and W is the number of microstates. The Boltzmann constant is related to the gas constant R and Avogadro's number, N_A, by the expression $k_B = R/N_A$. We can think of k_B as the gas constant per molecule. (Although we did not specifically introduce k_B in our discussion of kinetic-molecular theory, R/N_A appears in equation (6.19).) Using $R = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$ and $N_A = 6.0221 \times 10^{23} \text{ mol}^{-1}$, we obtain $k_B = 1.3807 \times 10^{-23} \text{ J K}^{-1}$. The constant k_B also appears in the following important relationship derived by Boltzmann for the probability, p, that a system has energy E.

$$p \propto e^{-E/k_B T}$$



Central Library for Physics, Vienna, Austria

▲ **A bust marking Ludwig Boltzmann's tomb in Vienna** Boltzmann's famous equation is inscribed on the tomb. At the time of Boltzmann's death, the term *log* was used for both natural logarithms and logarithms to the base ten; the symbol ln had not yet been adopted.

Bear in mind that the concept of quantization of energy was not developed during Boltzmann's lifetime (1844–1906), so he did not express his probability law in terms of the quantized energy levels of the particles in the system. A modern form of this law is

$$N_i \propto e^{-E_i/k_B T}$$

where N_i is the number of particles in the system having energy E_i. The expression above holds only when the number of particles is extremely large.

Equation (13.1) justifies our earlier assertion that entropy provides a measure of the dispersal of energy: the greater the value of *W*, the greater the number of ways of distributing the total energy of a system among the energy levels, and the greater the entropy, *S*.

The Boltzmann equation, equation (13.1), is deceptively simple. It suggests that *S* can be calculated simply by enumerating the possible microstates. As demonstrated earlier, the enumeration of microstates is straightforward when the system contains only five particles. For a system of containing a mole of particles, the number of microstates defies comprehension (see Exercise 3):

$$W \approx 10^{(10^{23})} = 10^{10,000,000,000,000,000,000,000}$$

◀ In this expression, the power of ten is a 1 followed by 23 zeros. The value of *W* is a 1 followed by 10^{23} zeros. If you could write down these digits on a piece of paper at a rate of one million digits every second, it would take you 10^{17} seconds or 3 billion years to complete the task.

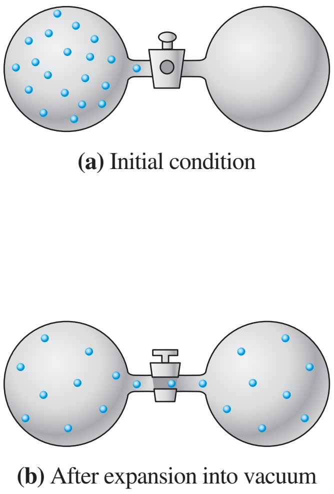
This number is not only incomprehensible but also uncountable. Fortunately, we don't have to count the microstates. We must simply accept that, for a given system, a very large number of microstates are possible.

The simplicity of equation (13.1) contrasts the enormity of Boltzmann's achievement. To obtain this result, he and others (particularly James Clerk Maxwell and J. Willard Gibbs) developed a new branch of physics for describing systems containing a large number of particles. This branch of physics is now called *statistical physics* or *statistical mechanics*. A key idea in statistical mechanics is that from the multitude of possible microstates, not all are equally likely. Think of flipping a coin a million times. Is it possible that you would flip heads each time? Yes. Is it likely? No. We can be quite certain that if we were to flip a coin a million times, the outcome will almost always be something very close to 50% heads and 50% tails. Boltzmann and others realized that, among all of the possible microstates, the most probable ones contribute the most to the macroscopic state. By focusing on the microstates of highest probability, Boltzmann was able to derive expressions for evaluating *W* for a given macroscopic state. With such expressions in hand, the impossibility of counting the microstates is circumvented.

Fortunately, we will not encounter or use the complicated expressions for *W* that are obtained by applying statistical mechanics. Our goal is to develop an understanding of how the number of microstates and entropy of a system change when, for example, the total energy, temperature, or volume changes. We have already established the following key ideas.

- When the space available to the particles of a system is fixed, *W* and *S* increase as the total energy, *U*, increases or as *T* increases.
- When the total energy of a system is fixed, *W* and *S* increase as the space available to the particles increases.

Let's reinforce these ideas by using equation (13.1) to help us understand, from a microscopic point of view, how *W* and *S* change for a few simple processes.



(a) Initial condition

(b) After expansion into vacuum

▲ FIGURE 13-2
Expansion of an ideal gas into a vacuum
(a) Initially, an ideal gas is confined to the bulb on the left at 1.00 bar pressure.
(b) When the stopcock is opened, the gas expands into the identical bulb on the right. The final condition is one in which the gas is equally distributed between the two bulbs at a pressure of 0.50 bar.

Microscopic Interpretation of Entropy Change

At the start of this chapter, we remarked that energy spontaneously disperses unless it is prevented from doing so. To decide whether or not the energy of a system has become "more dispersed" in some process, we must calculate changes in entropy.

Let's consider the isothermal expansion of an ideal gas as illustrated in Figure 13-2. This figure depicts two identical glass bulbs joined by a stopcock.

Initially, the bulb on the left contains an ideal gas at 1.00 bar pressure, and the bulb on the right is evacuated. When the valve is opened, the gas spontaneously expands into the evacuated bulb. After this expansion, the molecules are dispersed throughout the apparatus, with essentially equal numbers of molecules in both bulbs. The final pressure is 0.50 bar. In this spontaneous process, it is obvious that the volume of the gas changes. But what about the energy or entropy of the gas? Do either of these quantities change? To answer this question, we must calculate ΔU and ΔS.

One of the characteristics of an ideal gas is that its internal energy (U) does not depend on the gas pressure but only on the temperature. For example, the internal energy of a monatomic ideal gas, such as He or Ne, is $U = 3/2\, RT$ (see Section 6–7). Therefore, for the isothermal expansion of an ideal gas, $\Delta U = 0$. Also, the enthalpy change is zero: $\Delta H = 0$. This means that the expansion is not caused by the system dropping to a lower energy state. A convenient mental image to explain the expansion is that the gas molecules tend to spread out into the larger volume available to them at the reduced pressure. A more fundamental description of the underlying cause is that, for the same total energy, in the expanded volume there are more available translational energy levels among which the gas molecules can be distributed. That is, the number of microstates, W, is greater for the system in the larger volume than in the smaller volume. We can justify this idea by using Figure 13-1, which shows that the number of microstates increases when the space available to the particles increases (compare Figs. 13-1a and 13-1c). Thus, when a system expands, we have not only $V_f > V$ but also $W_f > W_i$ and $\ln W_f > \ln W_i$. Using Boltzmann's equation, equation (13.1), we obtain

▶ By definition, $H = U + PV$, so $\Delta H = \Delta U + \Delta(PV)$. For a fixed amount of an ideal gas, we can write $\Delta(PV) = \Delta(nRT) = nR\Delta T$ and so, $\Delta H = \Delta U + nR\Delta T$. For an isothermal process involving an ideal gas, we have $\Delta U = 0$ and $\Delta T = 0$. Thus, $\Delta H = 0$.

$$\Delta S = k_B \ln W_f - k_B \ln W_i = k_B(\ln W_f - \ln W_i) > 0$$

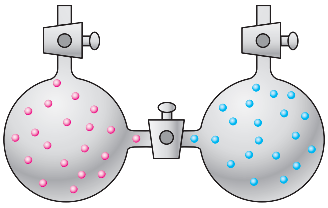
Therefore, entropy increases when a gas expands at constant temperature into a larger volume. Is the increase in entropy somehow connected to the spontaneity of this process? Let's explore this idea further by examining another spontaneous process.

Consider the situation depicted in Figure 13-3, which describes the spontaneous mixing of ideal gases. We can represent this process symbolically as

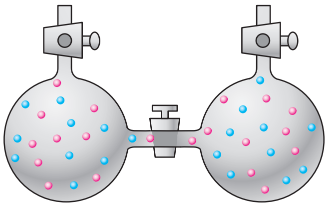
$$A(g) + B(g) \rightarrow \text{mixture of } A(g) \text{ and } B(g)$$

The final state is the mixed state, and the initial state is the un-mixed state. Let's demonstrate that $\Delta U = 0$ and $\Delta S > 0$ for this process. Because the molecules do not interact (they are ideal gases), the mixing is really just two spontaneous expansions occurring simultaneously. Let ΔU_A, ΔS_A, ΔU_B, and ΔS_B represent the internal energy and entropy changes for gases A and B. As described above, for the spontaneous expansion of a gas, the internal energy is constant and entropy increases: $\Delta U_A = \Delta U_B = 0$ and $\Delta S_A > 0$ and $\Delta S_B > 0$. Thus, $\Delta U = \Delta U_A + \Delta U_B = 0$ and $\Delta S = \Delta S_A + \Delta S_B > 0$.

So, for both the spontaneous expansion of an ideal gas and the spontaneous mixing of ideal gases, there is no change in internal energy (or enthalpy) but an increase in entropy. It seems possible that *increases in entropy underlie spontaneous processes.* We will soon see that the characteristic feature of a spontaneous process is that it causes the entropy of the universe to increase.



(a) Before mixing



(b) After mixing

● Gas A ● Gas B

▲ FIGURE 13-3
The mixing of ideal gases
The total volume of the system and the total gas pressure remain fixed. The net change is that **(a)** before mixing, each gas is confined to half the total volume (a single bulb) at a pressure of 1.00 bar, and **(b)** after mixing, each gas has expanded into the total volume (both bulbs) and exerts a partial pressure of 0.50 bar.

13-1 CONCEPT ASSESSMENT

Expansion of a gas into a vacuum is not only spontaneous but also instantaneous. Is it generally true that a spontaneous process is also instantaneous? Explain.

Let us explore the connection between the number of microstates (W) and entropy (S) a little further by using a small one-dimensional crystal of four nitrous oxide molecules, NO. Let's suppose that, at $T = 0$ K, the four NO molecules are aligned as [NO···NO···NO···NO]. This arrangement represents a microstate, and there are no other microstates like this one. Therefore, $W = 1$ and $S = 0$. Now consider what happens when the temperature is raised just enough to allow a single NO molecule to rotate. Such an increase in temperature corresponds to an increase in the internal energy of the system. Now four microstates are possible: [NO···NO···NO···ON], [NO···NO···ON···NO], [NO···ON···NO···NO], and [ON···NO···NO···NO]. W equals 4. By using Boltzmann's equation, we find that $S = k_B \ln 4 = (1.3807 \times 10^{-23}\ \text{J k}^{-1}) \ln 4 = 1.9141 \times 10^{-23}\ \text{J K}^{-1}$. This is yet another example illustrating that as the energy of the system increases, the number of microstates increases; therefore, entropy of the system will increase.

EXAMPLE 13-1 Relating Changes in the Number of Microstates to a Volume Change

A system containing four neon atoms is confined to a one-dimensional box. The system undergoes an expansion from 905 pm to 1810 pm at a fixed total energy of 14.0×10^{-24} J. **(a)** Determine the number of microstates for both the initial and final states of the system by illustrating, in the manner of Figure 13-1, the various possibilities for distributing the atoms among the particle-in-a-box energy levels. Use a different color for each atom. **(b)** Calculate the entropy change for the system.

Analyze

(a) We want to construct diagrams similar to those shown in Figure 13-1. To construct such diagrams, we use the particle-in-a-box energy level expression, $E_n = n^2h^2/(8mL^2)$, to calculate the energies of the levels for the initial ($L = 905$ pm) and final ($L = 1810$ pm) states. Then, we determine the number of different ways that the atoms can be placed in these energy levels, keeping in mind that for both the initial and final states, the total energy of the system must be equal to 14.0×10^{-24} J. **(b)** To calculate the entropy change $\Delta S = S_f - S_i$, we use the number of microstates for the initial and final states in Boltzmann's equation, $S = k_B \ln W$.

Solve

(a) Before using the particle-in-a-box energy level expression, we need to express the mass of a neon atom in the SI unit of kilograms.

$$m = 20.18\,\frac{\text{g}}{\text{mol}} \times \frac{10^{-3}\ \text{kg}}{1\ \text{g}} \times \frac{1\ \text{mol}}{6.022 \times 10^{23}\ \text{atoms}} = 3.351 \times 10^{-26}\,\frac{\text{kg}}{\text{atom}}$$

The energy levels for the 905 pm and 1810 pm boxes are given by

$$L = 905\ \text{pm:}\quad E_n = \frac{(6.626 \times 10^{-34}\ \text{J})^2}{(8)(3.351 \times 10^{-26}\ \text{kg})(905 \times 10^{-12}\ \text{m})^2} \times n^2 = (2.00 \times 10^{-24}\ \text{J}) \times n^2$$

$$L = 1810\ \text{pm:}\quad E_n = \frac{(6.626 \times 10^{-34}\ \text{J})^2}{(8)(3.351 \times 10^{-26}\ \text{kg})(1810 \times 10^{-12}\ \text{m})^2} \times n^2 = (0.500 \times 10^{-24}\ \text{J}) \times n^2$$

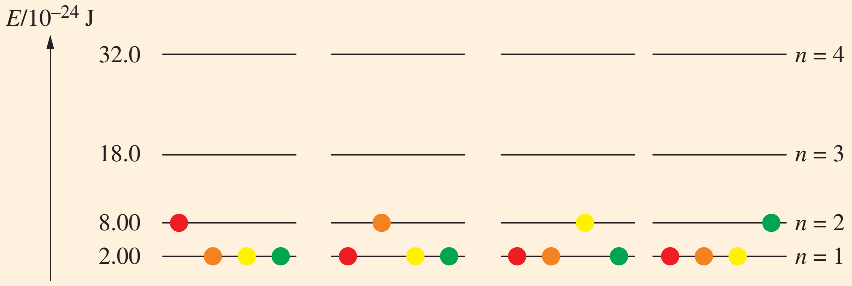
The energies of the first four levels are

	$E_n/10^{-24}$ J	
n	$L = 905$ pm	$L = 1810$ pm
1	2.00	0.500
2	8.00	2.00
3	18.0	4.50
4	32.0	8.00

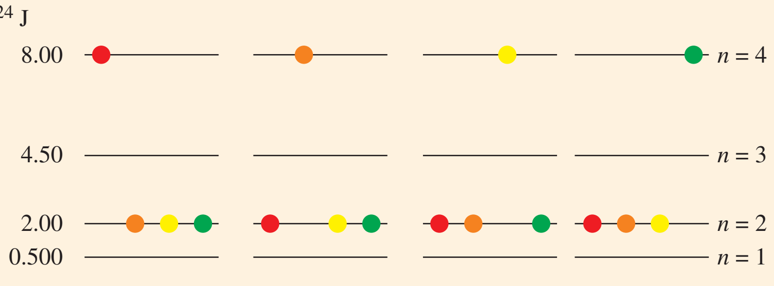
As shown in the diagrams that follow, there are 4 microstates for the system in the 905 pm box, and 8 microstates for the system in the 1810 pm box, each having a total energy of 14.0×10^{-24} J.

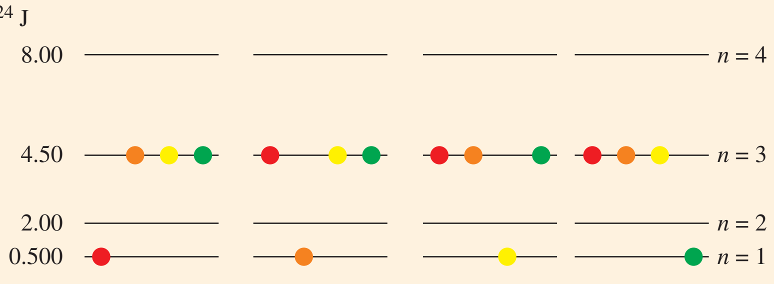
(continued)

For the 905 pm box: 4 microstates



For the 1810 pm box: 8 microstates





(b) The entropy change for the system is

$$\Delta S = k_B \ln 8 - k_B \ln 4 = k_B(\ln 8 - \ln 4) = k_B \ln (8/4) = k_B \ln 2$$

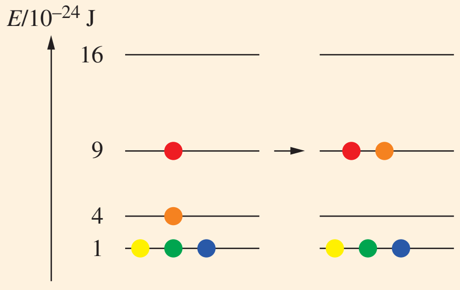
$$= 1.3807 \times 10^{-23}\ \mathrm{J/K} \times 0.693 = 9.57 \times 10^{-24}\ \mathrm{J/K}$$

Assess

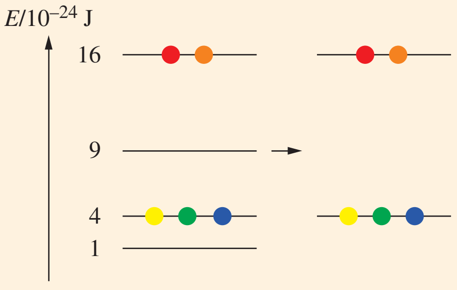
This example illustrates that for a fixed total energy, both the number of microstates and the entropy increase as volume increases.

PRACTICE PROBLEM A: How many microstates are there for four neon atoms confined to a 905 pm box if the total energy is 20.0×10^{-24} J?

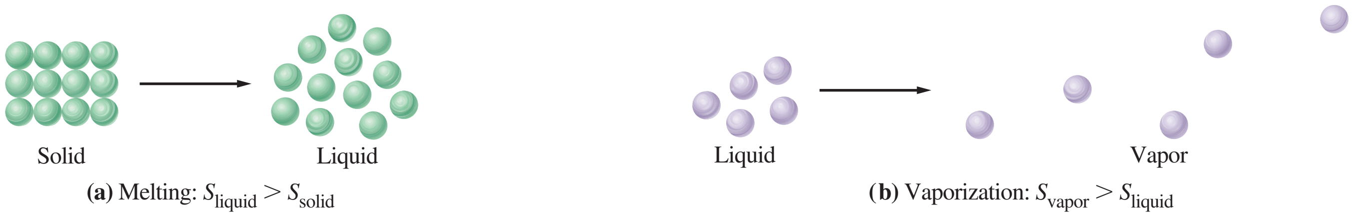
PRACTICE PROBLEM B: Which of the following, (a) or (b), represents a change in volume?



(a)

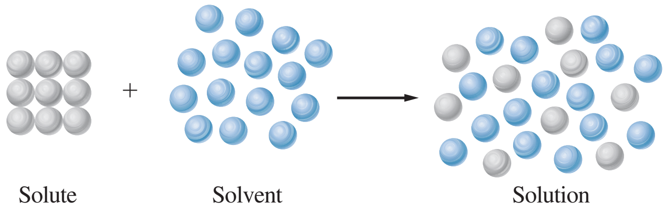


(b)



(a) Melting: $S_{\text{liquid}} > S_{\text{solid}}$

(b) Vaporization: $S_{\text{vapor}} > S_{\text{liquid}}$



(c) Dissolving: $S_{\text{soln}} > (S_{\text{solvent}} + S_{\text{solute}})$

▲ FIGURE 13-4
Three processes in which entropy increases
Each of the processes pictured—**(a)** the melting of a solid, **(b)** the evaporation of a liquid, and **(c)** the dissolving of a solute—results in an increase in entropy. For part (c), the generalization works best for nonelectrolyte solutions, in which ion–dipole forces do not exist.

Describing Entropy Changes for Some Simple Processes

We can use ideas from earlier sections to construct mental pictures for understanding how the entropy of a system changes during a process. We begin by noting that, in many cases, an increase or a decrease in the number of microstates (or the number of accessible energy levels) parallels an increase or decrease in the *number* of microscopic particles and the *space* available to them. As a consequence, we can often make qualitative predictions about entropy change by focusing on those two factors. Let's test this idea by considering the three spontaneous endothermic processes of melting, vaporization, and dissolution, as illustrated in Figure 13-4.

In the melting of ice, a crystalline solid is replaced by a less structured liquid. Molecules that were relatively fixed in position in the solid, being limited to vibrational motion, are now free to move about a bit. The molecules have gained some translational and rotational motion. The number of accessible microscopic energy levels has increased and so has the entropy. In the vaporization process, a liquid is replaced by an even less structured gas. Molecules in the gaseous state, because they can move within a large free volume, have many more accessible energy levels than do those in the liquid state. In the gas, energy can be spread over a much greater number of microscopic energy levels than in the liquid. The entropy of the gaseous state is much higher than that of the liquid state.

In the dissolving of ammonium nitrate in water, for example, a crystalline solid and a pure liquid are replaced by a mixture of ions and water molecules in the liquid (solution) state. This situation is somewhat more involved than the first two because some decrease in entropy is associated with the clustering of water molecules around the ions because of ion–dipole forces. The increase in entropy that accompanies the destruction of the solid's crystalline lattice predominates, however, and for the overall dissolution process, $\Delta S > 0$.

In each of the three spontaneous endothermic processes discussed here, the increase in entropy ($\Delta S > 0$) outweighs the fact that heat must be absorbed ($\Delta H > 0$), and each process is spontaneous.

In summary, four situations generally produce an *increase* in entropy:

- Pure liquids or liquid solutions are formed from solids.
- Gases are formed from either solids or liquids.
- The number of molecules of gas increases as a result of a chemical reaction.
- The temperature of a substance increases. (Increased temperature means an increased number of accessible energy levels for the increased molecular motion, whether it be vibrational motion of atoms or ions in a solid, or translational and rotational motion of molecules in a liquid or gas.)

We apply these generalizations in Example 13-2.

EXAMPLE 13-2 Making Qualitative Predictions of Entropy Changes in Physical and Chemical Processes

Predict whether each of the following processes involves an increase or a decrease in entropy or whether the outcome is uncertain.

(a) The decomposition of ammonium nitrate (a fertilizer and a highly explosive compound): $2\,NH_4NO_3(s) \longrightarrow 2\,N_2(g) + 4\,H_2O(g) + O_2(g)$.

(b) The conversion of SO_2 to SO_3 (a key step in the manufacture of sulfuric acid): $2\,SO_2(g) + O_2(g) \longrightarrow 2\,SO_3(g)$.

(c) The extraction of sucrose from cane sugar juice: $C_{12}H_{22}O_{11}(aq) \longrightarrow C_{12}H_{22}O_{11}(s)$.

(d) The "water gas shift" reaction (involved in the gasification of coal): $CO(g) + H_2O(g) \longrightarrow CO_2(g) + H_2(g)$.

Analyze

Apply the generalizations summarized on the previous page. Three of the processes are chemical reactions, and for those processes, we should first consider whether the number of molecules of gas increases or decreases.

Solve

(a) Here, a solid yields a large quantity of gas. Entropy increases.

(b) Three moles of gaseous reactants produce two moles of gaseous products. The loss of one mole of gas indicates a loss of volume available to a smaller number of gas molecules. This loss reduces the number of possible configurations for the molecules in the system and the number of accessible microscopic energy levels. Entropy decreases.

(c) The sucrose molecules are reduced in mobility and in the number of forms in which their energy can be stored when they leave the solution and arrange themselves into a crystalline state. Entropy decreases.

(d) The entropies of the four gases are likely to be different because their molecular structures are different. The number of moles of gases is the same on both sides of the equation, however, so the entropy change is likely to be small if the temperature is constant. On the basis of just the generalizations listed above, we cannot determine whether entropy increases or decreases.

Assess

As we will soon see, the ability to predict an increase or a decrease in entropy will help us to understand when a process will proceed spontaneously in the forward direction.

PRACTICE EXAMPLE A: Predict whether entropy increases or decreases in each of the following reactions. **(a)** The Claus process for removing H_2S from natural gas: $2\,H_2S(g) + SO_2(g) \longrightarrow 3\,S(s) + 2\,H_2O(g)$; **(b)** the decomposition of mercury(II) oxide: $2\,HgO(s) \longrightarrow 2\,Hg(l) + O_2(g)$.

PRACTICE EXAMPLE B: Predict whether entropy increases or decreases or whether the outcome is uncertain in each of the following reactions. **(a)** $Zn(s) + Ag_2O(s) \longrightarrow ZnO(s) + 2\,Ag(s)$; **(b)** the chlor-alkali process, $2\,Cl^-(aq) + 2\,H_2O(l) \xrightarrow{\text{electrolysis}} 2\,OH^-(aq) + H_2(g) + Cl_2(g)$.

13-2 CONCEPT ASSESSMENT

Figure 13-2 illustrates a spontaneous process through the expansion of an ideal gas into an evacuated bulb. Use the one-dimensional particle-in-a-box model to represent the initial condition of Figure 13-2. Use a second particle-in-a-box model to represent the system after expansion into the vacuum. Use these models to explain on a microscopic basis why this expansion is spontaneous. [*Hint:* Assume that the volume of the bulbs is analogous to the length of the box.]

13-2 Entropy Change: Clausius's View

▶ The word *entropy* is derived from the Greek words *en* (meaning "in") and *trope* (meaning "change or transformation").

Rudolf Clausius, a German physicist, introduced the term entropy in 1854, many years before Boltzmann presented his now famous equation. Clausius made significant contributions to thermodynamics, including providing a detailed analysis of an important thermodynamic cycle, called the Carnot cycle, on which the so-called ideal heat engine is based. A heat engine is designed to convert heat into work, and the ideal heat engine achieves the maximum possible efficiency for this conversion. During his analysis of the Carnot cycle, Clausius discovered a new thermodynamic property, or state function, *S*, that he called entropy. Although Clausius was not able to provide an interpretation of what *S* represents, he showed not only that *S* exists but also how it behaves.

The period between Clausius's discovery of entropy and Boltzmann's interpretation of it was remarkable in that scientists could not give a good answer to the question "What is entropy?" but they could answer very practical questions like "How does entropy change when a system expands at constant pressure?" or "How does entropy change when the temperature of a system increases at constant volume?" By asking and answering these very practical and precise questions, scientists discovered that *S* is a property that behaves in a certain way for all natural changes and exactly the opposite way for all unnatural changes.

Clausius proved that changes in *S* could be related to heat transfer, provided heat was transferred in a "reversible" way. As discussed in Chapter 7 (page 262), a reversible process involves changing the system variables by infinitesimal amounts. For example, to raise the temperature of a system from T_i to T_f in a reversible way means that the temperature is increased by infinitesimal amounts dT, as suggested below, until finally the temperature T_f is reached.

$$\overset{\text{Initial state}}{T_{\mathrm{i}}} \xrightarrow{\delta q_{\mathrm{rev}}} \overbrace{T_{\mathrm{i}} + dT \xrightarrow{\delta q_{\mathrm{rev}}} \cdots \xrightarrow{\delta q_{\mathrm{rev}}} \boxed{T \xrightarrow{\delta q_{\mathrm{rev}}} T + dT} \xrightarrow{\delta q_{\mathrm{rev}}} \cdots}^{\text{An infinite number of intermediate states}} \xrightarrow{\delta q_{\mathrm{rev}}} \overset{\text{Final state}}{T_{\mathrm{f}}}$$

The change in state is imagined to proceed through an infinite number of intermediate states by delivering infinitesimally small amounts of heat, δq_{rev}, each time. The subscript "rev" on δq emphasizes that we are considering a reversible process. In the reversible process illustrated above, the step for which the temperature changes from T to $T + dT$ (red box) represents any one of the infinite number of intermediate states. Clausius suggested that in each step of this reversible process, the entropy changes by a small amount, dS, given by

$$dS = \frac{\delta q_{\mathrm{rev}}}{T} \tag{13.2}$$

where T is the temperature just before delivering the small quantity of heat, δq_{rev}. The total entropy change, ΔS, for the system is obtained by adding the values of $dS = \delta q_{\mathrm{rev}}/T$ for each step. Mathematically, the summation of all these infinitesimal quantities is obtained by using the calculus technique of integration. See Are You Wondering? 13-1.

Let's try to rationalize equation (13.2) by using ideas from Section 13-1. We see that dS is directly proportional to the quantity of heat transferred. This seems reasonable because the more energy added to a system (as heat), the greater the number of energy levels available to the microscopic particles. Raising the temperature also increases the availability of energy levels, but for a given quantity of heat the proportional increase in number of energy levels is greatest at low temperatures. It seems reasonable then that dS should be inversely proportional to the Kelvin temperature. Notice that, because dS is proportional to δq_{rev} and inversely proportional to T, the unit of entropy change is J/K or J K^{-1}.

13-1 ARE YOU WONDERING?

How is equation (13.2) used to calculate a finite entropy change, ΔS?

The infinitesimal change in entropy, dS, that accompanies an infinitesimal reversible heat flow, δq_{rev}, is $dS = \delta q_{\text{rev}}/T$. Now imagine the change in a system from state 1 to state 2 is carried out in a series of such infinitesimal reversible steps. Summation of all these infinitesimal quantities through the calculus technique of integration yields ΔS.

$$\Delta S = \int \frac{\delta q_{\text{rev}}}{T}$$

If the change of state is isothermal (carried out at constant temperature), we can write

$$\Delta S = \int \frac{\delta q_{\text{rev}}}{T} = \frac{1}{T}\int \delta q_{\text{rev}} = \frac{q_{\text{rev}}}{T}$$

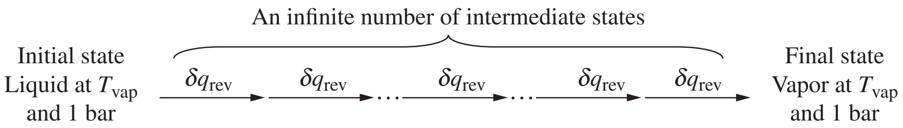
Starting from appropriate expressions for δq_{rev}, ΔS can be related to other system properties. For the isothermal, reversible expansion of an ideal gas, $\delta q_{\text{rev}} = -\delta w_{\text{rev}}$, leading to equation (13.6), which describes ΔS in terms of gas volumes. For a reversible change in temperature at constant pressure, $\delta q_{\text{rev}} = C_p\,dT$, which leads to the entropy change for a change in temperature (see Exercise 95).

Notice that an infinitesimal entropy change is represented by dS whereas an infinitesimal quantity of heat is represented by δq. The difference in notation arises because the results obtained by adding dS values or by adding δq values have fundamentally different interpretations. The dS values add to give a number that represents a *change* in a property of the system (in this case S). The δq values add to give q, the total quantity of heat transferred. Heat is energy in transition and not a system property, so notation such as dq or Δq is not appropriate.

The significance of equation (13.2) is that it relates S, more specifically, a small change in S, to quantities (heat and temperature) that are easily interpreted and measured. However, to calculate the entropy change for a system using this expression, we must devise a way to accomplish a given change in a reversible way. This is not always easy, but as we see below, it can be done fairly easily for certain types of changes.

Phase Transitions

We can use the expression $dS = \delta q_{\text{rev}}/T$ to obtain an equation for ΔS when a pure substance undergoes a phase change at constant temperature, T. Let's consider the constant pressure vaporization of a liquid at its vaporization temperature, T_{vap}. The process below shows that to carry out the vaporization in a reversible way, heat must be delivered in infinitesimal amounts. This is accomplished by placing the system in contact with another system having a temperature that is only infinitesimally greater than T_{vap}. (The vaporization process can be reversed at any time by lowering the temperature infinitesimally below T_{vap}.)



Each infinitesimal quantity of heat is used to convert a small amount of liquid to an equivalent amount of vapor at a constant temperature. That is, the heat is used to overcome the intermolecular forces of attraction, not to cause an increase in temperature. The total entropy change for the vaporization is obtained by adding the values of $dS = \delta q_{\text{rev}}/T_{\text{vap}}$. Because the temperature is constant, we can accomplish this by first adding the values of δq_{rev} and then dividing the result by T_{vap}. The total heat transferred is $q_{\text{vap}} = \Delta_{\text{vap}}H°$ and so, we can write

$$\Delta_{\text{vap}}S = \frac{q_{\text{vap}}}{T_{\text{vap}}} = \frac{\Delta_{\text{vap}}H°}{T_{\text{vap}}}$$

The equation above can be written more generally as

$$\Delta_{\text{tr}}S = \frac{\Delta_{\text{tr}}H°}{T_{\text{tr}}} \qquad \textbf{(13.3)}$$

where the symbol tr represents a transition. When applying equation (13.3), we are specific about which transition is involved by replacing tr with, for example, fus for the melting of solid or vap for the vaporization of liquid. Also, equation (13.3) applies only if the phase transition occurs at the usual or normal transition temperature. The reason is that a phase transition can be carried out reversibly only at the normal transition temperature.

Consider the reversible melting (fusion) of ice at its normal melting point, for which $\Delta_{\text{fus}}H° = 6.02$ kJ mol^{-1}.

$$\text{H}_2\text{O(s, 1 atm, 273.15 K)} \rightleftharpoons \text{H}_2\text{O(l, 1 atm, 273.15 K)}$$

(We are justified in using $\Delta_{\text{fus}}H°$ here because 1 atm $\approx$ 1 bar.) The standard entropy change is

$$\Delta_{\text{fus}}S° = \frac{\Delta_{\text{fus}}H°}{T_{\text{fus}}} = \frac{6.02 \times 10^3 \text{ J mol}^{-1}}{273.15 \text{ K}} = 22.0 \text{ J mol}^{-1} \text{ K}^{-1}$$

Entropy changes depend on the quantities of substances involved and are sometimes expressed on a per-mole basis.

A useful generalization known as Trouton's rule states that for many liquids at their normal boiling points, the standard molar entropy of vaporization has a value of about 87 J mol^{-1} K^{-1}.

KEEP IN MIND

that the normal melting point and normal boiling point are determined at 1 atm pressure. The difference between 1 atm and the standard state pressure of 1 bar is so small that we can usually ignore it.

$$\Delta_{\text{vap}}S° = \frac{\Delta_{\text{vap}}H°}{T_{\text{vap}}} \approx 87 \text{ J mol}^{-1} \text{ K}^{-1} \qquad \textbf{(13.4)}$$

For instance, the values of $\Delta_{\text{vap}}S°$ for benzene (C_6H_6) and octane (C_8H_{18}) are 87.1 and 86.2 J mol^{-1} K^{-1}, respectively. If the increased accessibility of microscopic energy levels produced in transferring one mole of molecules from liquid to vapor at 1 bar is roughly comparable for different liquids, then we should expect similar values of $\Delta_{\text{vap}}S°$.

Instances in which Trouton's rule fails are also understandable. In water and in ethanol, for example, hydrogen bonding among molecules produces a lower entropy than would otherwise be expected in the liquid state. Consequently, the entropy increase in the vaporization process is greater than normal, and so $\Delta_{\text{vap}}S° > 87$ J mol^{-1} K^{-1}.

EXAMPLE 13-3 Determining the Entropy Change for a Phase Transition

What is the standard molar entropy change for the vaporization of water at 373 K given that the standard molar enthalpy of vaporization is 40.7 kJ mol^{-1} at this temperature?

Analyze

This is an example of a phase transition, which means we can make use of $\Delta_{\text{tr}}S° = \dfrac{\Delta_{\text{tr}}H°}{T_{\text{tr}}}$.

(continued)

Solve

Although a chemical equation is not necessary, writing one can help us see the process we use to find the value of $\Delta_{\text{vap}}S^\circ$.

$$\mathrm{H_2O(l,\,1\,atm)} \rightleftharpoons \mathrm{H_2O(g,\,1\,atm)} \qquad \Delta_{\text{vap}}H^\circ = 40.7\ \text{kJ mol}^{-1}$$

$$\Delta_{\text{vap}}S^\circ = \,?$$

$$\Delta_{\text{vap}}S^\circ = \frac{\Delta_{\text{vap}}H^\circ}{T_{\text{vap}}} = \frac{40.7\ \text{kJ mol}^{-1}}{373\ \text{K}} = 0.109\ \text{kJ mol}^{-1}\,\text{K}^{-1}$$

$$= 109\ \text{J mol}^{-1}\,\text{K}^{-1}$$

Assess

When solving this type of problem, we should check the sign of ΔS. Here, we expect an increase in entropy (ΔS is positive) because, as discussed on page 587, the entropy of a gas is much higher than that of a liquid.

PRACTICE EXAMPLE A: What is the standard molar entropy of vaporization, $\Delta_{\text{vap}}S^\circ$, for CCl_2F_2, a chlorofluorocarbon that once was heavily used in refrigeration systems? Its normal boiling point is −29.79 °C, and $\Delta_{\text{vap}}H^\circ = 20.2\ \text{kJ mol}^{-1}$.

PRACTICE EXAMPLE B: The entropy change for the transition from solid rhombic sulfur to solid monoclinic sulfur at 95.5 °C is $\Delta_{\text{tr}}S^\circ = 1.09\ \text{J mol}^{-1}\,\text{K}^{-1}$. What is the standard molar enthalpy change, $\Delta_{\text{tr}}H^\circ$, for this transition?

Heating or Cooling at Constant Pressure

Equation (13.2) can also be used to obtain an expression for the entropy change, ΔS, for a substance that is heated (or cooled) at constant pressure—without a phase change—from an initial temperature T_{i} to a final temperature T_{f}. The heating of a substance from T_{i} to T_{f} can be carried out in a reversible way by making sure that, at each stage of the heating process, the substance is in contact with a heat source having a temperature that is only infinitesimally greater than the temperature, T, of the substance itself. At each stage of the heating process, the substance absorbs a quantity of heat equal to δq_{rev} and the temperature of the system increases from T to $T + dT$. The quantity of heat absorbed is, by applying equation (7.5), $\delta q_{\text{rev}} = C_p\,dT$, where C_p is the constant pressure heat capacity of the substance being heated. Thus, the corresponding entropy change is $dS = (C_p/T)dT$. By adding these infinitesimal entropy changes, for the infinite number of intermediate states between T_{i} and T_{f}, we obtain (using the calculus technique of integration) the result

$$\Delta S \approx C_p \ln\left(\frac{T_{\text{f}}}{T_{\text{i}}}\right) \qquad \text{constant pressure heating or cooling} \qquad \textbf{(13.5)}$$

▶ If you are familiar with the calculus technique of integration, then you will know that $\int_a^b (1/x)dx = \ln(b/a)$. Thus, $\int_{T_{\text{i}}}^{T_{\text{f}}} (C_p/T)dT = C_p \ln(T_{\text{f}}/T_{\text{i}})$ provided that C_p has the same (constant) value between T_{i} and T_{f}.

This result rests on the assumption that the heat capacity, C_p, has the same value for all temperatures between T_{i} and T_{f}. Using equation (13.5) with $T_{\text{f}} > T_{\text{i}}$, we obtain $\Delta S > 0$. In other words, the entropy of a substance increases when the temperature increases. Using equation (13.5) with $T_{\text{f}} < T_{\text{i}}$, we obtain $\Delta S < 0$. That is, the entropy decreases when the temperature decreases.

Changes in State for an Ideal Gas

Later in this chapter, we will discuss the thermodynamics of chemical reactions. Somewhat surprisingly, a reaction involving ideal gases is the starting point for applying thermodynamic principles to chemical reactions, and when such a reaction is assumed to occur at constant temperature, the amounts and the partial pressures of the gases will change. Therefore, we will want to know how, for example, the entropy of an ideal gas changes with pressure. We can establish some key ideas by using equation (13.2) to obtain an expression for the entropy change, ΔS, for an ideal gas that is expanded or compressed isothermally from an initial volume V_i to a final volume V_f. During the expansion or compression, the pressure of the gas will change from P_i to P_f.

To expand or compress a gas in a reversible way, we must ensure that the external pressure is different from the gas pressure by only an infinitesimal amount. (See Figure 7-12 for a method of expanding a gas in a nearly reversible fashion.) The reversible expansion of a gas can be represented by the following process.

$$\overset{\text{Initial state}}{\begin{pmatrix}V_\mathrm{i}\\P_\mathrm{i}\end{pmatrix}} \xrightarrow[P_\mathrm{ext}=P_i-dP]{\delta q_\mathrm{rev},\ \delta w_\mathrm{rev}} \overbrace{\begin{pmatrix}V_\mathrm{i}+dV\\P_\mathrm{i}-dP\end{pmatrix} \longrightarrow \cdots \longrightarrow \boxed{\begin{pmatrix}V\\P\end{pmatrix} \xrightarrow[P_\mathrm{ext}=P_i-dP]{\delta q_\mathrm{rev},\ \delta w_\mathrm{rev}} \begin{pmatrix}V+dV\\P-dP\end{pmatrix}} \longrightarrow \cdots \longrightarrow}^{\text{An infinite number of intermediate states}} \overset{\text{Final state}}{\begin{pmatrix}V_\mathrm{f}\\P_\mathrm{f}\end{pmatrix}}$$

At each stage, the external pressure, P_ext, is adjusted so that it is only infinitesimally smaller than the gas pressure, P. Because the gas pressure is slightly greater than the external pressure, the gas will expand but only by an infinitesimal amount dV. Let's focus on the step in which the volume changes from V to $V + dV$ and the pressure changes from P to $P - dP$ (red box). This step represents any one of the infinite number of intermediate states. For this step, the work done is

$$\delta w_\mathrm{rev} = -P_\mathrm{ext}dV = -(P - dP)dV = -PdV + dPdV \approx -PdV$$

We are justified in neglecting the term $dPdV$ because it is the product of two very small quantities whereas $-PdV$ is a product involving only one small quantity. For the isothermal expansion of an ideal gas, the change in internal energy is zero. (See page 583.) Thus, for this step, we must have $dU = 0 = \delta q_\mathrm{rev} + \delta w_\mathrm{rev}$, and

◀ To illustrate that we are justified in neglecting the term $dPdV$, let's use $P = 1$ bar, a typical value, and approximate the infinitesimal quantities dP and dV as 1×10^{-10} bar and 1×10^{-10} L, respectively. We have $dPdV \approx 1 \times 10^{-20}$ bar L and $-PdV \approx -1 \times 10^{-10}$ bar L. Therefore, $-PdV + dPdV$ $= -1 \times 10^{-10}$ bar L $+ 1 \times 10^{-20}$ bar L $\approx -1 \times 10^{-10}$ bar L $= -PdV$.

$$\delta q_\mathrm{rev} = -\delta w_\mathrm{rev} = PdV = \left(\frac{nRT}{V}\right)dV$$

Using this result in equation (13.2), we get

$$dS = \frac{\delta q_\mathrm{rev}}{T} = \left(\frac{nR}{V}\right)dV$$

By adding these infinitesimal entropy changes, for the infinite number of intermediate states between V_i and V_f, we obtain (using the calculus technique of integration)

$$\Delta S = nR\ln\left(\frac{V_\mathrm{f}}{V_\mathrm{i}}\right) \quad \text{isothermal volume change for an ideal gas} \qquad \mathbf{(13.6)}$$

Since the temperature is constant, we can write $P_\mathrm{f}V_\mathrm{f} = P_\mathrm{i}V_\mathrm{i}$ or $V_\mathrm{f}/V_\mathrm{i} = P_\mathrm{i}/P_\mathrm{f}$. Therefore, we can also write

$$\Delta S = nR\ln\left(\frac{P_\mathrm{f}}{P_\mathrm{i}}\right) = -nR\ln\left(\frac{P_\mathrm{f}}{P_\mathrm{i}}\right) \quad \text{isothermal pressure for an ideal gas} \qquad \mathbf{(13.7)}$$

Using equations (13.6) and (13.7), we can establish that the entropy of an ideal gas increases ($\Delta S > 0$) if the volume increases ($V_\mathrm{f} > V_\mathrm{i}$) or if the pressure decreases ($P_\mathrm{f} < P_\mathrm{i}$). These results are not unexpected because, as we saw earlier, the number of microstates and entropy increase as the space available to the particles increases.

Equation (13.7) is, in fact, a special case of the following general expression for calculating the entropy change of an ideal gas.

$$\Delta S = C_p\ln\left(\frac{T_\mathrm{f}}{T_\mathrm{i}}\right) - nR\ln\left(\frac{P_\mathrm{f}}{P_\mathrm{i}}\right) \qquad \mathbf{(13.8)}$$

Some important equations for calculating entropy changes are presented in Table 13.1, along with the conditions under which they may be used.

◀ To derive equation (13.8), we must make use of the first and second laws, the relationship between internal energy and enthalpy, certain characteristics of ideal gases, and a considerable amount of calculus. The derivation of this equation is typically presented in more advanced physical chemistry courses.

TABLE 13.1 Some Equations for Calculating Enthalpy and Entropy Changes

Process	Enthalpy Change	Entropy Change
Phase transition at the usual (normal) transition temperature	$\Delta_{tr}H^\circ$	$\Delta_{tr}S = \dfrac{\Delta_{tr}H^\circ}{T_{tr}}$
Heating or cooling at constant pressure (no phase transition; C_p has constant value)	$\Delta H = C_p\Delta T$	$\Delta S = C_p \ln\left(\dfrac{T_f}{T_i}\right)$
Change in state from (T_i, P_i) to (T_f, P_f) for an ideal gas*	$\Delta H = C_p\Delta T$	$\Delta S = C_p \ln\left(\dfrac{T_f}{T_i}\right) - nR\ln\left(\dfrac{P_f}{P_i}\right)$

*The enthalpy H of an ideal gas depends only on temperature, T. Consequently, ΔH depends only on ΔT.

Remember that each equation for ΔS was obtained by applying equation (13.2) to the appropriate process. We will find occasion to use these expressions for ΔS throughout this chapter.

▶ It is commonly stated that we are headed for a state of maximum entropy. Although this is true, it gives the incorrect notion that entropy, as defined here, and time are related. They are not. Entropy is a property of an equilibrium state. Here we calculate the difference between the entropies of two different equilibrium states.

13-2 ARE YOU WONDERING?

Is there a microscopic approach to obtaining equation (13.6)?

To do this, we use the ideas of Ludwig Boltzmann. Consider an ideal gas at an initial volume V_i and allow the gas to expand isothermally to a final volume V_f. By using the Boltzmann equation, we find that for the change in entropy,

$$\Delta S = S_f - S_i = k_B \ln W_f - k_B \ln W_i$$

$$\Delta S = k_B \ln\frac{W_f}{W_i}$$

where k_B is the Boltzmann constant, S_i and S_f are the initial and final entropies, respectively, and W_i and W_f are the number of microstates for the initial and final macroscopic states of the gas, respectively. We must now obtain a value for the ratio W_f/W_i. To do that, suppose that there is only a single gas molecule in a container. The number of microstates available to this single molecule should be proportional to the number of positions where the molecule can be and, hence, to the volume of the container. That is also true for each molecule in a system of $n \times N_A$ particles (n is the amount in moles and N_A is Avogadro's number). The number of microstates available to the whole system is

$$W_{\text{total}} = W_{\text{particle 1}} \times W_{\text{particle 2}} \times W_{\text{particle 3}} \times \cdots$$

Because the number of microstates for each particle is proportional to the volume V of the container, the number of microstates for $n \times N_A$ ideal gas molecules is

$$W \propto V^{nN_A}$$

Thus, the ratio of the microstates for isothermal expansion is

$$\frac{W_f}{W_i} = \left(\frac{V_f}{V_i}\right)^{nN_A}$$

We can now calculate ΔS as follows:

$$\Delta S = k_B \ln\frac{W_f}{W_i} = k_B \ln\left(\frac{V_f}{V_i}\right)^{nN_A} = nN_A k_B \ln\left(\frac{V_f}{V_i}\right) = nR\ln\left(\frac{V_f}{V_i}\right)$$

where R is the ideal gas constant. This equation, which gives the entropy change for the expansion of one mole of ideal gas, is equation (13.6).

EXAMPLE 13-4 Calculating the Entropy Change for Heating Ice Under Constant Pressure

Calculate the entropy change for the following constant pressure process.

$$\mathrm{H_2O(s, 100\ g, -10\ ^\circ C, 1\ bar)} \longrightarrow \mathrm{H_2O(l, 100\ g, 10\ ^\circ C, 1 bar)}$$

The molar heat capacities of ice and water are, respectively, $C_p(\text{ice}) = 37.12\ \mathrm{J\ mol^{-1}\ K^{-1}}$ and $C_p = 75.3\ \mathrm{J\ mol^{-1}\ K^{-1}}$. The enthalpy of fusion for ice is $\Delta_{\text{fus}}H^\circ = 6.01\ \mathrm{kJ\ mol^{-1}}$ at 0 °C.

Analyze

We must think of a way to carry out this process reversibly so that we may use the equations given in Table 13.1. Reversible, constant pressure heating is imagined to occur as the result of placing the system (100 g of H_2O) in contact with a heat source, the temperature of which is gradually increased from –10 to 10 °C and always just slightly greater than that of the H_2O. During this reversible heating process, several changes occur. First, the ice is heated reversibly from –10 °C to 0 °C and then melted reversibly at 0 °C. Finally, the water is heated reversibly from 0 °C to 10 °C. The entropy changes for these steps can be calculated by using equations from Table 13.1 and added together to give the total entropy change.

Solve

For the reversible heating of ice from –10 °C to 0 °C:

$$\Delta S_1^\circ = C_p(\text{ice}) \ln\left(\frac{T_f}{T_i}\right) = (5.55\ \text{mol})(37.12\ \mathrm{J\ mol^{-1}\ K^{-1}}) \ln\left(\frac{273\ \mathrm{K}}{263\ \mathrm{K}}\right)$$
$$= 7.69\ \mathrm{J\ K^{-1}}$$

For the reversible melting of ice at 0 °C:

$$\Delta S_2^\circ = \frac{\Delta_{\text{fus}}H^\circ}{T_{\text{fus}}} = \frac{(5.55\ \text{mol})(6010\ \mathrm{J\ mol^{-1}})}{273\ \mathrm{K}} = 122.18\ \mathrm{J\ K^{-1}}$$

For the reversible heating of water from 0 °C to 10 °C:

$$\Delta S_3^\circ = C_p(\text{water}) \ln\left(\frac{T_f}{T_i}\right) = (5.55\ \text{mol})(75.3\ \mathrm{J\ mol^{-1}\ K^{-1}}) \ln\left(\frac{283\ \mathrm{K}}{273\ \mathrm{K}}\right)$$
$$= 15.03\ \mathrm{J\ K^{-1}}$$

The total entropy change is the sum of the individual steps:

$$\Delta S_{\text{total}}^\circ = \Delta S_1^\circ + \Delta S_2^\circ + \Delta S_3^\circ = (7.69 + 122.18 + 15.03)\ \mathrm{J\ K^{-1}} = 144.90\ \mathrm{J\ K^{-1}}$$

Assess

The overall entropy change is positive, which is what we expect from an increase in temperature. More importantly, H_2O is converted from a solid—a state of lower entropy—to a liquid, a state of higher entropy. The phase change makes by far the largest contribution (+122.18 $\mathrm{J\ K^{-1}}$) to the total entropy change. The contributions from the heating of ice (+7.69 $\mathrm{J\ K^{-1}}$) and the heating of water (+15.03 $\mathrm{J\ K^{-1}}$) are much smaller. The entropy change is greater (almost double) for the heating of water than for the heating of ice even though the temperature increase is the same for both (+10 °C) because, as discussed in Section 7-2, liquid water has many more ways to disperse the energy entering the system than ice does.

PRACTICE EXAMPLE A: One mole of neon gas, initially at 300 K and 1.00 bar, expands adiabatically (i.e., with no heat lost to the surroundings) against a constant external pressure of 0.50 bar until the gas pressure is also 0.50 bar. The final temperature of the gas is 240 K. What is ΔS for the gas? The molar heat capacity of Ne(g) is 20.8 $\mathrm{J\ mol^{-1}\ K^{-1}}$.

PRACTICE EXAMPLE B: One mole of neon gas, initially at 300 K and 1.00 bar, expands isothermally against a constant external pressure of 0.50 bar until the gas pressure is also 0.50 bar. What is ΔS for the gas?

13-3 Combining Boltzmann's and Clausius's Ideas: Absolute Entropies

From the equation $S = k_B \ln W$, we see that if $W = 1$, then we must have $S = 0$. Is there any reason to expect that the macroscopic state of a system might be described by a single microstate? It turns out that the answer to this question is yes. Imagine lowering the temperature of a system to smaller and smaller values. As we lower the temperature, the total energy available to the particles of the system decreases. As a result, the particles are forced to occupy levels of lower and lower energy until finally all the particles in the system are in the lowest energy level. When all the particles are in the lowest energy level, we have $W = 1$ and so, $S = 0$. This idea is embodied in the following statement, which is one way of stating the **third law of thermodynamics**.

> The entropy of a pure perfect crystal at 0 K is zero.

We justified the statement above by using Boltzmann's equation for S. However, before Boltzmann presented his famous equation, scientists had already deduced the third law of thermodynamics by studying isothermal processes, such as phase transitions or reactions, at very low temperatures. They found that for a wide variety of isothermal processes, ΔS approached a value of zero as the temperature approached 0 K. This general observation suggests that the entropies of all substances must be the same at 0 K. When Boltzmann presented his equation for S, it was clear that $S = 0$ is the correct value for entropy at 0 K.

As we saw in the previous section, Clausius's approach to entropy provides equations for calculating entropy changes of substances that are heated or cooled, or that undergo a phase transition. It turns out that we can use these equations, together with the fact that $S = 0$ at $T = 0$ K, to assign a specific value to the entropy of any substance at 298.15 K. Consider the following process for a hypothetical substance X, which is assumed to be a solid at 0 K and 1 bar and a gas at 298.15 K and 1 bar.

$$\begin{array}{ccc} \text{X(s, 0 K, 1 bar)} & \longrightarrow & \text{X(g, 298.15 K, 1 bar)} \\ S_i^\circ = 0 & & S_f^\circ = ? \end{array}$$

This constant pressure process involves the following sequence of changes, where T_{low} represents a very low temperature. (Recall that 0 K is unattainable.)

▶ The expressions for ΔS_1°, ΔS_2°, and ΔS_3° are approximations because the heat capacity of each phase changes slightly over the large temperature ranges involved. Thus, the assumption that C_p is constant is not valid. More accurate results are obtained by taking into account the temperature variation of the various heat capacities. See Exercise 95.

1. Heating the solid from T_{low} to its melting point, T_{fus}.

$$X(\text{s}, T_{\text{low}}, 1\text{ bar}) \longrightarrow X(\text{s}, T_{\text{fus}}, 1\text{ bar}) \qquad \Delta S_1^\circ \approx C_p(\text{solid}) \ln (T_{\text{fus}}/T_{\text{low}})$$

2. Melting the solid at T_{fus}.

$$X(\text{s}, T_{\text{fus}}, 1\text{ bar}) \longrightarrow X(\text{l}, T_{\text{fus}}, 1\text{ bar}) \qquad \Delta S_2^\circ = \Delta_{\text{fus}}H^\circ/T_{\text{fus}}$$

3. Heating the liquid from T_{fus} to its boiling point, T_{vap}.

$$X(\text{l}, T_{\text{fus}}, 1\text{ bar}) \longrightarrow X(\text{l}, T_{\text{vap}}, 1\text{ bar}) \qquad \Delta S_3^\circ \approx C_p(\text{liquid}) \ln (T_{\text{vap}}/T_{\text{fus}})$$

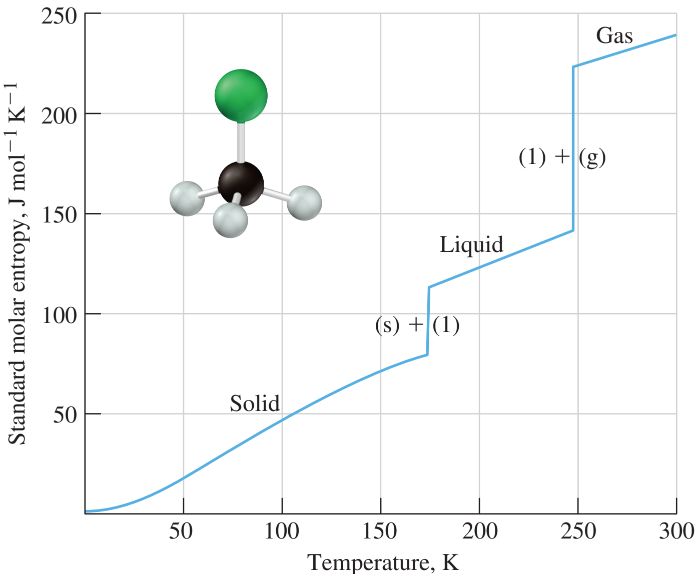
4. Vaporizing the liquid at T_{vap}.

$$X(\text{l}, T_{\text{vap}}, 1\text{ bar}) \longrightarrow X(\text{g}, T_{\text{vap}}, 1\text{ bar}) \qquad \Delta S_4^\circ = \Delta_{\text{vap}}H^\circ/T_{\text{vap}}$$

5. Heating the vapor from T_{vap} to 298.15 K.

$$X(\text{g}, T_{\text{vap}}, 1\text{ bar}) \longrightarrow X(\text{g}, 298.15\text{ K}, 1\text{ bar})\ \Delta S_5^\circ \approx C_p(\text{gas}) \ln (298.15\text{ K}/T_{\text{fus}})$$

The entropy changes for the phase changes can be calculated using equation (13.3), provided the corresponding enthalpy changes and transition temperatures are known. The entropy changes for the heating of solid, liquid, and gas can also be calculated provided the heat capacity of each phase is known. By adding the entropy changes for these steps, we obtain the total entropy change ΔS. Remembering that $S_i^\circ = 0$ and treating $\Delta S = S_f^\circ - S_i^\circ$ as a known quantity, we have $S_f^\circ = \Delta S$. In this manner, for any substance, we can assign a specific value to S° at 298.15 K. Figure 13-5 illustrates the method for CH_3Cl.



▲ FIGURE 13-5

Molar entropy as a function of temperature

The standard molar entropy of methyl chloride, CH_3Cl, is plotted at various temperatures from 0 to 298.15 K, with the phases noted. The vertical segment between the solid and liquid phases corresponds to $\Delta_{fus}S$; the other vertical segment, to $\Delta_{vap}S$. By the third law of thermodynamics, an entropy of *zero* is expected at 0 K. Experimental methods cannot be carried to that temperature, however, so an extrapolation is required.

The absolute entropy of one mole of substance in its standard state is called the **standard molar entropy**, **$S°$**. Standard molar entropies of a number of substances at 298.15 K are tabulated in Appendix D. These values may be used to calculate the **standard reaction entropy, $\Delta_r S°$**, for a reaction. Consider the following general equation for a reaction.

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

In the equation above, the uppercase letters A, B, C, D, etc., represent different substances and the lowercase letters a, b, c, d, etc., represent the coefficients required to balance the equation. $\Delta_r S°$ for the reaction is obtained using the following equation, which has a familiar form (recall equation 7.22).

$$\Delta_r S° = \underbrace{[c\,S°_{\mathrm{C}} + d\,S°_{\mathrm{D}} + \dots]}_{\text{Weighted sum of } S° \text{ values for products}} - \underbrace{[a\,S°_{\mathrm{A}} + b\,S°_{\mathrm{B}} + \dots]}_{\text{Weighted sum of } S° \text{ values for reactants}} \qquad \textbf{(13.9)}$$

In these weighted sums, the terms are formed by multiplying the standard molar entropy by the corresponding stoichiometric coefficient. The coefficients are simply numbers (without units) and so $\Delta_r S°$ has the same unit as $S°$, that is J mol^{-1} K^{-1}. Example 13–5 shows how to use this equation.

EXAMPLE 13-5 Calculating the Standard Entropy of Reaction

Use data from Appendix D to calculate the standard molar entropy change at 298.15 K for the conversion of nitrogen monoxide to nitrogen dioxide (a step in the manufacture of nitric acid).

$$2\,NO(g) + O_2(g) \longrightarrow 2\,NO_2(g) \qquad \Delta_r S° = ?$$

(continued)

Analyze

The standard reaction entropy, $\Delta_r S°$, is calculated from standard molar entropies by applying equation (13.5).

Solve

Equation (13.5) takes the form

$$\begin{aligned}\Delta_r S° &= 2S°_{NO_2(g)} - 2S°_{NO(g)} - S°_{O_2(g)}\\ &= [(2 \times 240.1) - (2 \times 210.8)] - 205.1\ \text{J mol}^{-1}\,\text{K}^{-1} = -146.5\ \text{J mol}^{-1}\text{K}^{-1}\end{aligned}$$

Assess

Some qualitative reasoning can be applied as a useful check on this calculation. If three moles of gaseous reactants are completely converted it two moles of gaseous products (a net decrease in the number of moles of gas), then the entropy of the system should decrease. That is, we should expect $\Delta_r S° < 0$.

PRACTICE EXAMPLE A: Use data from Appendix D to calculate the standard molar entropy change at 298.15 K for the synthesis of ammonia from its elements.

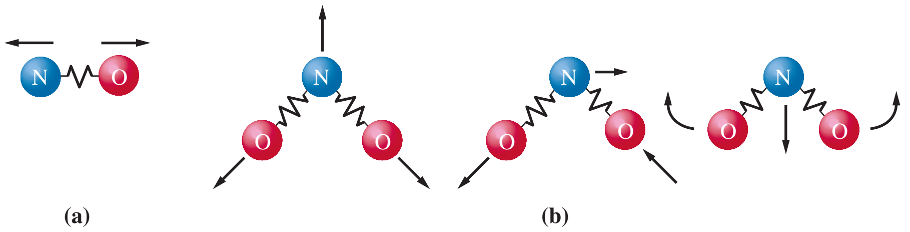
$$N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g) \qquad \Delta_r S° = ?$$

PRACTICE EXAMPLE B: N_2O_3 is an unstable oxide that readily decomposes. The decomposition of 1.00 mol of N_2O_3 to nitrogen monoxide and nitrogen dioxide at 25 °C is accompanied by the entropy change $\Delta_r S° = 138.5\ \text{J mol}^{-1}\,\text{K}^{-1}$. What is the standard molar entropy of $N_2O_3(g)$ at 25 °C?

▶ In general, at low temperatures, because the quanta of energy are so small, translational energies are most important in establishing the entropy of gaseous molecules. As the temperature increases and the quanta of energy become larger, first rotational energies become important, and finally, at still higher temperatures, vibrational modes of motion start to contribute to the entropy.

Example 13-5 uses the standard molar entropies of $NO_2(g)$ and NO(g). Why is the value for $NO_2(g)$, 210.8 J mol^{-1} K^{-1}, greater than that of NO(g), 240.1 J mol^{-1} K^{-1}? The simple answer is that because the NO_2 molecule has a greater number of atoms and a somewhat more complex structure than does the NO molecule, a system of NO_2 molecules has a greater number of ways to make use of a fixed amount of energy than does a system of NO molecules. For example, when a gas absorbs energy (e.g. heat), some of the energy goes into raising the average translational energy of the molecules. However, there are other ways for energy to be used. One possibility, shown in Figure 13-6, is that the vibrational energies of molecules can be increased. In the *diatomic* molecule NO, only one type of vibration is possible; in the *triatomic* molecule NO_2, three types are possible. Because there are more ways of distributing energy among NO_2 molecules than among NO molecules, $NO_2(g)$ has a higher molar entropy than does NO(g) at the same temperature. In general, we can say that

> Standard molar entropy, $S°$, increases as molecular complexity increases (i.e., as the number of atoms per molecule increases).

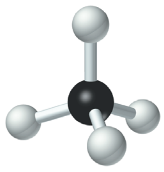


▲ FIGURE 13-6

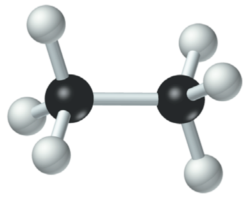
Vibrational energy and entropy

The movement of atoms is suggested by the arrows. **(a)** The NO molecule has only one type of vibrational motion, whereas **(b)** the NO_2 molecule has three. This difference helps account for the fact that the molar entropy of $NO_2(g)$ is greater than that of NO(g).

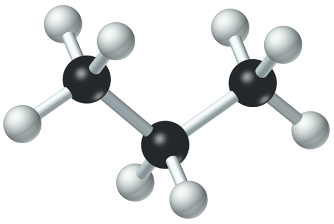
The idea that standard molar entropy increases with the number of atoms in a molecule is illustrated in Figure 13.7.



Methane, CH_4
$S° = 186.3\ \text{J mol}^{-1}\ \text{K}^{-1}$



Ethane, C_2H_6
$S° = 229.6\ \text{J mol}^{-1}\ \text{K}^{-1}$



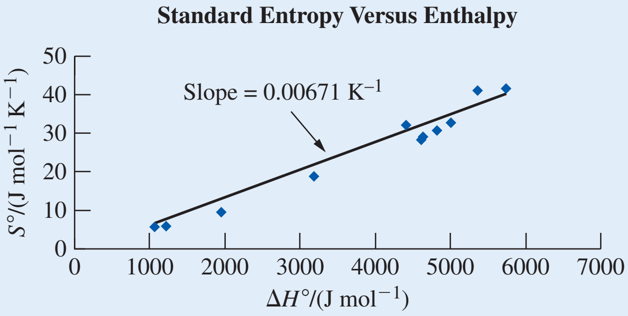
Propane, C_3H_8
$S° = 270.3\ \text{J mol}^{-1}\ \text{K}^{-1}$

▲ FIGURE 13-7
Standard molar entropies of some hydrocarbons

13-3 ARE YOU WONDERING?

Is the standard molar entropy related to the amount of energy stored in a substance?

The answer to this question is yes, provided we focus only on substances that are solids at 298.15 K, and we interpret the energy stored in a substance to be the amount of heat required to raise the temperature of the solid from 0 K to 298.15 K at a constant pressure of 1 bar. The following figure is a plot of standard molar entropy, $S°$, versus $\Delta H°$, for several monatomic solids. Here, $\Delta H°$ represents the enthalpy change per mole of solid when it is heated from 0 to 298.15 K at a constant pressure equal to 1 bar.



From the graph, we see that, for monatomic solids,

$$S°_{298.15} \approx \Delta H° \times 0.00671\ K^{-1}$$

The result indicates that the standard entropy value, $S°$, at 298.15 K is proportional to the heat absorbed by that solid to get it from 0 to 298.15 K with the proportionality constant 0.00671 K^{-1}. The heat that is absorbed by the solid in this process is dispersed through the various energy levels of the solid. The simple relationship clearly shows that the greater the amount of heat (energy) that is absorbed when one mole of the solid is heated from 0 to 298.15 K, the greater its standard molar entropy. Thus, the standard molar entropy of a solid is a direct measure of the amount of energy stored in the solid.

The proportionality constant 0.00671 K^{-1} may be expressed as a temperature by taking the reciprocal of this value: $1/(0.00671\ \text{K}^{-1}) = 149$ K. This temperature is exactly half way between 0 K and 298.15 K. We explore reasons for this in Exercise 94.

13-4 Criterion for Spontaneous Change: The Second Law of Thermodynamics

In Section 13-1, we came to the tentative conclusion that processes in which the entropy increases should be spontaneous and that processes in which entropy decreases should be nonspontaneous. But this statement can present difficulties, for example, of how to explain the spontaneous freezing of liquid water at –10 °C. Because crystalline ice has lower molar entropy than does liquid water, the freezing of water is a process for which entropy *decreases*. The way out of this dilemma is to recognize that *two* entropy changes must always be considered simultaneously: the entropy change of the system itself, $\Delta S_{\text{sys}} = \Delta S$, and the entropy change of the surroundings, ΔS_{surr}. The criterion for spontaneous change must be based on the sum of the two, called the entropy change of the universe, ΔS_{univ}. Although it is beyond the scope of this discussion to verify the following expression, or explain how scientists came to recognize its validity, the expression provides the basic criterion for spontaneous change.

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0 \qquad \textbf{(13.10)}$$

Equation (13.10) is one way of stating the **second law of thermodynamics**. Another way is through the following statement.

> All spontaneous processes produce an increase in the entropy of the universe.

▶ We will usually use ΔS to represent the entropy change for the system. However, in some instances, we use the symbol ΔS_{sys} for extra emphasis.

▶ As established on page 275 for $\Delta_r H°$, the equation for $\Delta_r S°$ can also be expressed in the form

$$\Delta_r S° = \sum_{\text{all substances}} \nu_j S°$$
$$= \sum_{\text{products}} \nu_j S_j^\circ - \sum_{\text{reactants}} |\nu_j| S_j^\circ$$

According to expression (13.10), if a process produces positive entropy changes in both the system and its surroundings, the process is surely spontaneous. If both entropy changes are negative, the process is just as surely nonspontaneous. If one of the entropy changes is positive and the other negative, whether the sum of the two is positive or negative depends on the relative magnitudes of the two changes. To illustrate this point let us consider the freezing of super-cooled water at –10 °C. The corresponding Kelvin temperature is $T = 263.15$ K.

$$H_2O(l, 263.15\text{ K}) \longrightarrow H_2O(s, 263.15\text{ K})$$

Everyday experience tells us that water spontaneously freezes at 263.15 K. Let's use equation (13.10) to demonstrate that the freezing of super-cooled water is spontaneous at 263.15 K, and the reverse process is nonspontaneous.

Before we attempt to calculate the entropy changes for the system and its surroundings, we must think about how to carry out the desired change in a reversible way. Because the water is below its normal freezing point, we cannot carry out this process in a reversible way by keeping the temperature at 263.15 K. To carry out the process in a reversible way, we must first carefully raise the temperature of the water to 273.15 K. At this temperature, water freezes reversibly. Once all the water has frozen, we slowly lower the temperature back to 263.15 K. The following thermodynamic cycle summarizes how super-cooled water can be converted to ice at 263.15 K in a reversible way. The overall process is shown in black and the reversible path representing the overall process is shown in blue.

$$\begin{tikzcd}
H_2O(l, 263.15\text{ K}) \arrow[r, "{\Delta S = ?,\ \Delta H = ?}"] \arrow[d, "{\Delta S_1,\ \Delta H_1}"'] & H_2O(s, 263.15\text{ K}) \\
H_2O(l, 273.15\text{ K}) \arrow[r, "{\Delta S_2,\ \Delta H_2}"] & H_2O(s, 273.15\text{ K}) \arrow[u, "{\Delta S_3,\ \Delta H_3}"']
\end{tikzcd}$$

The enthalpy and entropy changes for the three steps shown in blue can be calculated using equations from Table 13.1, assuming the system contains exactly 1 mole. (The constant pressure heat capacities of ice and water are 37.3 and 75.3 J mol^{-1} K^{-1}, respectively. The enthalpy of fusion of ice is 6.01 kJ mol^{-1} K^{-1} at 273.15 K.)

1. Reversible heating of water from 263.15 K to 273.15 K

$$\begin{aligned}\Delta H_1 &= C_p(\text{water})\Delta T\\ &= (1\text{ mol})(75.3\text{ J mol}^{-1}\text{ K}^{-1})(+10\text{ K}) = +753\text{ J}\end{aligned}$$

$$\begin{aligned}\Delta S_1 &= C_p(\text{water})\ln(T_f/T_i)\\ &= (1\text{ mol})(75.3\text{ J mol}^{-1}\text{ K}^{-1})\ln(273.15\text{ K}/263.15\text{ K}) = +2.81\text{ J/K}\end{aligned}$$

2. Reversible freezing of water at 273.15 K

$$\Delta H_2 = -(1\text{ mol})\Delta_{\text{fus}}H° = -(1\text{ mol})(6.01 \times 10^3\text{ J mol}^{-1}) = -6010\text{ J}$$

$$\begin{aligned}\Delta S_2 &= -(1\text{ mol})\Delta_{\text{fus}}H°/T_{\text{fus}}\\ &= -(1\text{ mol})(6.01 \times 10^3\text{ J mol}^{-1}/273.15\text{ K}) = -22.0\text{ J mol}^{-1}\end{aligned}$$

3. Reversible cooling of ice from 273.15 K to 263.15 K

$$\begin{aligned}\Delta H_3 &= C_p(\text{ice})\Delta T\\ &= (1\text{ mol})(37.3\text{ J mol}^{-1}\text{ K}^{-1})(-10\text{ K}) = -373\text{ J}\end{aligned}$$

$$\begin{aligned}\Delta S_3 &= C_p(\text{ice})\ln(T_{\text{f}}/T_{\text{i}})\\ &= (1\text{ mol})(37.3\text{ J mol}^{-1}\text{ K}^{-1})\ln(263.15\text{ K}/273.15\text{ K}) = -1.39\text{ J mol}^{-1}\end{aligned}$$

Notice that the enthalpy and entropy changes are both positive for the heating process, but they are both negative for the freezing and cooling processes. The values of ΔS and ΔH for the overall process are obtained by adding the corresponding values for the individual steps.

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 = 753\text{ J} - 6010\text{ J} - 373\text{ J} = -5630\text{ J}$$

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 = 2.81\text{ J mol}^{-1} - 22.0\text{ J mol}^{-1} - 1.39\text{ J mol}^{-1} = -20.6\text{ J mol}^{-1}$$

The entropy of the system decreases because, in the solid, the molecules are more restricted in their motions; therefore, there are fewer ways to distribute the total energy of the system among the molecules. So, why is the freezing of super-cooled water spontaneous? It must be because the entropy change for the surroundings is greater than 20.6 J mol^{-1}. Let's calculate ΔS_{surr} to verify that this is indeed the case.

The entropy change for the surroundings is determined by the total amount of heat that flows into the surroundings and the temperature of the surroundings. Let's assume the surroundings are, in general, large enough that any quantity of heat released to (or absorbed from) the surroundings causes no more than an infinitesimal change in the temperature of the surroundings. Therefore, we can calculate the entropy change for the surroundings as

$$\Delta S_{\text{surr}} = \frac{-q_{\text{sys}}}{T_{\text{surr}}} \tag{13.11}$$

where q_{sys} represents the actual amount of heat that is absorbed or released by the system. Following the usual sign conventions, established in Chapter 7 (see page 249), $q_{\text{sys}} > 0$ when the system absorbs heat and $q_{\text{sys}} < 0$ when the system releases heat.

For the overall process described above, we have $q_{\text{sys}} = \Delta H = -5630$ kJ, which means that 5630 kJ of heat flows into the surroundings. The entropy change for the surroundings is

$$\Delta S_{\text{surr}} = \frac{+5630\text{ J}}{263.15\text{ K}} = +21.4\text{ J mol}^{-1}$$

and that of the universe is

$$\Delta S_{\text{univ}} = \Delta S + \Delta S_{\text{surr}} = -20.6\text{ J mol}^{-1} + 21.4\text{ J mol}^{-1} = +0.8\text{ J mol}^{-1} > 0$$

Since $\Delta S_{\text{univ}} > 0$, the freezing of super-cooled water at 263.15 K is spontaneous.

What about the reverse process, the conversion of $H_2O(s)$ to $H_2O(l)$ at 263.15 K? For this process, we would have $\Delta H = +5630$ J, $\Delta S = +20.6$ J mol^{-1}, $\Delta S_{\text{surr}} = -21.4$ J mol^{-1} and $\Delta S_{\text{univ}} = -0.8$ J mol^{-1}. The second law requires that $\Delta S_{\text{univ}} > 0$, so we conclude that the melting of ice at 263.15 K is nonspontaneous.

The ideas above can be summarized as follows.

- If $\Delta S_{\text{univ}} > 0$, the process is *spontaneous*.
- If $\Delta S_{\text{univ}} < 0$, the process is *nonspontaneous*.
- If $\Delta S_{\text{univ}} = 0$, the process is *reversible*.

13-3 CONCEPT ASSESSMENT

Using ideas from this section, explain why highly exothermic processes tend to be spontaneous. Under what condition(s) will a highly exothermic process be nonspontaneous?

Gibbs Energy and Gibbs Energy Change

We could use expression (13.10) as the basic criterion for spontaneous change, but it would be preferable to have a criterion that could be applied to *the system itself*, without having to worry about changes in the surroundings. Such a criterion can be developed in a straightforward manner for processes such as phase changes and chemical reactions that occur at constant temperature and constant pressure.

To develop this new criterion, let us explore a hypothetical process that occurs at constant temperature T and constant pressure P, with work limited to pressure-volume work. We will assume that the surroundings also have temperature T. Because pressure is constant, we have $\Delta H_{\text{sys}} = q_p$ and by equation (13.11), the entropy change in the surroundings is $\Delta S_{\text{surr}} = -H_{\text{sys}}T$.* Now substitute this value for ΔS_{surr} into equation (13.10) and multiply by T. We obtain

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

Finally, multiply by –1 (change signs).

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

The right side of this equation has terms involving *only the system*. On the left side appears the term ΔS_{univ}, which embodies the criterion for spontaneous change, that for a spontaneous process, $\Delta S_{\text{univ}} > 0$.

The equation above is generally cast in a somewhat different form by introducing a new thermodynamic function, called the **Gibbs energy, *G*.** The Gibbs energy for a system is defined by the equation

$$G = H - TS \qquad \textbf{(13.12)}$$

The **Gibbs energy change, Δ*G***, for a process at constant T is

$$\Delta G = \Delta H - T\Delta S \qquad \textbf{(13.13)}$$

In equation (13.13), all the terms refer to *changes for the system*. All reference to the surroundings has been eliminated. Also, when we compare the expressions for $-T\Delta S_{\text{univ}}$ and ΔG given above, we get

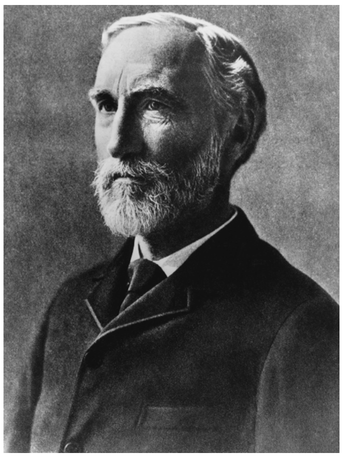
$$\Delta G = -T\Delta S_{\text{univ}}$$

Now, by noting that ΔG is *negative* when ΔS_{univ} is *positive*, we have our final criterion for spontaneous change based on properties of only the system itself.

For a process occurring at constant T and P, the following statements hold true.

- If $\Delta G < 0$ (*negative*), the process is *spontaneous*.
- If $\Delta G > 0$ (*positive*), the process is *nonspontaneous.*
- If $\Delta G = 0$ (*zero*), the process is *reversible* and the system has reached equilibrium.

Table 13.2 provides a summary of the criteria we can use for determining whether or not a particular process is spontaneous, nonspontaneous, or reversible.



Bettmann/Corbis

▲ **J. Willard Gibbs (1839–1903)—a great "unknown" scientist** Gibbs, a Yale University professor of mathematical physics, spent most of his career without recognition, partly because his work was abstract and partly because his important publications were in little-read journals. Yet today, Gibbs's ideas serve as the basis of most of chemical thermodynamics.

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*We cannot similarly substitute $\Delta H_{\text{sys}}/T$ for ΔS_{sys}. A process that occurs spontaneously is generally far removed from an equilibrium condition and is therefore *irreversible*. We cannot substitute δq for an irreversible process into equation (13.2).

TABLE 13.2 Criteria for Spontaneous Change

	Criteria	
Type of Change	General Conditions	Constant T and P
Spontaneous	$\Delta S_{\text{univ}} > 0$	$\Delta G < 0$
Nonspontaneous	$\Delta S_{\text{univ}} < 0$	$\Delta G > 0$
Reversible	$\Delta S_{\text{univ}} = 0$	$\Delta G = 0$

◀ For cases 2 and 3, there is a particular temperature at which a process switches from being spontaneous to being nonspontaneous. Section 13-5 explains how to determine such a temperature.

Applying the Gibbs Energy Criteria for Spontaneous Change

We can use ideas from Table 13.2 together with equation (13.13) to make some qualitative predictions. Altogether there are four possibilities for ΔG on the basis of the signs of ΔH and ΔS. These possibilities are outlined in Table 13.3 and demonstrated in Example 13-6.

If ΔH is *negative* and ΔS is *positive*, the expression $\Delta G = \Delta H - T\Delta S$ is negative at all temperatures. The process is spontaneous at all temperatures. This corresponds to the situation noted previously in which both ΔS_{sys} and ΔS_{surr} are positive and ΔS_{univ} is also positive.

Unquestionably, if a process is accompanied by an *increase* in enthalpy (heat is absorbed) and a *decrease* in entropy, ΔG is positive at all temperatures and the process is nonspontaneous. This corresponds to a situation in which both ΔS_{sys} and ΔS_{surr} are negative and ΔS_{univ} is also negative.

The questionable cases are those in which the entropy and enthalpy changes work in opposition—that is, with ΔH and ΔS *both* negative or *both* positive. In these cases, whether a reaction is spontaneous or not (that is, whether ΔG is negative or positive) depends on temperature. In general, if a reaction has negative values for both ΔH and ΔS, it is spontaneous at *lower* temperatures, whereas if ΔH and ΔS are both positive, the reaction is spontaneous at *higher* temperatures.

◀ For cases 2 and 3, there is a particular temperature at which a process switches from being spontaneous to being nonspontaneous. Section 13-8 explains how to determine such a temperature.

TABLE 13.3 Applying the Criteria for Spontaneous Change: $\Delta G - \Delta H - T\Delta S$

Case	ΔH	ΔS	ΔG	Result	Example
1.	−	+	−	spontaneous at all temp.	$2\,N_2O(g) \longrightarrow 2\,N_2(g) + O_2(g)$
2.	−	−	− +	spontaneous at low temp. nonspontaneous at high temp.	$H_2O(l) \longrightarrow H_2O(s)$
3.	+	+	+ −	nonspontaneous at low temp. spontaneous at high temp.	$2\,NH_3(g) \longrightarrow N_2(g) + 3\,H_2(g)$
4.	+	−	+	nonspontaneous at all temp.	$3\,O_2(g) \longrightarrow 2\,O_3(g)$

13-4 CONCEPT ASSESSMENT

The normal boiling point of water is 100 °C. At 120 °C and 1 atm, is ΔH or $T\Delta S$ greater for the vaporization of water?

EXAMPLE 13-6 Using Enthalpy and Entropy Changes to Predict the Direction of Spontaneous Change

Under what temperature conditions would the following reactions occur spontaneously?

(a) $2\,NH_4NO_3(s) \longrightarrow 2\,N_2(g) + 4\,H_2O(g) + O_2(g) \qquad \Delta_r H° = -236.0\text{ kJ mol}^{-1}$

(b) $I_2(g) \longrightarrow 2\,I(g)$

(continued)

Analyze

(a) The reaction is exothermic, and in Example 13-3(a) we concluded that $\Delta S > 0$ because large quantities of gases are produced.

(b) Because one mole of gaseous reactant produces two moles of gaseous product, we expect entropy to increase. But what is the sign of ΔH? We could calculate ΔH from enthalpy of formation data, but there is no need to. In the reaction, covalent bonds in $I_2(g)$ are broken and no new bonds are formed. Because energy is absorbed to break bonds, ΔH must be positive. With $\Delta H > 0$ and $\Delta S > 0$, case 3 in Table 13.3 applies.

Solve

(a) With $\Delta H < 0$ and $\Delta S > 0$, this reaction should be spontaneous at all temperatures (case 1 in Table 13.3). $NH_4NO_3(s)$ exists only because the decomposition occurs very slowly. (We will investigate the factors affecting the rates of chemical reactions in Chapter 20.)

(b) ΔH is larger than $T\Delta S$ at low temperatures, and the reaction is nonspontaneous. At high temperatures, the $T\Delta S$ term becomes larger than ΔH, ΔG becomes negative, and the reaction is spontaneous.

Assess

We observe that reaction spontaneity depends on a balance of enthalpy, entropy, and temperature. Table 13.3 is a good summary of the conditions in which reactions will be spontaneous or nonspontaneous.

PRACTICE EXAMPLE A: Which of the four cases in Table 13.3 would apply to each of the following reactions?

(a) $N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g), \qquad \Delta_r H^\circ = -92.22 \text{ kJ mol}^{-1}$

(b) $2\,C(\text{graphite}) + 2\,H_2(g) \longrightarrow C_2H_4(g), \qquad \Delta_r H^\circ = 52.26 \text{ kJ mol}^{-1}$

PRACTICE EXAMPLE B: Under what temperature conditions would the following reactions occur spontaneously? **(a)** The decomposition of calcium carbonate into calcium oxide and carbon dioxide. The reaction is endothermic. **(b)** The "roasting" of zinc sulfide in oxygen to form zinc oxide and sulfur dioxide. This exothermic reaction releases 439.1 kJ for every mole of zinc sulfide that reacts.

▶ A related observation is that only a small fraction of the mass of the universe is in molecular form.

Example 13-6(b) illustrates why there is an upper temperature limit for the stabilities of chemical compounds. No matter how positive the value of ΔH for dissociation of a molecule into its atoms, the term $T\Delta S$ will eventually exceed ΔH in magnitude for sufficiently large values of T. For those temperatures, dissociation will be spontaneous. Known temperatures range from near absolute zero to the interior temperatures of stars (about 3×10^7 K). Molecules exist only at limited temperatures (up to about 1×10^4 K or about 0.03% of this total temperature range).

Gibbs Energy Change and Work

Up to this point, we have made use of the fact that, for a process occurring at constant T and constant P, the Gibbs energy change is less than or equal to zero: $\Delta G \leq 0$. This result was developed on page 602 by focusing on a process in which work is limited to pressure-volume work. How is this result changed if other types of work are possible? Before answering this question, let us first mention some examples of non-PV work that are relevant to chemistry. Examples include the work associated with forcing electrons through a circuit (electrical work), the work associated with raising a column of liquid, the work of stretching an elastic material (e.g., a muscle), or the work of sustaining nerve activity. It turns out that, if other types of work are possible, then the second law guarantees that $\Delta G \leq w_{\text{non-}PV}$, where $w_{\text{non-}PV}$ represents the sum total of all other forms of work. Clearly, if $w_{\text{non-}PV} = 0$, then we get back the usual condition that $\Delta G \leq 0$.

According to the sign conventions established for work in Chapter 7 (w is positive when work is done on the system; w is negative when work is done by the system), we can write $w_{\text{non-}PV} = -|w_{\text{non-}PV}|$ when the system does non-PV work on the surroundings, where $|w_{\text{non-}PV}|$ is the magnitude of the amount of non-*PV* work we can obtain from the process. Thus, we may write $\Delta G \leq -|w_{\text{non-}PV}|$ and from this we can say

$$|w_{\text{non-}PV}| \leq -\Delta G$$

What does this result imply? First, we get nonzero, non-*PV* work only if ΔG for the process is negative. Second, $-\Delta G$ represents the maximum amount of energy available to do non-*PV* work. Thus, for example, if ΔG for a process is –100 kJ, then the maximum amount of energy available for non-*PV* work is 100 kJ. Finally, if the process is carried out reversibly, then the maximum amount of energy available for non-*PV* work is $|\Delta G|$, otherwise it is less than $|\Delta G|$. Because $|\Delta G|$ determines how much energy is available to do non-*PV* work, *G* was once called the Gibbs free energy or simply free energy by most chemists. In this context, “free” refers to the availability of energy for doing non-*PV* work and is not meant to imply that the actual financial cost of obtaining this energy is zero. (Without a doubt, there are always nonzero financial costs associated with obtaining energy from a process.) In Chapter 19, we will see how the Gibbs energy change for a system can be converted into electrical work.

As discussed above, ΔG for a process reflects the amount of energy that is available to perform non-*PV* work. An important application is to use the energy generated by a spontaneous process to do the work of making another nonspontaneous process occur. For example, the biochemical oxidation of one mole of glucose, $C_6H_{12}O(s)$, at 37 °C gives $\Delta G = -37$ kJ. The energy obtained from this process is used in living systems to drive the formation of adenosine triphosphate (ATP) from adenosine diphosphate (ADP) and phosphate. ATP is needed to sustain reactions involved in muscle expansion and contraction.

13-5 Gibbs Energy Change of a System of Variable Composition: $\Delta_r G°$ and $\Delta_r G$

As established in the preceding section, the Gibbs energy change of a system is the key quantity for predicting the spontaneity of change under the condition of constant *T* and constant *P*, a condition that is frequently encountered (e.g., with phase transitions and chemical reactions). In such situations, the Gibbs energy change arises not because of changes in *T* or *P*, but from changes in the amounts of substances, that is, from a change in composition of the system. For example, in a phase transition occurring at constant *T* and constant *P*, the composition of the system changes because a certain amount of a substance is converted from one phase to another. In a chemical reaction, the composition of the system changes because certain amounts of reactants are converted into products. In this section, we introduce the concepts needed to evaluate the change in Gibbs energy that arises from a change in composition.

Standard Gibbs Energy of Reaction, $\Delta_r G°$

The **standard Gibbs energy of reaction**, $\Delta_r G°$, is defined as the Gibbs energy change per mole of reaction for the following process.

$$\begin{array}{lcl} \text{Pure, unmixed reactants} & \longrightarrow & \text{Pure, unmixed products} \\ \text{(each in its standard state)} & & \text{(each in its standard state)} \end{array}$$

The process involves the complete conversion of stoichiometric amounts of pure, unmixed reactants in their standard states to stoichiometric amounts of pure, unmixed products in their standard states. The Gibbs energy change for this process can be obtained from tabulated thermochemical data of pure substances in their standard states (see Appendix D). To see how this is done, consider the following general equation representing the process above.

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

Following the same approach that was used in Chapter 7 to establish the result given in equation (7.22) for $\Delta_r H^\circ$, it is possible to show that

$$\Delta_r G^\circ = \underbrace{[c\,\Delta_f G^\circ_C + d\,\Delta_f G^\circ_D + \ldots]}_{\text{Weighted sum of } \Delta_f G^\circ \text{ values for products}} \quad - \quad \underbrace{[a\,\Delta_f G^\circ_A + b\,\Delta_f G^\circ_B +]\ldots}_{\text{Weighted sum of } \Delta_f G^\circ \text{ values for reactants}} \qquad \mathbf{(13.14)}$$

where $\Delta_f G^\circ$, the **standard Gibbs energy of formation**, is the Gibbs energy change *per mole* for a reaction in which a substance in its standard state is formed from its elements in their reference forms in their standard states. As was the case for standard enthalpies of formation, we have $\Delta_f G^\circ = 0$ for an element in its reference form at a pressure of 1 bar. Standard Gibbs energies of formation for a variety of substances are tabulated in Appendix D. The value of $\Delta_r G^\circ$ calculated using equation (13.14) has the unit J mol^{-1} because $\Delta_f G^\circ$ values have the unit J mol^{-1} and the coefficients a, b, c, d, etc., are simply numbers with no units.

Some additional relationships involving $\Delta_r G^\circ$ are similar to those presented for enthalpy in section 7-7: (1) $\Delta_r G^\circ$ changes sign when a process is reversed; (2) $\Delta_r G^\circ$ for an overall reaction can be obtained by adding together the $\Delta_r G^\circ$ values for the individual steps; and (3) $\Delta_r G^\circ$ is equal to $\Delta_r H^\circ - T\Delta_r S^\circ$. The last relationship is helpful in situations for which $\Delta_r H^\circ$ and $\Delta_r S^\circ$ values are known or more easily obtained, as illustrated in Example 13-7.

EXAMPLE 13-7 Calculating $\Delta_r G^\circ$ for a Reaction

Determine $\Delta_r G^\circ$ at 298.15 K for the reaction

$$2\,\text{NO(g)} + \text{O}_2\text{(g)} \longrightarrow 2\,\text{NO}_2\text{(g)} \quad \text{(at 298.15 K)} \qquad \begin{aligned} \Delta_r H^\circ &= -114.1 \text{ kJ mol}^{-1} \\ \Delta_r S^\circ &= -146.5 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

Analyze

Because we have values of $\Delta_r H^\circ$ and $\Delta_r S^\circ$, the most direct method of calculating $\Delta_r G^\circ$ is to use the expression $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$.

Solve

Note that the unit for the standard molar enthalpy is kJ mol^{-1}, and for the standard molar entropy it is mol^{-1} J K^{-1}. Before combining the $\Delta_r H^\circ$ and $\Delta_r S^\circ$ values to obtain a $\Delta_r G^\circ$ value, the $\Delta_r H^\circ$ and $\Delta_r S^\circ$ values must be expressed in the same energy unit (for instance, kJ).

$$\begin{aligned} \Delta_r G^\circ &= -114.1 \text{ kJ mol}^{-1} - (298.15 \text{ K} \times -0.1465 \text{ kJ mol}^{-1} \text{ K}^{-1}) \\ &= -114.1 \text{ kJ mol}^{-1} + 43.68 \text{ kJ mol}^{-1} \\ &= -70.4 \text{ kJ mol}^{-1} \end{aligned}$$

Assess

This example says that all the reactants and products are maintained at 25 °C and 1 bar pressure. Under these conditions, the Gibbs energy change is −70.4 kJ for oxidizing two moles of NO to two moles of NO_2. To do this, it is necessary to replenish the reactants so as to maintain the standard conditions.

PRACTICE EXAMPLE A: Determine $\Delta_r G^\circ$ at 298.15 K for the reaction $4\,\text{Fe(s)} + 3\,\text{O}_2\text{(g)} \longrightarrow 2\,\text{Fe}_2\text{O}_3\text{(s)}$. $\Delta_r H^\circ = -1648 \text{ kJ mol}^{-1}$ and $\Delta_r S^\circ = -549.3 \text{ J mol}^{-1} \text{ K}^{-1}$.

PRACTICE EXAMPLE B: Determine $\Delta_r G^\circ$ for the reaction in Example 13-7 by using data from Appendix D. Compare the two results.

13-5 CONCEPT ASSESSMENT

For the reaction below, $\Delta_r G^\circ = 326.4 \text{ kJ mol}^{-1}$:

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

What is the Gibbs energy change for the system when 1.75 mol O_2(g) at 1 bar reacts completely to give O_3(g) at 1 bar?

Gibbs Energy of Reaction for Nonstandard Conditions, $\Delta_r G$

In Section 13-4, we established that for a spontaneous process at constant T and constant P, the Gibbs energy of the system always decreases: $(\Delta G)_{T,P} < 0$. Consequently, to predict the direction of spontaneous chemical change, we need an equation that relates a change in G to a change in composition. With such an equation, we can decide whether G will increase or decrease when the composition of a system changes by some amount. With that knowledge, we can state unequivocally whether reaction to the left or to the right is spontaneous, for a given initial condition. In this section we present the equation, without derivation, and focus on interpreting and using it properly. We defer the derivation of this equation to Section 13-8. The motivation for this approach is quite simply stated: For most applications, knowing the meaning of the equation and how to use it is ultimately more helpful than knowing or remembering how it can be derived.

To place this discussion on firmer ground, let's consider a system containing $N_2(g)$, $H_2(g)$, and $NH_3(g)$, treated as ideal gases, and let n_{N_2}, n_{H_2} and n_{NH_3} represent the initial amounts, in moles, of each gas. Suppose that the composition of the system changes, at constant T and constant P, because the following reaction advances by an infinitesimal amount, $d\xi$. The changes occurring in the system are summarized below.

$$N_2(g) + 3\,H_2(g) \underset{d\xi < 0}{\overset{d\xi > 0}{\rightleftarrows}} 2\,NH_3(g)$$

	$N_2(g)$	$3\,H_2(g)$	$2\,NH_3(g)$	
Initial state:	n_{N_2}	n_{H_2}	n_{NH_3}	G_i
Change:	$-\,d\xi$	$-\,3\,d\xi$	$+\,2\,d\xi$	$+\,dG$
Final state:	$n_{N_2} - d\xi$	$n_{H_2} - 3\,d\xi$	$n_{NH_3} + 2\,d\xi$	$G_f = G_i + dG$

We have arrows pointing to the left and to the right because we want to consider the effect on G of a change in composition arising from reaction toward the right ($\longrightarrow$) or toward the left ($\longleftarrow$). The sign of $d\xi$ determines the direction of reaction. A positive value ($d\xi > 0$) describes reaction from left to right, whereas a negative value ($d\xi < 0$) describes reaction from right to left. As suggested by the summary above, an infinitesimally small change in composition, represented by $d\xi$, causes an infinitesimally small change, dG, in the Gibbs energy of the system.

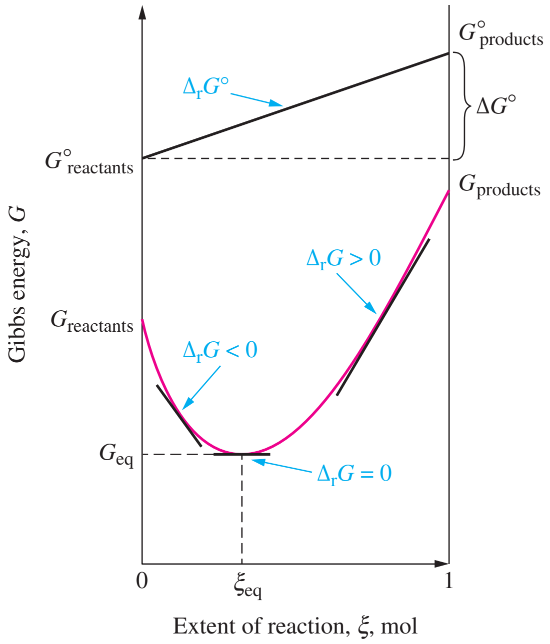
To decide whether the reaction to the right or to the left is spontaneous, we need to know how G changes with ξ, the extent of reaction, and more specifically, the rate of change of G with respect to ξ. The rate of change of G with respect to the extent of reaction is represented by the symbol $\Delta_r G$ and it is called the **Gibbs energy of reaction**. As we will demonstrate in Section 13-8, the equation for $\Delta_r G$ has the following remarkably simple form.

$$\Delta_r G = \Delta_r G° + RT \ln Q \qquad \textbf{(13.15)}$$

We have already discussed the meaning of the term $\Delta_r G°$. In the term $RT \ln Q$, the quantity Q is called the **reaction quotient**. Because equation (13.15) relates the value of $\Delta_r G$ for arbitrary nonstandard conditions to its value under standard conditions, we anticipate that the term $RT \ln Q$ includes the effects of bringing the system from standard conditions (pure, unmixed substances, each at $P° = 1$ bar) to the actual nonstandard conditions (a mixture of substances with a total pressure of 1 bar). For the present example, the reaction quotient takes the following form, a result that will be established in Section 13-8.

$$Q = \frac{(P_{NH_3}/P°)^2}{(P_{N_2}/P°)\,(P_{H_2}/P°)^3}$$

In general, the reaction quotient depends on the composition of the system, in this case through the partial pressures of the gases. So, for a specified composition (e.g., for given values of the partial pressures), we can calculate



▲ FIGURE 13-8

Variation of G at constant T and constant P

At $\xi = 0$ mol, the system contains stoichiometric amounts of reactants only and at $\xi = 1$ mol, it contains stoichiometric amounts of products only. The quantities $G^\circ_{\text{reactants}}$ and $G^\circ_{\text{products}}$ are the Gibbs energies for stoichiometric amounts of pure, unmixed reactants and of pure, unmixed products in their standard states. $\Delta G^\circ = G^\circ_{\text{products}} - G^\circ_{\text{reactants}}$ is the Gibbs energy change for converting stoichiometric amounts of pure, unmixed reactants in their standard states to stoichiometric amounts of pure, unmixed products in their standard states, whereas the standard Gibbs energy of reaction, $\Delta_rG^\circ = \Delta G^\circ/(1\text{ mol})$, is the slope of the line joining the points marked by $G^\circ_{\text{products}}$ and $G^\circ_{\text{reactants}}$. The quantities $G_{\text{reactants}}$ and G_{products} represent the Gibbs energies of reactants and of products after stoichiometric amounts of them are brought to a total pressure P. The Gibbs energy of reaction, Δ_rG, is the rate of change of G with respect to the extent of reaction. Its value at any point is equal to the slope of the tangent to the curve at that point. At equilibrium, G reaches its minimum value and $\Delta_rG = 0$. The extent of reaction and the Gibbs energy at equilibrium are denoted by ξ_{eq} and G_{eq}, respectively. When the extent of reaction is less than ξ_{eq}, the slope (Δ_rG) is negative and, therefore, G decreases as ξ increases. When the extent of reaction is greater than ξ_{eq}, the slope (Δ_rG°) is positive and G increases as ξ increases.

a value of Q and, by applying equation (13.15), a value of Δ_rG. Figure 13-8 can help us understand the meaning of the value of Δ_rG and also how to decide whether the reaction to the left or to the right is spontaneous for the conditions specified. Notice from Figure 13-8 that Δ_rG is the slope of the tangent at a particular point in a graph of G versus the extent of the reaction. With the help of Figure 13-8, we can establish the following important ideas.

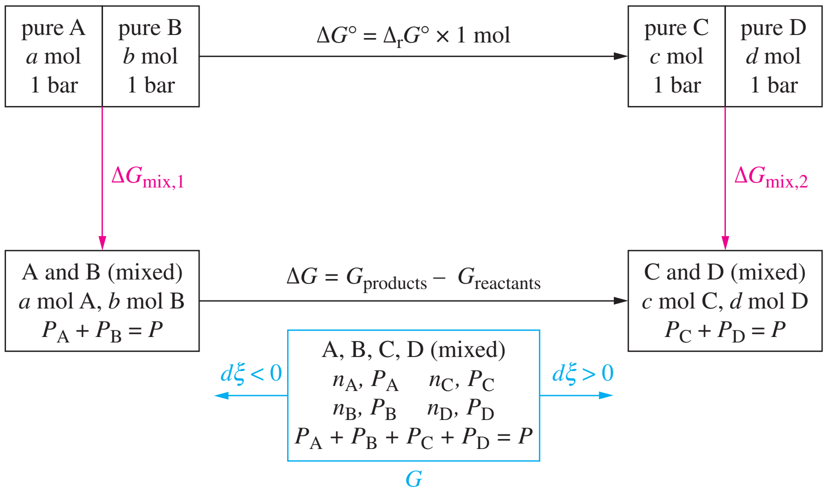
1. **If $\Delta_rG < 0$, then G decreases as ξ increases.** When $\Delta_rG < 0$, the reaction proceeds spontaneously from left to right to achieve a decrease in the value of G. The reverse reaction, from right to left, causes the value of G to increase and is therefore nonspontaneous.
2. **If $\Delta_rG > 0$, then G increases as ξ increases.** To achieve a decrease in the value of G, the value of ξ must decrease. This means the reaction must proceed in the reverse direction, from right to left. Thus, when $\Delta_rG > 0$, reaction from right to left is spontaneous and reaction from left to right is nonspontaneous.
3. **When $\Delta_rG = 0$, the system has attained the minimum possible value of G.** We say that the system has reached equilibrium. When $\Delta_rG = 0$, reaction to the right (increasing ξ) or to the left (decreasing ξ) is accompanied by an increase in G.

These results are summarized in Table 13.4.

TABLE 13.4 Predicting the Direction of Spontaneous Chemical Change

Δ_rG	Spontaneous Reaction
< 0	Left to right ($\longrightarrow$)
> 0	Right to left ($\longleftarrow$)
$= 0$	Equilibrium ($\rightleftharpoons$)

An alternative explanation of Figure 13-8 is illustrated in the following diagram for the generalized reaction $a\mathrm{A(g)} + b\mathrm{B(g)} \longrightarrow c\mathrm{C(g)} + d\mathrm{D(g)}$.



The top portion of this diagram highlights that ΔG° is the change in Gibbs energy for the system when stoichiometric amounts of unmixed reactants in their standard states are converted completely into stoichiometric amounts of unmixed products in their standard states. Although this conversion does not correspond to any real situation (it is a hypothetical process), we observe that ΔG° is equal to $\Delta_r G^\circ$ times one mole of reaction. The bottom portion of the diagram describes a more realistic situation, in which a mixture initially containing only A and B is converted to a mixture containing only C and D. The conversion is carried out at a constant pressure P. The Gibbs energy change for the complete conversion of a mixture of A and B to a mixture of C and D is ΔG. As suggested in diagram, the hypothetical and realistic processes can be related by two mixing processes (red arrows), one involving the mixing of reactants and the other involving the mixing of products. The mixing processes also involve bringing the mixture to a total pressure P. The Gibbs energy changes for these two mixing processes are denoted by $\Delta G_{\text{mix},1}$ and $\Delta G_{\text{mix},2}$. From the diagram, we can establish the result $\Delta G = \Delta G^\circ - \Delta G_{\text{mix},1} + \Delta G_{\text{mix},2}$.

Now, let's turn our focus to the box in blue in the bottom portion of the diagram. This box represents the system containing arbitrary amounts of A, B, C, and D at total pressure P, somewhere between a mixture of stoichiometric amounts of reactants and a mixture of stoichiometric amounts of products. The Gibbs energy of the system at that particular point is G. Depending on the values of n_A, n_B, n_C, and n_D, the reaction goes either to the left ($d\xi < 0$) or to the right ($d\xi > 0$), the corresponding change in G given by $dG = \Delta_r G \times d\xi$. It is the sign of $\Delta_r G$ that indicates whether the reaction to the left or right is spontaneous.

Equation (13.15) is the relationship we need to predict whether the reaction to the right or to the left is spontaneous under any conditions of composition, provided that the temperature and pressure at which we observe the reaction are constant. Because of the importance of this equation, it is imperative that we are perfectly clear about the meaning of the quantities appearing in it.

- $\Delta_r G^\circ$ is the standard Gibbs energy of reaction in J mol^{-1}. As discussed previously, it is the Gibbs energy change per mole of reaction when stoichiometric amounts of pure unmixed reactants in their standard states are completely converted into stoichiometric amounts of pure unmixed products in their standard states. The Gibbs energy change for this process is $\Delta_r G^\circ \times 1$ mol. The value of $\Delta_r G^\circ$ is often calculated using thermochemical data for pure substances in their standard states (equation 13.14).

- Q represents the reaction quotient, and its value depends on the composition of the system. Therefore, the effect of composition is contained in the term $RT \ln Q$. We will say more about Q in the discussion that follows.
- $\Delta_r G$ represents the rate of change of Gibbs energy with respect to the extent of reaction for a system under the specified conditions of composition. It has the unit J mol^{-1}. Its value is easily calculated once the values of $\Delta_r G°$ and Q have been determined. As shown in Table 13.4, it is the sign of $\Delta_r G$ that matters most. The value of $\Delta_r G$ can be used to the estimate the change in G that is caused by a given change in composition. For example, when the composition of a system changes because of a reaction that advances by an infinitesimal amount $d\xi$, the corresponding change in Gibbs energy is $dG = \Delta_r G\, d\xi$.

In Example 13-8, we apply these concepts to a system containing specified amounts of $N_2(g)$, $H_2(g)$, and $NH_3(g)$. Following this example, we discuss the general form for the reaction quotient, Q, so that we can apply equation (13.15) to any reaction.

Example 13-8 Calculating $\Delta_r G$ from Thermodynamic Data and Specified Reaction Conditions

A system contains H_2, N_2, and NH_3 gases, each with a partial pressure of 0.100 bar. The temperature is held constant at 298 K. Calculate the Gibbs energy of reaction, $\Delta_r G$, for the formation of $NH_3(g)$ from $N_2(g)$ and $H_2(g)$ under these conditions, and predict whether formation or consumption of NH_3 is spontaneous.

Analyze

We are asked to calculate the Gibbs energy of reaction for a specified reaction and an initial condition. To calculate $\Delta_r G$, we can use equation (13.15), which means we need values for the standard Gibbs energy of reaction, $\Delta_r G°$, and the reaction quotient Q.

Solve

The first step is to write a balanced equation for the reaction.

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

The expression to be evaluated is equation (13.15).

$$\Delta_r G = \Delta_r G° + RT \ln Q$$

Next, determine $\Delta_r G°$ by using equation (13.14) and $\Delta_f G°$ values from Appendix D.

$$\begin{aligned}\Delta_r G° &= 2\Delta_f G°[NH_3(g)] - \Delta_f G°[N_2(g)] - 3\Delta_f G°[H_2(g)]\\ &= [2(-46.11) - 1(0) - 3(0)]\ \text{kJ mol}^{-1}\\ &= -92.22\ \text{kJ mol}^{-1}\end{aligned}$$

The value of Q is calculated from the data given in the problem. We make use of the fact that $P° = 1$ bar.

$$Q = \frac{(P_{NH_3}/P°)^2}{(P_{N_2}/P°)(P_{H_2}/P°)^3} = \frac{(0.10)^2}{(0.10)(0.10)^3} = 100$$

Now we use equation (13.15) to obtain the value of $\Delta_r G$.

$$\begin{aligned}\Delta_r G &= \Delta_r G° + RT \ln Q\\ &= -92.22\ \text{kJ mol}^{-1} + (8.314 \times 10^{-3}\ \text{kJ mol}^{-1}\ \text{K}^{-1})(298\ \text{K})\\ &\quad \ln 100 = -80.8\ \text{kJ mol}^{-1}\end{aligned}$$

The value of –80.8 kJ mol^{-1} for $\Delta_r G$ represents the rate of change of Gibbs energy with respect to the extent of reaction for the system under the specified conditions of composition. The sign of $\Delta_r G$ indicates that the rate of change is negative (G decreases as the reaction proceeds in the forward direction). Therefore, for the given initial conditions, the reaction proceeds spontaneously from left to right, leading to the formation of more NH_3.

Assess

For the given initial conditions, reaction to the right (formation of more NH_3) is spontaneous. However, different initial conditions might lead to spontaneous consumption of NH_3. For example, if the initial partial pressures were $P_{NH_3} = 10$ bar, and $P_{N_2} = P_{H_2} = 1.0 \times 10^{-4}$ bar, then $Q = 1 \times 10^{20}$ and

$\Delta_r G = 22 \text{ kJ mol}^{-1} > 0$. In this case, the forward reaction is nonspontaneous and the reverse reaction (consumption of NH_3) is spontaneous.

PRACTICE EXAMPLE A: What is the partial pressure of NH_3 in the ammonia synthesis reaction if the Gibbs energy of reaction is –82.00 kJ mol^{-1} and the partial pressures of hydrogen and nitrogen are each 0.500 bar? The temperature is 298 K.

PRACTICE EXAMPLE B: What is the minimum value of Q required to make the reverse reaction, conversion of NH_3 to N_2 and H_2, spontaneous at 298 K?

The Thermodynamic Reaction Quotient, Q

We saw earlier that the reaction quotient for the reaction

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

is given by

$$Q = \frac{(P_{NH_3}/P°)^2}{(P_{N_2}/P°)(P_{H_2}/P°)^3}$$

We can rewrite this expression in a slightly different but more general way by defining $a = P/P°$ as the **activity** of an ideal gas. Thus, for an ideal gas, the activity is simply the partial pressure of the gas divided by $P° = 1$ bar, the standard state pressure. Although we will have more to say about activity in Section 13-8, for now we need only say that ultimately, the activity of a substance depends not only on the amount of substance but also on the form in which it appears in the system. The following rules summarize how the activity of various substances is defined (see also Table 13.5). It is beyond the scope of this discussion to explain the reasons for defining activities in these ways, so we will simply accept these definitions and use them. However, it is important to note that the activity of a substance is defined with respect to a specific reference state.

TABLE 13.5 Activities of Solids, Liquids, Gases, and Solutes*

Form of Substance	Activity
X(s)	$a = 1$
X(l)	$a = 1$
X(g)	$a = P_X/P°$
X(aq)	$a = [X]/c°$

*In these relationships, $P° = 1$ bar and $c° = 1 \text{ mol L}^{-1}$.

- **For solids and liquids:** The activity $a = 1$. The reference state is the pure solid or liquid.
- **For gases:** With ideal gas behavior assumed, the activity is replaced by the numerical value of the gas pressure in bar. The reference state is an ideal gas at 1 bar at the temperature of interest. Thus, the activity of a gas at 0.50 bar pressure is $a = (0.50 \text{ bar})/(1 \text{ bar}) = 0.50$. (Recall also that 1 bar of pressure is almost identical to 1 atm.)
- **For solutes in aqueous solution:** With ideal solution behavior assumed (for example, no interionic interactions), the activity is replaced by the numerical value of the molarity. The reference state is an ideal solution having a concentration of 1 M at the temperature of interest. Thus, the activity of the solute in a 0.25 M solution is $a = (0.25 \text{ M})/(1 \text{ M}) = 0.25$.

In terms of activities, the expression above for Q may be written as

$$Q = \frac{(a_{NH_3})^2}{(a_{N_2})(a_{H_2})^3}$$

Although this expression for Q is for a very specific reaction, it reveals that (1) Q is a quotient formed by writing the activities of the products in the numerator and the activities of the reactants in the denominator; and (2) the activity of each reactant or product is raised to a power equal to the corresponding coefficient from the balanced equation for the reaction. To illustrate the general procedure for writing the reaction quotient, consider again the following general equation for a chemical reaction.

$$aA + bB + \ldots \longrightarrow cC + dD + \ldots$$

To write the reaction quotient for a reaction, we proceed as follows.

1. Form a quotient in which the activities of products appear in the numerator and those of reactants appear in the denominator. In both the numerator and the denominator, the activities are combined by multiplying them. (The resulting expression is not yet the reaction quotient.)

$$\frac{a_C \times a_D \times \cdots}{a_A \times a_B \times \cdots}$$

2. To obtain the reaction quotient, Q, raise each activity to a power equal to the corresponding coefficient from the balanced chemical equation.

$$Q = \frac{a_C^c \times a_D^d \times \cdots}{a_A^a \times a_B^b \times \cdots} \tag{13.16}$$

The value of the reaction quotient depends on the composition of the system because, as described in the preceding discussion, the activities typically depend on the pressures or concentrations of the substances involved.

Relationship of $\Delta_r G^\circ$ to the Equilibrium Constant K

We encounter an interesting situation when we apply equation (13.15) to a reaction at equilibrium. We have learned that at equilibrium, $\Delta_r G = 0$ and so, we can write

$$0 = \Delta_r G^\circ + RT \ln Q_{eq}$$

The subscript eq on Q emphasizes that the equation, as written, applies only if the system has reached equilibrium. If we rearrange the expression above for $\ln Q_{eq}$, we get $\ln Q_{eq} = -\Delta_r G^\circ / RT$. For a given reaction at a particular temperature, $\Delta_r G^\circ$ has a specific value, as demonstrated by Example 13-7. Therefore, $\ln Q_{eq}$ and Q_{eq} also have certain fixed values once the reaction and the temperature are specified. Let's use the symbol K to represent the value of Q_{eq} and call it the **equilibrium constant**. So, by definition, the equilibrium constant, K, represents the value of the reaction quotient, Q, at equilibrium. By replacing Q_{eq} with K, we can write the equation above in the following form.

$$\Delta_r G^\circ = -RT \ln K \tag{13.17}$$

If we have a value of $\Delta_r G^\circ$ for a reaction at a given temperature, we can use equation (13.17) to calculate an equilibrium constant K. This means that the tabulation of thermodynamic data in Appendix D can serve as a direct source of countless equilibrium constant values at 298.15 K. Knowing the value of K for a reaction turns out to be extremely useful because, as we will see in Chapter 15, the value of K and a set of initial reaction conditions are all that we need to be able to predict the equilibrium composition of a system.

We can use equation (13.17) to rewrite equation (13.15) as

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q = -RT \ln K + RT \ln Q$$

By combining the logarithmic terms, we obtain

$$\Delta_r G = RT \ln (Q/K) \tag{13.18}$$

This equation can be used to establish a method for predicting the direction of spontaneous change. The method involves comparing the values of Q and K. Again, there are three specific cases to consider. They are described below and summarized in Table 13.6.

1. **$Q < K$:** In this case, $Q/K < 1$ and $\Delta_r G = RT \ln (Q/K) < 0$. As already established, when $\Delta_r G < 0$, the forward reaction is spontaneous. In this situation, the reaction proceeds spontaneously in the direction that causes the value of Q to increase.

TABLE 13.6 Using Q and K to Predict the Direction of Spontaneous Chemical Change

Condition	Spontaneous Reaction
$Q < K$	Left to right ($\longrightarrow$)
$Q > K$	Right to left ($\longleftarrow$)
$Q = K$	Equilibrium ($\rightleftharpoons$)

2. **$Q > K$:** Here we have $Q/K > 1$ and $\Delta_r G = RT \ln (Q/K) > 0$. Therefore, the reverse reaction is spontaneous. The reaction proceeds spontaneously in the direction that causes the value of Q to decrease.
3. **$Q = K$:** When the reaction quotient is equal to the equilibrium constant, $\Delta_r G = RT \ln (1) = 0$ and the system has reached equilibrium.

Different Forms of the Equilibrium Constant

When the reaction quotient for a reaction is written in terms of activities, the corresponding equilibrium constant is called the **thermodynamic equilibrium constant**. Activities are dimensionless (unitless) quantities and therefore, the thermodynamic equilibrium constant is also a dimensionless quantity. The thermodynamic equilibrium constant is appropriate for use in equation (13.15).

KEEP IN MIND

that by writing an equation for a reaction with double arrows, each with a half arrowhead ($\rightleftharpoons$), we are emphasizing that the reaction has reached equilibrium.

Consider again the general equation for a reaction that has reached equilibrium.

$$a\,\mathrm{A} + b\,\mathrm{B} + \ldots \rightleftharpoons c\,\mathrm{C} + d\,\mathrm{D} + \ldots$$

We may write the equilibrium condition $Q_{eq} = K$ for this reaction as follows.

$$K = \frac{(a_{\mathrm{C,eq}})^c\,(a_{\mathrm{D,eq}})^d \cdots}{(a_{\mathrm{A,eq}})^a\,(a_{\mathrm{B,eq}})^b \cdots} \qquad \textbf{(13.19)}$$

The subscript eq on the activities emphasizes that equilibrium values for these quantities must be used. Although the notation used above is clear, few chemists use it because the numerous subscripts and parentheses make the resulting expression appear rather cluttered. Many chemists would instead write the expression above in the abbreviated form

$$K = \frac{a_{\mathrm{C}}^c\,a_{\mathrm{D}}^d}{a_{\mathrm{A}}^a\,a_{\mathrm{B}}^b}$$

The expression above is much simpler, but it hides the true meaning of what is intended and can be easily misinterpreted. It seems to imply that the value of K changes as the values of the activities change. However, that is not the intended meaning. To the left of the equal sign, we have K, the equilibrium constant. To the right of the equal sign, we have the reaction quotient, Q, expressed in terms of the activities. By setting these two things equal, we mean that the reaction quotient has the value K, which is of course only true at equilibrium. Thus, when writing or using the simplified expressions above for K, equilibrium values of the activities are implied. This seems an obvious, and perhaps even a trivial, point but it is important to remember that the value of Q changes as the composition of the system changes, not the value of K.

Because the activities are expressed in different ways for different types of substances, the equilibrium condition—equation (13.19)—is also expressed in different ways, depending on the types of substances involved. Let us explore this issue in more detail.

Reactions Involving Gases. For a reaction that involves only gases, we may write equation (13.19) as (assuming ideal behavior)

$$K = \frac{(P_{\text{C,eq}}/P°)^c\,(P_{\text{D,eq}}/P°)^d \cdots}{(P_{\text{A,eq}}/P°)^a\,(P_{\text{B,eq}}/P°)^b \cdots} = \frac{P^c_{\text{C,eq}}\,P^d_{\text{D,eq}} \cdots}{P^a_{\text{A,eq}}\,P^b_{\text{B,eq}} \cdots} \times \left(\frac{1}{P°}\right)^{\Delta\nu}$$

where $P° = 1$ bar and $\Delta\nu = (c + d + \cdots) - (a + b + \cdots)$ is the sum of coefficients for products minus the sum of coefficients for reactants. Let us define

$$K_P = \frac{P^c_{\text{C,eq}}\,P^d_{\text{D,eq}}}{P^a_{\text{A,eq}}\,P^b_{\text{B,eq}}} \qquad \textbf{(13.20)}$$

Notice that K_p has the same form as K, equation (13.19), except that partial pressures have taken the place of activities. Now, we can express K as

$$K = K_p \times (1/P°)^{\Delta\nu} \qquad \textbf{(13.21)}$$

In principle, when using equation (13.21), we can express the pressures in any pressure unit, but using a unit other than bar requires an extra calculation, that is, the evaluation of the factor $(1/P°)^{\Delta\nu}$. If we express pressures in bar, then this factor has a numerical value of 1. However, if we choose instead to express pressures in atmospheres (atm), then $P° = 1\text{ bar} = 1/1.01325\text{ atm}$ and $(1/P°)^{\Delta\nu}$ has a value of $(1/1.01325\text{ atm})^{\Delta\nu}$. This complication can be avoided entirely if we simply agree to express all pressures in bar and substitute their values *without units* into the expression for K_p. By doing so, we obtain the correct value of K without having to worry about units.

Reactions in Aqueous Solution. For a reaction that occurs in aqueous solution, the activities are expressed in terms of concentrations (page 611). For example, the activity of A(aq) is expressed as $a_A = [A]/c°$, where $c° = 1\text{ mol/L}$. We can write similar expressions for B(aq), C(aq), D(aq), etc. For a reaction in aqueous solution, equation (13.19) takes the form

$$K = K_c \times (1/c°)^{\Delta\nu} \qquad \textbf{(13.22)}$$

where, as before, $\Delta\nu = (c + d + \cdots) - (a + b + \cdots)$ and

$$K_c = \frac{[\text{C}]^c_{\text{eq}}\,[\text{D}]^d_{\text{eq}} \cdots}{[\text{A}]^a_{\text{eq}}\,[\text{B}]^b_{\text{eq}} \cdots} \qquad \textbf{(13.23)}$$

The factor $(1/c°)^{\Delta\nu}$ appearing in equation (13.22) has the unit $(\text{mol/L})^{-\Delta\nu}$. As discussed above for reactions involving gases, the issue of units can be avoided and the use of equation (13.23) simplified if we choose judiciously to express concentrations in mol/L and substitute their values *without units* into the expression for K_c.

Reactions in a Heterogeneous System. In the previous cases, the substances involved in the reaction were either all gases or all dissolved in aqueous solution. Those systems are *homogeneous* because all the substances are in the same phase and constitute a homogeneous mixture. As established in the previous discussion, for a reaction in a homogeneous system, the thermodynamic equilibrium constant, K, may expressed in terms of either K_p or K_c. This is not necessarily the case for a heterogeneous system, where the substances exist in different phases. To make this point clear, let us consider the following reaction which involves substances in a variety of different forms.

$$2\,\text{Al(s)} + 6\,\text{H}^+\text{(aq)} \rightleftharpoons 2\,\text{Al}^{3+}\text{(aq)} + 3\,\text{H}_2\text{(g)}$$

For this reaction, the equilibrium condition is

$$K = \frac{(a_{Al^{3+},eq})^2 (a_{H_2,eq})^3}{(a_{Al,eq})^2 (a_{H^+,eq})^6} \approx \frac{([Al^{3+}]_{eq}/c°)^2 (P_{H_2,eq}/P°)^3}{(1)^2 ([H^+]_{eq}/c°)^6}$$

$$= \frac{[Al^{3+}]^2_{eq} P^3_{H_2,eq}}{[H^+]^6_{eq}} \times (c°)^4 \times \left(\frac{1}{P°}\right)^3$$

That is, for reactions in heterogeneous systems, the thermodynamic equilibrium constant might involve both pressures and concentrations. In such cases, it is not appropriate to associate K with either K_p or K_c.

EXAMPLE 13-9 Writing Thermodynamic Equilibrium Constant Expressions

For the following reversible reactions, write thermodynamic equilibrium constant expressions, making appropriate substitutions for activities. Then relate K to K_c or K_p, where this can be done.

(a) The water gas reaction

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

(b) Formation of a saturated aqueous solution of lead(II) iodide, a very slightly soluble solute

$$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\,I^-(aq)$$

(c) Oxidation of sulfide ion by oxygen gas (used in removing sulfides from wastewater, as in pulp and paper mills)

$$O_2(g) + 2\,S^{2-}(aq) + 2\,H_2O(l) \rightleftharpoons 4\,OH^-(aq) + 2\,S(s)$$

Analyze

In each case, once we have made the appropriate substitutions for activities, if all factors in our expression are molarities, the thermodynamic equilibrium constant is easily related to K_c. If all factors are partial pressures, K is easily related to K_p. If both molarities *and* partial pressures appear in the expression, however, K is not related simply to K_c or K_p.

Solve

(a) The activity of solid carbon is 1. Activities of the gases are expressed in terms of partial pressures.

$$K = \frac{a_{CO(g)} a_{H_2(g)}}{a_{C(s)} a_{H_2O(g)}} = \frac{(P_{CO}/P°)(P_{H_2}/P°)}{(P_{H_2O}/P°)} = \frac{(P_{CO})(P_{H_2})}{(P_{H_2O})} \times \frac{1}{P°} = K_p \times \frac{1}{P°}$$

(b) The activity of solid lead(II) iodide is 1. Activities of the aqueous ions are expressed in terms of molarities.

$$K = \frac{a_{Pb^{2+}(aq)} a^2_{I^-(aq)}}{a_{PbI_2(s)}} = \left(\frac{[Pb^{2+}]}{c°}\right)\left(\frac{[I^-]}{c°}\right)^2 = [Pb^{2+}][I^-]^2 \times \left(\frac{1}{c°}\right)^3 = K_c \times \left(\frac{1}{c°}\right)^3$$

(c) The activity of both the solid sulfur and the liquid water is 1. The activities of $OH^-(aq)$ and $S^{2-}(aq)$ are expressed in terms of molarities and the activity of $O_2(g)$ is expressed in terms of partial pressure. Thus, the resulting K is neither a K_c nor a K_p.

$$K = \frac{a^4_{OH^-(aq)} a^2_{S(s)}}{a_{O_2(g)} a^2_{S^{2-}(aq)} a^2_{H_2O(l)}} = \frac{([OH^-]/c°)^4 (1)^2}{(P_{O_2}/P°)([S^{2-}]/c°)^2 (1)^2} = \frac{[OH^-]^4}{P_{O_2}[S^{2-}]^2} \times \left(\frac{1}{c°}\right)^2 \times P°$$

Assess

For each of the expressions given above, equilibrium values of activities, partial pressures, and molarities are implied. Also, these are thermodynamic equilibrium expressions since they are written in terms of their activities. The values of the thermodynamic equilibrium constant will be dimensionless. All the expressions given above for K include factors involving powers of $c°$ or $P°$. As described in the text (page 611), we can avoid the complication of having to evaluate these factors by judiciously choosing to express concentrations in mol/L and pressures in bar.

PRACTICE EXAMPLE A: Write thermodynamic equilibrium constant expressions for each of the following reactions. Relate these to K_c or K_p where appropriate.

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

(b) $Cl_2(g) + H_2O(l) \rightleftharpoons HOCl(aq) + H^+(aq) + Cl^-(aq)$

(continued)

PRACTICE EXAMPLE B: Write a thermodynamic equilibrium constant expression to represent the reaction of solid lead(II) sulfide with aqueous nitric acid to produce solid sulfur, a solution of lead(II) nitrate, and nitrogen monoxide gas. Base the expression on the balanced net ionic equation for the reaction.

We have now acquired all the tools with which to perform one of the most practical calculations of chemical thermodynamics: *determining the equilibrium constant for a reaction from tabulated data*. Example 13-10, which demonstrates this application, uses thermodynamic properties of ions in aqueous solution as well as of compounds. An important idea to note about the thermodynamic properties of ions is that they are relative to $H^+(aq)$, which, by convention, is assigned values of *zero* for $\Delta_f H^\circ$, $\Delta_f G^\circ$, and S°. This means that entropies listed for ions are not absolute entropies, as they are for compounds. Negative values of S° simply denote an entropy less than that of $H^+(aq)$.

EXAMPLE 13-10 Calculating the Equilibrium Constant of a Reaction from the Standard Gibbs Energy of Reaction

Determine the equilibrium constants K and K_c at 298.15 K for the dissolution of magnesium hydroxide in an acidic solution.

$$\mathrm{Mg(OH)_2(s)} + 2\,\mathrm{H^+(aq)} \rightleftharpoons \mathrm{Mg^{2+}(aq)} + 2\,\mathrm{H_2O(l)}$$

Analyze

The key to solving this problem is to find a value of $\Delta_r G^\circ$ and then to use the expression $\Delta_r G^\circ = -RT \ln K$.

Solve

We can obtain $\Delta_r G^\circ$ from standard Gibbs energies of formation listed in Appendix D. Note that because its value is zero, the term $\Delta_r G^\circ[\mathrm{H^+(aq)}]$ is not included.

$$\begin{aligned}\Delta_r G^\circ &= 2\,\Delta_r G^\circ[\mathrm{H_2O(l)}] + \Delta_r G^\circ[\mathrm{Mg^{2+}(aq)}] - \Delta_r G^\circ[\mathrm{Mg(OH)_2(s)}]\\ &= 2(-237.1\ \mathrm{kJ\ mol^{-1}}) + (-454.8\ \mathrm{kJ\ mol^{-1}}) - (-833.5\ \mathrm{kJ\ mol^{-1}})\end{aligned}$$

$$\Delta_r G^\circ = -RT\ln K = -95.5\ \mathrm{kJ\ mol^{-1}} = -95.5 \times 10^3\ \mathrm{J\ mol^{-1}}$$

Now solve for $\ln K$ and K.

$$\ln K = \frac{-\Delta_r G^\circ}{RT} = \frac{-(-95.5\times 10^3\ \mathrm{J\ mol^{-1}})}{8.3145\ \mathrm{J\ mol^{-1}\ K^{-1}} \times 298.15\ \mathrm{K}} = 38.5$$

$$K = e^{38.5} = 5 \times 10^{16}$$

The value of K obtained above is the thermodynamic equilibrium constant. Because the activities of both $\mathrm{Mg(OH)_2(s)}$ and $\mathrm{H_2O(l)}$ are 1, the expression for K may be written as

$$K = \frac{a_{\mathrm{Mg^{2+}(aq)}}\, a^2_{\mathrm{H_2O(l)}}}{a_{\mathrm{Mg(OH)_2(s)}}\, a^2_{\mathrm{H^+(aq)}}} = \frac{([\mathrm{Mg^{2+}}]/c^\circ)}{([\mathrm{H^+}]/c^\circ)^2} = \frac{[\mathrm{Mg^{2+}}]}{[\mathrm{H^+}]^2} \times c^\circ = K_c \times c^\circ$$

Therefore,

$$K_c = K \times \left(\frac{1}{c^\circ}\right) = 5 \times 10^{16} \times \left(\frac{1}{1\ \mathrm{M}}\right) = 5 \times 10^{16}\ \mathrm{M^{-1}}$$

Assess

Notice that the thermodynamic equilibrium constant is dimensionless (no units) and that although K_c has the same value as K, it has the unit $\mathrm{M^{-1}}$. Finally, because the activities of both $\mathrm{Mg(OH)_2(s)}$ and $\mathrm{H_2O(l)}$ are 1 and the activities of $\mathrm{Mg^{2+}(aq)}$ and $\mathrm{H^+(aq)}$ can be expressed in terms of molarities, we could have obtained the relationship between K and K_c directly by applying equation (13.22):

$$K = K_c \times \left(\frac{1}{c^\circ}\right)^{\Delta\nu} = K_c \times \left(\frac{1}{c^\circ}\right)^{1-2} = K_c \times \left(\frac{1}{c^\circ}\right)^{-1} = K_c \times c^\circ$$

PRACTICE EXAMPLE A: Determine the thermodynamic equilibrium constant at 298.15 K for $\mathrm{AgI(s)} \rightleftharpoons \mathrm{Ag^+(aq)} + \mathrm{I^-(aq)}$.

PRACTICE EXAMPLE B: What is the value of the thermodynamic equilibrium constant at 298.15 K for the reaction of solid manganese dioxide with HCl(aq) to give manganese(II) ion in solution and chlorine gas?

TABLE 13.7 Significance of the Magnitude of $\Delta_r G^\circ$ and K (at 298 K)

$\Delta_r G^\circ$	K	Significance
$+200\ \text{kJ mol}^{-1}$	9.1×10^{-36}	Equilibrium favors reactants
$+100$	3.0×10^{-18}	
$+50$	1.7×10^{-9}	
$+10$	1.8×10^{-2}	
$+1.0$	6.7×10^{-1}	Equilibrium calculation is necessary
0	1.0	
-1.0	1.5	
-10	5.6×10^{1}	
-50	5.8×10^{8}	Equilibrium favors products
-100	3.3×10^{17}	
-200	1.1×10^{35}	

Interpreting the Values of $\Delta_r G^\circ$ and K

By solving equation (13.17) for K, we see that the value of K is determined by the value of $\Delta_r G^\circ$.

$$K = e^{-\frac{\Delta_r G^\circ}{RT}}$$

The expression above can be used to calculate values of K at 298 K for different values of $\Delta_r G^\circ$. Several values are presented in Table 13.7. Notice that positive values of $\Delta_r G^\circ$ give values of K that are less than one, and the more positive the $\Delta_r G^\circ$ value, the smaller the value of K. Negative values of $\Delta_r G^\circ$ give values of K that are greater than one, and the more negative the $\Delta_r G^\circ$ value, the greater the value of K.

If we think of $\Delta_r G^\circ$ as providing a measure of the thermodynamic stability of products relative to reactants, then $\Delta_r G^\circ < 0$ means that products in their standard states are thermodynamically more stable than reactants in their standard states. Conversely, $\Delta_r G^\circ > 0$ means that products in their standard states are thermodynamically less stable than reactants in their standard states. Because the values of $\Delta_r G^\circ$ and K are related, K may also be considered a measure of the thermodynamic stability of products relative to reactants. A large value of K implies that products are thermodynamically more stable than reactants and, thus, equilibrium favors products. A small value of K implies that products are thermodynamically less stable than reactants and equilibrium favors reactants.

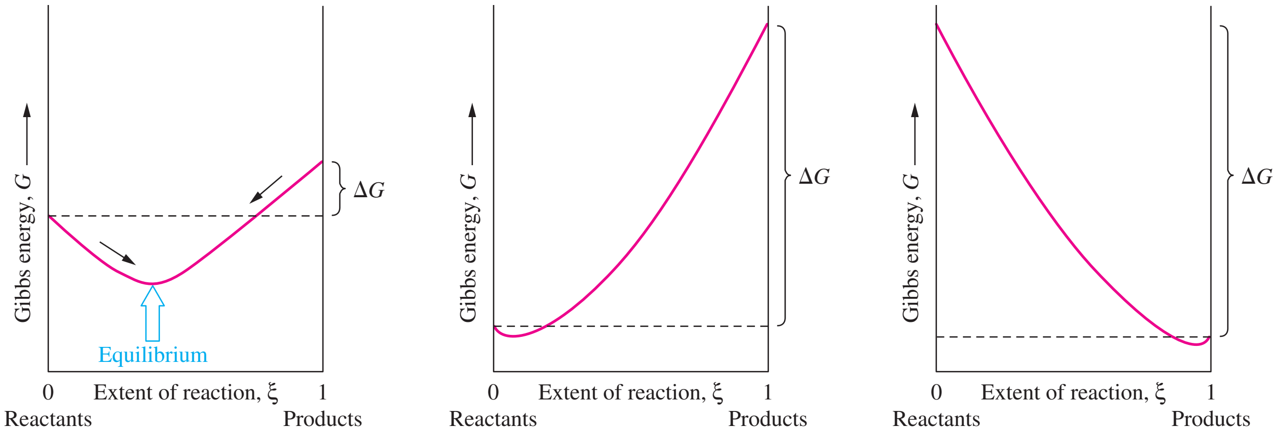
Let us explore in more detail how the Gibbs energy of a system changes with composition, with the intention of developing an understanding of how the position of equilibrium correlates with the magnitude of the equilibrium constant K. The graphs in Figure 13-9 are plots of G versus the extent of reaction, ξ, for three different situations: an intermediate value of K (Fig. 13-9a), a very small value of K (Fig. 13-9b), and a very large value of K (Fig. 13-9c). To interpret the graphs, it will be helpful to focus on the meaning of the magnitude of K. Without loss of generality, we can focus on the following gas-phase reaction

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

for which

$$K = \frac{P_{\text{C,eq}}^{c}\, P_{\text{D,eq}}^{d} \cdots}{P_{\text{A,eq}}^{a}\, P_{\text{B,eq}}^{b} \cdots} \times \left(\frac{1}{P^\circ}\right)^{\Delta\nu}$$

A small value of K suggests that the values of $P_{\text{C,eq}}$ and $P_{\text{D,eq}}$ are small compared with those of $P_{\text{A,eq}}$ and $P_{\text{B,eq}}$. If the values of $P_{\text{C,eq}}$ and $P_{\text{D,eq}}$ are small,



(a) K approximately equal to 1 **(b)** K much less than 1 **(c)** K much greater than 1

▲ FIGURE 13-9

The position of equilibrium for small, large, and intermediate values of K

Gibbs energy is plotted against the extent of reaction for a reaction $aA + bB \longrightarrow cC + dD$. For $\xi = 0$ mol, the system contains stoichiometric amounts of reactants (a mol A and b mol B) at a total pressure P. For $\xi = 1$ mol, the system contains stoichiometric amounts of products (c mol C and d mol D) at a total pressure P. As described in the text, $\Delta G = -1 \text{ mol} \times RT \ln K +$ constant. **(a)** When $K \approx 1$, the value of ΔG is small and the equilibrium position corresponds to having appreciable amounts of both reactants and products. **(b)** When $K \ll 1$, ΔG has a large, positive value and the equilibrium position corresponds to an equilibrium position closer to reactants (a small value of ξ). **(c)** When $K \gg 1$, ΔG has a large negative value and the equilibrium position corresponds to an equilibrium position closer to products (a larger value of ξ).

it is because the conversion of A and B to C and D has not occurred to an appreciable extent. Thus, a small value of K corresponds to an equilibrium position that is closer to reactants than to products, as suggested by Figure 13-9(b). Conversely, a large value of K corresponds to an equilibrium position that is closer to products (Fig. 13-9c). Between these two extremes, the equilibrium position corresponds to a situation in which appreciable amounts of both reactants and products are present (Fig. 13-9a). Figure 13-9 also illustrates that, from a theoretical standpoint, no chemical reaction goes totally to completion.

Figure 13-9 can also help us understand the relationship between ΔG and the value of K. When K is not too large or too small, ΔG is also relatively small (Fig. 13-9a). However, if K is very small, complete conversion of reactants to products would be accompanied by a very large increase in Gibbs energy (Fig. 13-9b). Finally, when K is very large, complete conversion of reactants to products would give a very large decrease in Gibbs energy.

Equation (13.17) shows that the value of K is related in a simple way to the value of $\Delta_r G°$. But what is the relationship between ΔG and K? To obtain an answer to this question, we refer to the diagram on page 609, which helped us establish the result

$$\Delta G = \Delta_r G° \times 1 \text{ mol} - \Delta G_{\text{mix},1} + \Delta G_{\text{mix},2}$$

In the expression above, $\Delta G_{\text{mix},1}$ represents the Gibbs energy changes for converting pure reactants, each at 1 bar, to a mixture of reactants at pressure P. Similarly, $\Delta G_{\text{mix},2}$ represents the Gibbs energy changes for converting pure products, each at 1 bar, to a mixture of products at pressure P. From equation (13.17), we have $\Delta_r G° = -RT \ln K$ and thus, we may write the expression above as

$$\Delta G = -RT \ln K - \Delta G_{\text{mix},1} + \Delta G_{\text{mix},2} = -RT \ln K + C$$

where $C = -\Delta G_{\text{mix},1} + \Delta G_{\text{mix},2}$ represents a constant, the value of which includes the effects of bringing pure reactants each at a pressure of 1 bar to a mixture of reactants with total pressure P, and of bringing pure products each at a pressure of 1 bar to a mixture of products with total pressure P. The expression above for ΔG suggests that (1) the larger the value of K, the more negative the value of ΔG and thus, the greater the decrease in G; and (2) the smaller the value of K, the more positive the value of ΔG and the greater the increase in G.

In summary,

- A large K value ($K \gg 1$) indicates that products in their standard states are thermodynamically more stable than reactants in their standard states and the equilibrium position is closer to products. Complete conversion of reactants to products would be accompanied by a large decrease in G.
- A small K value ($K \ll 1$) indicates that products in their standard states are thermodynamically less stable than reactants in their standard states and the equilibrium position is closer to reactants. Complete conversion of reactants to products would be accompanied by a large increase in G.
- When $K \approx 1$, the equilibrium position corresponds to having appreciable amounts of both reactants and products. Complete conversion of reactants to products would be accompanied by a relatively small change in G.

13-6 $\Delta_r G°$ and K as Functions of Temperature

In this section, we will describe how to use the value of $\Delta_r G°$ or K at one temperature to obtain their values at another temperature. In the method illustrated in Example 13-11, we assume that $\Delta_r H°$ and $\Delta_r S°$ are independent of temperature. Even with this assumption, $\Delta_r G° = \Delta_r H° - T\Delta_r S°$ is strongly temperature-dependent because the temperature factor, T, multiplies $\Delta_r S°$.

◀ The assumption that $\Delta_r H°$ and $\Delta_r S°$ are independent of temperature is valid provided that the heat capacity of the reacting system does not change substantially when stoichiometric amounts of pure reactants are converted completely into stoichiometric amounts of pure products.

EXAMPLE 13-11 Determining the Relationship Between an Equilibrium Constant and Temperature by Using Equations for Gibbs Energy of Reaction

At what temperature will the equilibrium constant for the formation of NOCl(g) be $K = 1.00 \times 10^3$? Data for this reaction at 25 °C are

$$2\,\text{NO(g)} + \text{Cl}_2\text{(g)} \rightleftharpoons 2\,\text{NOCl(g)} \quad \Delta_r G° = -40.9\ \text{kJ mol}^{-1} \quad \Delta_r H = -77.1\ \text{kJ mol}^{-1} \quad \Delta_r S° = -121.3\ \text{J mol}^{-1}\,\text{K}^{-1}$$

Analyze

To determine an unknown temperature from a known equilibrium constant, we need an equation in which both of these terms appear. The required equation is $\Delta_r G° = -RT \ln K$. However, to solve for the unknown temperature, we need the value of $\Delta_r G°$ at that temperature. We know the value of $\Delta_r G°$ at 25 °C (-40.9 kJ mol^{-1}), but we also know that this value will be different at other temperatures. We can assume, however, that the values of $\Delta_r H°$ and $\Delta_r S°$ will not change much with temperature. This means that we can obtain a value of $\Delta_r G°$ from the equation $\Delta_r G° = \Delta_r H° - T\Delta_r S°$, where T is the *unknown* temperature and the values of $\Delta_r H°$ and $\Delta_r S°$ are those at 25 °C. Now we have two equations that we can set equal to each other.

Solve

That is,

$$\Delta_r G° = \Delta_r H° - T\Delta_r S° = -RT \ln K$$

(continued)

We can gather the terms with T on the right,

$$\Delta_r H^\circ = T\Delta_r S^\circ - RT \ln K = T(\Delta_r S^\circ - R \ln K)$$

and solve for T.

$$T = \frac{\Delta_r H^\circ}{\Delta_r S^\circ - R \ln K}$$

Now substitute values for $\Delta_r H^\circ$, $\Delta_r S^\circ$, R, and $\ln K$.

$$\begin{aligned} T &= \frac{-77.1 \times 10^3 \text{ J mol}^{-1}}{-121.3 \text{ J mol}^{-1}\text{ K}^{-1} - [8.3145 \text{ J mol}^{-1}\text{ K}^{-1} \times \ln(1.00 \times 10^3)]} \\ &= \frac{-77.1 \times 10^3 \text{ J mol}^{-1}}{-121.3 \text{ J mol}^{-1}\text{ K}^{-1} - (8.3145 \times 6.908) \text{ J mol}^{-1}\text{ K}^{-1}} \\ &= \frac{-77.1 \times 10^3 \text{ J mol}^{-1}}{-178.7 \text{ J mol}^{-1}\text{ K}^{-1}} = 431 \text{ K} \end{aligned}$$

Assess

Although the answer shows three significant figures, the final result should probably be rounded to just two significant figures. The assumption we made about the constancy of $\Delta_r H^\circ$ and $\Delta_r S^\circ$ is probably no more valid than that.

PRACTICE EXAMPLE A: At what temperature will the formation of $NO_2(g)$ from NO(g) and $O_2(g)$ have $K_p = 1.50 \times 10^2$? For the reaction $2\,NO(g) + O_2(g) \rightleftharpoons 2\,NO_2(g)$ at 25 °C, $\Delta_r H^\circ = -114.1 \text{ kJ mol}^{-1}$ and $\Delta_r S^\circ = -146.5 \text{ J mol}^{-1}\text{K}^{-1}$.

PRACTICE EXAMPLE B: For the reaction $2\,NO(g) + Cl_2(g) \rightleftharpoons 2\,NOCl(g)$, what is the value of K at **(a)** 25 °C; **(b)** 75 °C? Use data from Example 13-11.

An alternative to the method outlined in Example 13-11 is to relate the equilibrium constant and temperature directly, without specific reference to a Gibbs energy change. We start with the same two expressions as in Example 13-11

$$-RT \ln K = \Delta_r G^\circ = \Delta_r H^\circ - T\,\Delta_r S^\circ$$

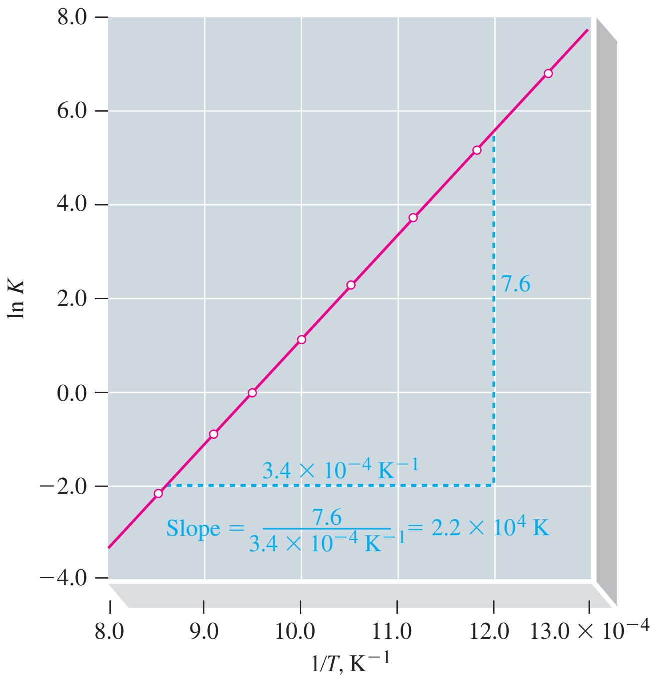
and divide by $-RT$

$$\ln K = \frac{-\Delta_r H^\circ}{RT} + \frac{\Delta_r S^\circ}{R} \qquad \textbf{(13.24)}$$

If we assume that $\Delta_r H^\circ$ and $\Delta_r S^\circ$ are constant, equation (13.24) implies that a plot of $\ln K$ versus $1/T$ is a straight line with a slope of $-\Delta_r H^\circ/R$ and a y-intercept of $\Delta_r S^\circ/R$. Table 13.8 lists equilibrium constants as a function of the

TABLE 13.8 Equilibrium Constants, K, for the Reaction $2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$ at Several Temperatures

T, K	$1/T$, K^{-1}	K	ln K
800	12.5×10^{-4}	9.1×10^2	6.81
850	11.8×10^{-4}	1.7×10^2	5.14
900	11.1×10^{-4}	4.2×10^1	3.74
950	10.5×10^{-4}	1.0×10^1	2.30
1000	10.0×10^{-4}	3.2×10^0	1.16
1050	9.52×10^{-4}	1.0×10^0	0.00
1100	9.09×10^{-4}	3.9×10^{-1}	−0.94
1170	8.5×10^{-4}	1.2×10^{-1}	−2.12



◀ FIGURE 13-10
Temperature dependence of the equilibrium constant K for the reaction

$$2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$$

This graph can be used to establish the enthalpy of reaction, $\Delta_r H°$ (see equation 13.25).

$$\begin{aligned} \text{slope} &= -\Delta_r H°/R = 2.2 \times 10^4\ \text{K} \\ \Delta_r H° &= -8.3145\ \text{J mol}^{-1}\ \text{K}^{-1} \times 2.2 \times 10^4\ \text{K} \\ &= -1.8 \times 10^5\ \text{J mol}^{-1} \\ &= -1.8 \times 10^2\ \text{kJ mol}^{-1} \end{aligned}$$

reciprocal of Kelvin temperature for the reaction of $SO_2(g)$ and $O_2(g)$ that forms $SO_3(g)$. The ln K and $1/T$ data from Table 13.8 are plotted in Figure 13-10 and yield the expected straight line.

Now we can follow the procedure used in Appendix A-4 to derive the Clausius–Clapeyron equation. We can write equation (13.24) twice, for two different temperatures and with the corresponding equilibrium constants. Then, if we subtract one equation from the other, we obtain the result shown here,

$$\ln \frac{K_2}{K_1} = -\frac{\Delta_r H°}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{13.25}$$

where T_2 and T_1 are two Kelvin temperatures; K_2 and K_1 are the equilibrium constants at those temperatures; $\Delta_r H°$ is the enthalpy of reaction, expressed in J mol^{-1}; and R is the gas constant, expressed as 8.3145 J mol^{-1} K^{-1}. Jacobus van't Hoff (1852–1911) derived equation (13.25), which is often referred to as *the van't Hoff equation.*

◀ For endothermic reactions, K increases as T increases whereas for exothermic reactions, K decreases as T increases. You can verify this through equation (13.25) by setting $T_1 = 100$ K, $T_2 = 1000$ K and $K_1 = 1$ and solving for K_2, first with $\Delta_r H° = +1.0 \times 10^5$ J mol^{-1} and then with $\Delta_r H° = -1.0 \times 10^5$ J mol^{-1}.

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that the Clausius–Clapeyron equation (12.2) is just a special case of equation (13.25) in which the equilibrium constants are equilibrium vapor pressures and $\Delta_r H° = \Delta_{vap} H°$.

EXAMPLE 13-12 Relating Equilibrium Constants and Temperature Through the van't Hoff Equation

Use data from Table 13.8 and Figure 13-10 to estimate the temperature at which $K = 1.0 \times 10^6$ for the reaction

$$2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$$

Analyze

By consulting Table 13.8, we see that $K = 9.1 \times 10^2$ at 800 K for this reaction and the value of K increases as T decreases. Thus, the value of K will be equal to 1.0×10^6 at a temperature lower than 800 K. To find this temperature, we can use equation (13.25) with $T_1 = ?$ K, $K_1 = 1.0 \times 10^6$, $T_2 = 800$ K, $K_2 = 9.1 \times 10^2$, and $\Delta_r H° = -1.8 \times 10^5$ J mol^{-1} (from Figure 13-10). We expect $T_1 < T_2$.

(continued)

Solve

We substitute $K_1 = 1.0 \times 10^6$, $T_2 = 800$ K, $K_2 = 9.1 \times 10^2$, and $\Delta_r H° = -1.8 \times 10^5$ J mol^{-1} into equation (13.25) and solve for T_1.

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta_r H°}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{9.1 \times 10^2}{1 \times 10^6}\right) = -\frac{(-1.8 \times 10^5\,\text{J mol}^{-1})}{8.3145\,\text{J mol}^{-1}\,\text{K}^{-1}}\left(\frac{1}{800\,\text{K}} - \frac{1}{T_1}\right)$$

$$-7.00 = 2.2 \times 10^4\,\text{K}\left(\frac{1}{800\,\text{K}} - \frac{1}{T_1}\right)$$

$$\frac{-7.00}{2.2 \times 10^4\,\text{K}} = \frac{1}{800\,\text{K}} - \frac{1}{T_1}$$

$$\frac{1}{T_1} = \frac{1}{800\,\text{K}} + \frac{-7.00}{2.2 \times 10^4\,\text{K}}$$

$$\frac{1}{T_1} = (1.25 \times 10^{-5}\,\text{K}^{-1}) + (3.2 \times 10^{-4}\,\text{K}^{-1}) = 1.57 \times 10^{-3}\,\text{K}^{-1}$$

$$T_1 = \frac{1}{1.57 \times 10^{-3}\,\text{K}^{-1}} = 637\,\text{K}$$

Assess

A common error in this type of problem is the use of incorrect temperature units. It should be Kelvin (K).

PRACTICE EXAMPLE A: Estimate the temperature at which $K = 5.8 \times 10^{-2}$ for the reaction in Example 13-12. Use data from Table 13.8 and Figure 13-10.

PRACTICE EXAMPLE B: What is the value of K_p for the reaction $2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$ at 235 °C? Use data from Table 13.8, Figure 13-10, and the van't Hoff equation (13.25).

13-7 Coupled Reactions

We have seen two ways to obtain product from a nonspontaneous reaction: (1) change the reaction conditions to ones that make the reaction spontaneous (mostly by changing the temperature), and (2) combine a pair of reactions, one with a positive $\Delta_r G$ and one with a negative $\Delta_r G$, to obtain a spontaneous overall reaction. Such paired reactions are called **coupled reactions**. Consider the extraction of a metal from its oxide.

When copper(I) oxide is heated to 673 K, no copper metal is obtained. The decomposition of Cu_2O to form products in their standard states (for instance, $P_{O_2} = 1.00$ bar) is nonspontaneous at 673 K.

▶ In general chemistry, simple examples of reactions are generally used. In fact, in almost all interesting cases, one reaction is coupled to another, and so forth. No better example exists than the complex cycles of coupled chemical reactions in biological processes.

$$Cu_2O(s) \xrightarrow{\Delta} 2\,Cu(s) + \frac{1}{2}O_2(g) \qquad \Delta_r G°_{673\,\text{K}} = +125\ \text{kJ mol}^{-1} \tag{13.26}$$

Suppose this nonspontaneous decomposition reaction is coupled with the partial oxidation of carbon to carbon monoxide—a spontaneous reaction. The overall reaction (13.27) is spontaneous when reactants and products are in their standard states because $\Delta_r G°$ has a negative value.

$$\begin{aligned}
Cu_2O(s) &\longrightarrow 2\,Cu(s) + \cancel{\tfrac{1}{2}O_2(g)} && \Delta_r G°_{673\,\text{K}} = +125\ \text{kJ mol}^{-1}\\
C(s) + \cancel{\tfrac{1}{2}O_2(g)} &\longrightarrow CO(g) && \Delta_r G°_{673\,\text{K}} = -175\ \text{kJ mol}^{-1}\\
Cu_2O(s) + C(s) &\longrightarrow 2\,Cu(s) + CO(g) && \Delta_r G°_{673\,\text{K}} = -50\ \text{kJ mol}^{-1} \qquad (13.27)
\end{aligned}$$

Note that reactions (13.26) and (13.27) are not the same, even though each has Cu(s) as a product. The purpose of coupled reactions, then, is to produce a spontaneous overall reaction by combining two other processes: one nonspontaneous and one spontaneous. Many metallurgical processes employ coupled reactions, especially those that use carbon or hydrogen as reducing agents.

To sustain life, organisms must synthesize complex molecules from simpler ones. If carried out as single-step reactions, these syntheses would generally be accompanied by increases in enthalpy, decreases in entropy, and increases in Gibbs energy—in short, they would be nonspontaneous and would not occur. In living organisms, changes in temperature and electrolysis are not viable options for dealing with nonspontaneous processes. Here, coupled reactions are crucial. See Focus On 13-1 on the MasteringChemistry website for an example.

13-8 Chemical Potential and Thermodynamics of Spontaneous Chemical Change

In this section, we focus on deriving equation (13.15), the equation that is used to predict the direction of spontaneous change in a system that undergoes a change in composition at constant T and constant P. Perhaps surprisingly, the concepts we need to derive equation (13.15) find their origin in an equation that describes how the Gibbs energy of an ideal gas depends on temperature, pressure, and the amount, n. The equation obtained for an ideal gas can be generalized to all substances by introducing the concepts of chemical potential and activity, arguably two of the most important concepts in chemical thermodynamics. As we will see, the concepts of chemical potential and activity are intertwined; it is nearly impossible to speak of one without reference to the other. However, they are precisely what we need to describe the Gibbs energy change for a system undergoing a change in composition at constant T and constant P.

Gibbs Energy of an Ideal Gas

To begin, consider the following the isothermal process for an ideal gas, X.

$$\mathrm{X}(\mathrm{g}, T, P^\circ = 1\ \mathrm{bar}) \longrightarrow \mathrm{X}(\mathrm{g}, T, P)$$

In this process, the pressure of the gas is changed isothermally from 1 bar to a final pressure P. Because T is constant, we can write $\Delta G = \Delta H - T\Delta S$ for this process. Recall that $\Delta H = 0$ for an isothermal process involving an ideal gas (page 583) and so we have $\Delta G = -T\Delta S$. Using equation (13.7) for ΔS with $P_\mathrm{f} = P$ and $P_\mathrm{i} = P^\circ$, we obtain

$$\Delta G = nRT \ln\left(\frac{P}{P^\circ}\right)$$

If we use the symbols G° and G to represent the Gibbs energy of the gas in the initial and final states, respectively, we have $\Delta G = G - G^\circ$ and we can express the equation above in the form

$$G = G^\circ + nRT \ln\left(\frac{P}{P^\circ}\right) \tag{13.28}$$

This equation shows how the Gibbs energy of an ideal gas changes with pressure at constant temperature. If we divide all terms by n, we obtain

$$G_\mathrm{m} = G^\circ_\mathrm{m} + RT \ln\left(\frac{P}{P^\circ}\right) \tag{13.29}$$

where $G_\mathrm{m} = G/n$ and $G^\circ_\mathrm{m} = G^\circ/n$ are the molar Gibbs energies (Gibbs energy per mole) for, respectively, the gas at T and P and the gas at T and 1 bar. Both quantities have the unit J mol^{-1}.

Gibbs Energy of an Ideal Gas Mixture

Let's now consider a mixture containing several ideal gases A(g), B(g), C(g), etc. If the amounts of these gases are denoted by n_A, n_B, n_C, etc., then the Gibbs energy of the mixture is

$$G = n_A G_{m,A} + n_B G_{m,B} + n_C G_{m,C} + \cdots \qquad \textbf{(13.30)}$$

where $G_{m,A}$, $G_{m,B}$, $G_{m,C}$, etc. are the molar Gibbs energies of the gases, each of which has the form given by equation (13.29) with P replaced by the appropriate partial pressure P_A, P_B, P_C, etc. We now ask, what is the change in Gibbs energy for the system if the amount of A(g) is changed by an amount Δn_A without changing the amounts of the other gases? The Gibbs energy change is

$$\begin{aligned}\Delta G &= G_f - G_i \\ &= [(n_A + \Delta n_A)G_{m,A} + n_B G_{m,B} + n_C G_{m,C} + \cdots] \\ &\quad - [n_A G_{m,A} + n_B G_{m,B} + n_C G_{m,C} + \cdots] \\ &= G_{m,A}\Delta n_A\end{aligned}$$

Notice that ΔG for the system is directly proportional to Δn_A, with $G_{m,A}$ providing the link between these two quantities. Thus, for an ideal gas mixture, the molar Gibbs energy $G_{m,A}$ allows us to relate the change in Gibbs energy to a change in the amount of gas A.

Chemical Potential and Activity

Gilbert N. Lewis, a leader in the development of thermodynamics, recognized that equation (13.29) could be generalized so that it applies to any substance (solid, liquid, gas, dissolved solute, etc.) by writing

$$\mu = \mu^\circ + RT \ln a \qquad \textbf{(13.31)}$$

Through this expression, Lewis introduced not only the concept of chemical potential, represented by the symbol μ (Greek letter mu), but also the concept of activity, represented by the symbol a. The quantity μ is the chemical potential of the substance for the given conditions of T and P, whereas μ° is the chemical potential of the substance in a well-defined reference state at temperature T and a pressure of 1 bar. By comparing equations (13.29) and (13.31), we see that, for an ideal gas, $\mu = G_m$, $\mu^\circ = G^\circ{}_m$ and $a = P/P^\circ$. That is, for an ideal gas, the chemical potential is simply the molar Gibbs energy and the activity is P/P°.

Equation (13.30) can also be expressed more generally by writing

$$G = n_A\mu_A + n_B\mu_B + n_C\mu_C + \cdots \qquad \textbf{(13.32)}$$

This equation relates the Gibbs energy of a mixture of substances to the amounts and chemical potentials of those substances. As argued above for $G_{m,A}$, the chemical potential μ_A relates the change in G to a change in the amount of substance A.

Let us explore the concept of chemical potential a little further. The **chemical potential, μ**, of a substance refers to its ability or potential to change the Gibbs energy of the system. If a substance has a high chemical potential, it means that a small change in the amount of that substance will cause a relatively large change in the Gibbs energy of the system. On the other hand, if the chemical potential is low, then even a large change in amount produces only a small change in the Gibbs energy. More precisely, when the amount of substance A in a system is changed by an infinitesimally small amount dn_A, the corresponding change in Gibbs energy is

$$\begin{aligned}dG &= G_f - G_i \\ &= [(n_A + dn_A)\mu_A + n_B\mu_B + n_C\mu_C + \cdots] - [n_A\mu_A + n_B\mu_B + n_C\mu_C + \cdots]\end{aligned}$$

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that dn_A represents an infinitesimally small change in the amount of substance A.

which simplifies to

$$dG = \mu_A dn_A \tag{13.33}$$

Equation (13.33) shows that the change in Gibbs energy is directly proportional to the change in amount of A; the constant of proportionality is μ_A, the chemical potential of A. We may also think of μ_A as the rate of change of G with respect to the amount of substance A. For example, if the chemical potential of a substance A in a system is constant and equal to $\mu_A = 10\ \text{J mol}^{-1}$, then increasing the amount of that substance by 0.01 mol causes the Gibbs energy of the system to increase by approximately $10\ \text{J mol}^{-1} \times 0.01\ \text{mol} = 0.1\ \text{J}$. (This calculation is approximate because 0.01 mol is not infinitesimally small.)

With the chemical potential, μ, of a substance expressed in the form of equation (13.31), $\mu = \mu^\circ + RT \ln a$, we can see that as the activity a increases, then so too does the chemical potential. This, in essence, is the meaning of activity: a direct measure of the chemical potential of a substance and, therefore, of the ability or potential of a substance to change the Gibbs energy of a system. The greater the activity, the greater the chemical potential and the greater the ability of that substance to change the Gibbs energy of the system.

We must emphasize that the concept of activity was introduced by Lewis for a rather simple reason: to ensure that the chemical potential of a substance always has the form given by equation (13.31). To ensure that this is so, activities of various substances must be defined as described on page 611.

Can we say more about what the activity of a substance might represent? Not really, but we can say a little about what it does not represent. The activity of a substance is sometimes described as an “effective pressure” or an “effective concentration,” but such vague descriptions are not at all illuminating and are somewhat misleading because these terms incorrectly suggest that (1) activity is designed to provide a different or better measure of pressure or concentration, and (2) activities have the unit of pressure or concentration when in fact they are dimensionless quantities. So, it is not particularly helpful to think of activity as an effective pressure or an effective concentration. It is much better to think of pressure and concentration as providing a measure of activity.

The significance of the concept of chemical potential cannot be overstated. For example, a recurring theme in thermodynamics is that a substance moves spontaneously from a region of high chemical potential to a region of low chemical potential. Typically, the spontaneity of physical and chemical changes may be explained with reference to not only entropy changes but also differences in chemical potentials.

Our interest in chemical potentials (and activities) arises from the fact that the Gibbs energy of a mixture can be expressed in terms of the amounts of the substances and their chemical potentials, as shown by equations (13.31) and (13.32). These two equations, and the second law of thermodynamics, can be used to develop the criterion for predicting the direction of spontaneous chemical change.

Expressing $\Delta_r G^\circ$ in Terms of Chemical Potentials

Although the standard Gibbs energy of reaction, $\Delta_r G^\circ$, is usually expressed in terms of $\Delta_f G^\circ$ values, as shown by equation (13.14), it is also possible to express it in terms of the chemical potentials of the substances involved. To see how this is done, consider the following change in composition.

<u>Initial State</u>	<u>Final State</u>
Pure A at 1 bar, $n_A = a$ mol	Pure C at 1 bar, $n_C = c$ mol
Pure B at 1 bar, $n_B = b$ mol	Pure D at 1 bar, $n_D = d$ mol
$G_i = n_A\mu_A^\circ + n_B\mu_B^\circ$	$G_f = n_C\mu_C^\circ + n_D\mu_D^\circ$

The change in Gibbs energy is

$$\begin{aligned}\Delta G &= G_{\mathrm{f}} - G_{\mathrm{i}}\\ &= [(c\ \mathrm{mol})\mu_{\mathrm{C}}^{\circ} + (d\ \mathrm{mol})\mu_{\mathrm{D}}^{\circ} + \cdots] - [(a\ \mathrm{mol})\mu_{\mathrm{A}}^{\circ} + (b\ \mathrm{mol})\mu_{\mathrm{B}}^{\circ} + \cdots]\\ &= \{[c\,\mu_{\mathrm{C}}^{\circ} + d\,\mu_{\mathrm{D}}^{\circ} + \cdots] - [a\,\mu_{\mathrm{A}}^{\circ} + b\,\mu_{\mathrm{B}}^{\circ} + \cdots]\} \times 1\ \mathrm{mol}\end{aligned}$$

Since $\Delta_{\mathrm{r}}G^{\circ}$ is the Gibbs energy change *per mole*, we have $\Delta_{\mathrm{r}}G^{\circ} = \Delta G/(1\ \mathrm{mol})$ and thus,

$$\Delta_{\mathrm{r}}G^{\circ} = \underbrace{[c\,\mu_{\mathrm{C}}^{\circ} + d\,\mu_{\mathrm{D}}^{\circ} + \cdots]}_{\text{Weighted sum of } \mu^{\circ} \text{ values for products}} - \underbrace{[a\,\mu_{\mathrm{A}}^{\circ} + b\,\mu_{\mathrm{B}}^{\circ} + \cdots]}_{\text{Weighted sum of } \mu^{\circ} \text{ values for reactants}} \qquad \mathbf{(13.34)}$$

The chemical potentials have the unit J mol^{-1} and the coefficients *a*, *b*, *c*, and *d* are simply numbers (no units). Again, we see that $\Delta_{\mathrm{r}}G^{\circ}$ has the unit J mol^{-1}. We will encounter this last expression for $\Delta_{\mathrm{r}}G^{\circ}$ again.

Criterion for Predicting the Direction of Spontaneous Chemical Change

In Section 13-4, we established that, for a spontaneous process at constant T and constant P, the Gibbs energy of the system always decreases: $(\Delta G)_{T,P} < 0$. This idea can also be expressed as $(dG)_{T,P} < 0$, for a system that undergoes a spontaneous change that is infinitesimally small. We will find this second expression the most useful for developing an equation that can be used for predicting the direction of spontaneous change in a system in which a chemical reaction occurs.

Consider a system containing substances A, B, C, and D, and let n_{A}, n_{B}, n_{C}, and n_{D} represent the initial amounts, in moles, of each substance. Suppose that the composition of the system changes, at constant T and constant P, because the following reaction advances by an infinitesimal amount, $d\xi$. The changes occurring in the system are summarized below.

	$a\,\mathrm{A}$	+	$b\,\mathrm{B}$	$\underset{d\xi < 0}{\overset{d\xi > 0}{\rightleftharpoons}}$	$c\,\mathrm{C}$	+	$d\,\mathrm{D}$	
Initial:	n_{A}		n_{B}		n_{C}		n_{D}	G_{i}
Change:	$-a\,d\xi$		$-b\,d\xi$		$+c\,d\xi$		$+d\,d\xi$	$+dG$
Final:	$n_{\mathrm{A}} - a\,d\xi$		$n_{\mathrm{B}} - b\,d\xi$		$n_{\mathrm{C}} + c\,d\xi$		$n_{\mathrm{D}} + d\,d\xi$	$G_{\mathrm{f}} = G_{\mathrm{i}} + dG$

We have arrows pointing to the left and to the right because we want to consider the effect on G of a change in composition arising from reaction toward the right ($\longrightarrow$) or toward the left ($\longleftarrow$). The sign of $d\xi$ determines the direction of reaction: A positive value ($d\xi > 0$) describes reaction from left to right whereas a negative value ($d\xi < 0$) describes reaction from right to left. As suggested by the summary above, an infinitesimally small change in composition, represented by $d\xi$, causes an infinitesimally small change, dG, in the Gibbs energy of the system. We can use equation (13.30) to write expressions for G_{f} and G_{i}, and thus relate the change, dG, in Gibbs energy to the chemical potentials of A, B, C, and D:

$$\begin{aligned}dG &= G_{\mathrm{f}} - G_{\mathrm{i}}\\ &= [(n_{\mathrm{A}} - ad\xi)\mu_{\mathrm{A}} + (n_{\mathrm{B}} - bd\xi)\mu_{\mathrm{B}} + (n_{\mathrm{C}} + cd\xi)\mu_{\mathrm{C}} + (n_{\mathrm{D}} + dd\xi)\mu_{\mathrm{D}}]\\ &\quad - [n_{\mathrm{A}}\mu_{\mathrm{A}} + n_{\mathrm{B}}\mu_{\mathrm{B}} + n_{\mathrm{C}}\mu_{\mathrm{C}} + n_{\mathrm{D}}\mu_{\mathrm{D}}]\\ &= -a\mu_{\mathrm{A}}d\xi - b\mu_{\mathrm{B}}d\xi + c\mu_{\mathrm{C}}d\xi + d\mu_{\mathrm{D}}d\xi\\ &= [-a\mu_{\mathrm{A}} - b\mu_{\mathrm{B}} + c\mu_{\mathrm{C}} + d\mu_{\mathrm{D}}]d\xi\\ &= [(c\mu_{\mathrm{C}} + d\mu_{\mathrm{D}}) - (a\mu_{\mathrm{A}} + b\mu_{\mathrm{B}})]d\xi\end{aligned}$$

TABLE 13.9 Using the Expression $dG = \Delta_r G \times d\xi \leq 0$

$\Delta_r G$	$d\xi$	dG	Conclusion
+	+	+	The forward reaction is nonspontaneous.
+	–	–	The reverse reaction is spontaneous.
–	+	–	The forward reaction is spontaneous.
–	–	+	The reverse reaction is nonspontaneous.
0	+ or –	0	The system has reached equilibrium.

The quantity in square brackets has a form similar to that given in equation (13.34) for $\Delta_r G°$, except that it refers to nonstandard conditions. Therefore, let's represent the quantity in square brackets by the symbol $\Delta_r G$. Thus, we have

$$dG = \Delta_r G \times d\xi \qquad \textbf{(13.35)}$$

where

$$\Delta_r G = (c\mu_C + d\mu_D) - (a\mu_A + b\mu_B) \qquad \textbf{(13.36)}$$

We see immediately that $\Delta_r G$ has the unit J mol^{-1}. (The unit of $\Delta_r G$ can be established by considering the units of dG and $d\xi$, or by remembering that the chemical potentials themselves have the unit J mol^{-1}.)

Equation (13.35) is the key to predicting the direction of spontaneous change, so we must be certain to interpret it properly. It shows clearly that if $\Delta_r G < 0$, then we must have reaction occurring in the forward direction ($d\xi > 0$) to ensure that G decreases ($dG < 0$), as required by the second law. On the other hand, if $\Delta_r G > 0$, then we must have reaction occurring in the reverse direction ($d\xi < 0$) to ensure that G decreases. Table 13.9 summarizes the various possibilities.

The task that remains is to obtain an expression for $\Delta_r G$, and we do this by writing the chemical potentials for A, B, C, and D in the form of equation (13.31). For example, the chemical potential of A is

$$\mu_A = \mu_A^\circ + RT \ln a_A$$

Similar expressions hold for μ_B, μ_C, and μ_D. Thus, we may write equation (13.36) as

$$\begin{aligned}
\Delta_r G &= (c\mu_C + d\mu_D) - (a\mu_A + b\mu_B)\\
&= c(\mu_C^\circ + RT \ln a_C) + d(\mu_D^\circ + RT \ln a_D) - [a(\mu_A^\circ + RT \ln a_A) + b(\mu_B^\circ + RT \ln a_B)]\\
&= c\mu_C^\circ + d\mu_D^\circ - (a\mu_A^\circ + b\mu_B^\circ) + cRT \ln a_C + dRT \ln a_D - aRT \ln a_A - bRT \ln a_B\\
&= c\mu_C^\circ + d\mu_D^\circ - (a\mu_A^\circ + b\mu_B^\circ) + RT \ln a_C^c + RT \ln a_D^d - RT \ln a_A^a - RT \ln a_B^b\\
&= c\mu_C^\circ + d\mu_D^\circ - (a\mu_A^\circ + b\mu_B^\circ) + RT \ln\left(\frac{a_C^c\, a_D^d}{a_A^a\, a_B^b}\right)\\
&= \Delta_r G^\circ + RT \ln\left(\frac{a_C^c\, a_D^d}{a_A^a\, a_B^b}\right)
\end{aligned}$$

In the last step, we have made use of the fact that $\Delta_r G^\circ = c\mu_C^\circ + d\mu_D^\circ - (a\mu_A^\circ + b\mu_B^\circ)$ because, shown by equation (13.34), $\Delta_r G^\circ$ can be expressed in terms of standard chemical potentials. The quotient in the logarithmic term is the general form of the thermodynamic reaction quotient, Q. Thus, we can write the equation above in its most general form as

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q$$

The relationship above is equation (13.15), which is what we set out to derive.

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Adenosine triphosphate (ATP) is the energy currency used in nature to drive reactions. The conversion of adenosine diphosphate (ADP) to ATP is a nonspontaneous process. For a discussion of how nature is able to convert ADP to ATP, go to the Focus On feature for Chapter 13, Coupled Reactions in Biological Systems, on the MasteringChemistry site.

Summary

13-1 Entropy: Boltzmann's View—**Entropy, S**, is a thermodynamic property that is related to the way in which the energy of a system is distributed among the available energy levels. A **microstate** is a specific microscopic configuration describing how the particles of a system are distributed among the available energy levels. Boltzmann's formula for entropy (equation 13.1) indicates that entropy is proportional to ln W, where W is the number of microstates and, therefore, Boltzmann's formula provides the basis for a microscopic view of entropy. For example, the spontaneous expansion of ideal gases involves an increase in entropy that can be rationalized in terms of an increase in the number of accessible energy levels and an increase in the number of microstates.

13-2 Entropy Changes: Clausius's View—Clausius, using macroscopic observations, proposed that the entropy change for a process can be related to the amount of heat transferred divided by the temperature (equation 13.2), provided the process is imagined to occur in a reversible way. Consequently, an entropy change, ΔS, has the unit $\mathrm{J\,K^{-1}}$. Clausius's formula can be used to obtain expressions for calculating entropy changes for a variety of physical changes, including phase transitions, constant pressure heating or cooling, or the isothermal expansion or compression of an ideal gas. Table 13.1 summarizes formulas for calculating entropy changes for these different processes.

13-3 Combining Boltzmann's and Clausius's Ideas: Absolute Entropies—A statement of the **third law of thermodynamics** is that the entropy of a pure perfect crystal at 0 K is zero. Thus, we can assign a specific (absolute) value to the entropy of a pure substance. This is in marked contrast to the situation for other thermodynamic properties, such internal energy and enthalpy, for which absolute values cannot be assigned. The absolute entropy of one mole of substance in its standard state is called the **standard molar entropy, S°**. Standard molar entropies of reactants and products can be used to calculate the **standard reaction entropy, $\Delta_r S^\circ$** (equation 13.9).

13-4 Criterion for Spontaneous Change: The Second Law of Thermodynamics—The basic criterion for spontaneous change is that the entropy change of the universe, which is the sum of the entropy change of the system plus that of the surroundings (equation 13.11), must be greater than zero (equation 13.10). This statement is known as the **second law of thermodynamics.** An equivalent criterion applied to the system alone is based on a thermodynamic function known as the **Gibbs energy, G**. For an isothermal process, the **Gibbs energy change, $\Delta_r G$**, is the enthalpy change for the system (ΔH) minus the product of the temperature and entropy change for the system ($T\Delta S$) (equation 13.13). Table 13.3 summarizes the criteria for spontaneous change based on Gibbs energy change.

13-5 Gibbs Energy of a System of Variable Composition: $\Delta_r G^\circ$ and $\Delta_r G$—The **standard Gibbs energy of reaction, $\Delta_r G^\circ$**, is based on the conversion of stoichiometric amounts of reactants in their standard states to stoichiometric amounts of products in their standard states. Values of $\Delta_r G^\circ$ are often calculated from tabulated values of **standard Gibbs energies of formation**, $\Delta_f G^\circ$ at 298.15 K (equation 13.14). For nonstandard conditions, the **Gibbs energy of reaction, $\Delta_r G$**, is equal to $\Delta_r G^\circ$ plus $RT \ln Q$ (equation 13.15) where Q, the **reaction quotient**, takes account of the initial (nonstandard) conditions. The value of $\Delta_r G$ can be used to predict the direction of spontaneous chemical change as described in Table 13.4. The relationship between the standard Gibbs energy change and the **equilibrium constant** for a reaction is $\Delta_r G^\circ = -RT \ln K$ (equation 13.17). The constant, K, is the value of the reaction quotient Q at equilibrium and is called the **thermodynamic equilibrium constant** (equation 13.19). Both Q and K are expressed in terms of the activities of reactants and products (equations 13.16 and 13.19). The activities can be related to molarities and gas partial pressures by means of a few simple conventions (Table 13.5). The direction of spontaneous chemical change can also be predicted by comparing the values of Q and K (Table 13.6).

13-6 $\Delta_r G^\circ$ and K as Functions of Temperature—By starting with the relationship between standard Gibbs energy change and the equilibrium constant, the van't Hoff equation—relating the equilibrium constant and temperature—can be written (equation 13.25). With this equation, tabulated data at 25 °C can be used to determine equilibrium constants not just at 25 °C but at other temperatures as well.

13-7 Coupled Reactions—Nonspontaneous processes can be made spontaneous by coupling them with spontaneous reactions and by taking advantage of the state function property of G. **Coupled reactions**, that is, paired reactions that yield a spontaneous overall reaction, occur in metallurgical processes and in biochemical transformations.

13-8 Chemical Potential and Thermodynamics of Spontaneous Chemical Change—G. N. Lewis introduced the concept of chemical potential, represented by the symbol μ and the concept of activity, represented by the symbol a. The **chemical potential, μ**, of a substance refers to its ability or potential to change the Gibbs energy of the system. The activity is defined in a way that ensures that the chemical potential has a specific form (equation 13.31). The criterion for predicting the direction of spontaneous chemical change can be obtained by considering the Gibbs energy of a mixture, which can be expressed in terms of the chemical potentials of the substances involved (equation 13.32).

Integrative Example

The synthesis of methanol is of great importance because methanol can be used directly as a motor fuel, mixed with gasoline for fuel use, or converted to other organic compounds. The synthesis reaction, carried out at about 500 K, is

$$\mathrm{CO(g)} + 2\,\mathrm{H_2(g)} \rightleftharpoons \mathrm{CH_3OH(g)}$$

What is the values of K and K_p at 500 K?

Analyze

Our approach to this problem begins with determining $\Delta_r G^\circ$ from Gibbs energy of formation data and using $\Delta_r G^\circ$ to find K at 298 K. The next step is to calculate $\Delta_r H^\circ$ from enthalpy of formation data and use this value together with K at 298 K in expression (13.25) to find K at 500 K. Finally, we obtain K_p by using equation (13.21).

Solve

Write the equation for methanol synthesis; place Gibbs energy of formation data from Appendix D under formulas in the equation, and use these data to calculate $\Delta_r G^\circ$ at 298 K.

$$\begin{array}{lccc} & \mathrm{CO(g)} & +\ 2\,\mathrm{H_2(g)} \rightleftharpoons & \mathrm{CH_3OH(g)} \\ \Delta_f G^\circ,\ \mathrm{kJ\ mol^{-1}} & -137.2 & 0 & -162.0 \end{array}$$

$$\Delta_r G^\circ = 1 \times (-162.0\ \mathrm{kJ\ mol^{-1}}) - 1 \times (-137.2\ \mathrm{kJ\ mol^{-1}}) = -24.8\ \mathrm{kJ\ mol^{-1}}$$

To calculate K_p at 298 K, use $\Delta_r G^\circ$ at 298 K, written as $-24.8 \times 10^3\ \mathrm{J\ mol^{-1}}$, in the expression $\Delta_r G^\circ = -RT \ln K$.

$$\ln K = -\Delta_r G^\circ/RT = \frac{-(-24.8 \times 10^3\ \mathrm{J\ mol^{-1}})}{8.3145\ \mathrm{J\ mol^{-1}\ K^{-1}} \times 298\ \mathrm{K}} = 10.0$$

$$K = e^{10.0} = 2.2 \times 10^4$$

To determine $\Delta_r H^\circ$ at 298 K, use standard enthalpy of formation data from Appendix D, applied in the same manner as was previously used for $\Delta_r G^\circ$.

$$\begin{array}{lccc} & \mathrm{CO(g)} & +\ 2\,\mathrm{H_2(g)} \rightleftharpoons & \mathrm{CH_3OH(g)} \\ \Delta_f H^\circ,\ \mathrm{kJ\ mol^{-1}} & -110.5 & 0 & -200.7 \end{array}$$

$$\Delta_r H^\circ = 1 \times (-200.7\ \mathrm{kJ\ mol^{-1}}) - 1\ \mathrm{mol\ CO} \times (-110.5\ \mathrm{kJ\ mol^{-1}}) = -90.2\ \mathrm{kJ\ mol^{-1}}$$

Use the van't Hoff equation with $K = 2.2 \times 10^4$ at 298 K and $\Delta_r H^\circ = -90.2 \times 10^3\ \mathrm{J\ mol^{-1}}$. Solve for K at 500 K.

$$\ln \frac{K}{2.2 \times 10^4} = \frac{-90.2 \times 10^3\ \mathrm{J\ mol^{-1}}}{8.3145\ \mathrm{J\ mol^{-1}\ K^{-1}}}\left(\frac{1}{500\ \mathrm{K}} - \frac{1}{298\ \mathrm{K}}\right)$$

$$= -14.7$$

To obtain K_p, we use equation (13.21) with $\Delta\nu = 1 - (1 + 2) = -2$

$$\frac{K}{2.2 \times 10^4} = e^{-14.7} = 4 \times 10^{-7} \qquad K = 9 \times 10^{-3}$$

$$K = K_p \times (1/P^\circ)^{-2}$$

$$K_p = K \times (1/P^\circ)^2 = 9 \times 10^{-3}\ \mathrm{bar^{-2}}$$

Assess

There are two important points to make. First, notice that the thermodynamic equilibrium constant, K, has no units and that K_p has the unit $(1/\mathrm{bar})^2$ in this case. However, their numerical values are equal. Sometimes, chemists give K_p and K_c values without units, but they do so in the knowledge that the appropriate power of bar or mol $\mathrm{L^{-1}}$ can be easily included again when explicitly required. Second, notice that, for this exothermic reaction ($\Delta_r H^\circ < 0$), an increase in temperature causes the value of K to decrease and thus, causes the equilibrium position to shift from products towards reactants. For an endothermic reaction ($\Delta_r H^\circ > 0$), the opposite is true: Increasing the temperature causes the value of K to increase and the equilibrium position to shift from reactants toward products.

PRACTICE EXAMPLE A: Dinitrogen pentoxide, N_2O_5, is a solid with a high vapor pressure. Its vapor pressure at 7.5 °C is 100 mmHg, and the solid sublimes at a pressure of 1.00 atm at 32.4 °C. What is $\Delta_r G^\circ$ 25 °C for the reaction $\mathrm{N_2O_5(s)} \longrightarrow \mathrm{N_2O_5(g)}$?

PRACTICE EXAMPLE B: A plausible reaction for the production of ethylene glycol (used as antifreeze) is

$$2\,\mathrm{CO(g)} + 3\mathrm{H_2(g)} \longrightarrow \mathrm{CH_2(OH)CH_2OH(l)}$$

The following thermodynamic properties of $CH_2(OH)CH_2OH(l)$ at 25 °C are given: $\Delta_f H° = -454.8\ kJ\ mol^{-1}$ and $\Delta_f G° = -323.1\ kJ\ mol^{-1}$. Use these data, together with values from Appendix D, to obtain a value of $S°$, the standard molar entropy of $CH_2(OH)CH_2OH(l)$ at 25 °C.

Exercises

Entropy and Spontaneous Change

1. Consider a system of five distinguishable particles confined to a one-dimensional box of length L. Describe how the following actions affect the number of accessible microstates and the entropy of the system:
   (a) increasing the length of the box to $2L$ for fixed total energy
   (b) increasing the total energy for constant length L
2. Consider a sample of ideal gas initially in a volume V at temperature T and pressure P. Does the entropy of this system increase, decrease, or stay the same in the following processes?
   (a) The gas expands isothermally.
   (b) The pressure is increased at constant temperature.
   (c) The gas is heated at constant pressure.
3. The standard molar entropy of $H_2(g)$ is $S° = 130.7\ J\ mol^{-1}\ K^{-1}$ at 298 K. Use this value, together with Boltzmann's equation, to determine the number of microstates, W, for one mole of $H_2(g)$ at 298 K and 1 bar. Reflect on the magnitude of your calculated value by describing how to write the number in decimal form. [*Hint*: To write the number 1×10^{15}, for example, in decimal form, we would write down a 1 followed by 15 zeros. The relationship $\ln W = 2.303 \log W$ might also be useful.]
4. In a 1985 paper in the *Journal of Chemical Thermodynamics*, the standard molar entropy of chalcopyrite, $CuFeS_2$, is given as $0.012\ J\ mol^{-1}\ K^{-1}$ at 5 K. [See R. A. Robie et. al., *J. Chem. Thermodyn.*, **17**, 481 (1985).] Use this value to estimate the number of microstates for one picogram (1×10^{-12} g) of $CuFeS_2$ at 5 K and 1 bar. Report your answer in the manner described in Exercise 3.
5. Indicate whether each of the following changes represents an increase or a decrease in entropy in a system, and explain your reasoning: **(a)** the freezing of ethanol; **(b)** the sublimation of dry ice; **(c)** the burning of a rocket fuel.
6. Arrange the entropy changes of the following processes, all at 25 °C, in the expected order of increasing ΔS, and explain your reasoning:
   (a) $H_2O(l, 1\ bar) \longrightarrow H_2O(g, 1\ bar)$
   (b) $CO_2(s, 1\ bar) \longrightarrow CO_2(g, 0.01\ bar)$
   (c) $H_2O(l, 1\ bar) \longrightarrow H_2O(g, 0.01\ bar)$
7. Use ideas from this chapter to explain this famous remark attributed to Rudolf Clausius (1865): "Die Energie der Welt ist konstant; die Entropie der Welt strebt einem Maximum zu." ("The energy of the world is constant; the entropy of the world increases toward a maximum.")
8. Comment on the difficulties of solving environmental pollution problems from the standpoint of entropy changes associated with the formation of pollutants and with their removal from the environment.
9. Indicate whether entropy increases or decreases in each of the following reactions. If you cannot be certain simply by inspecting the equation, explain why.
   (a) $CCl_4(l) \longrightarrow CCl_4(g)$
   (b) $CuSO_4 \cdot 3\,H_2O(s) + 2\,H_2O(g) \longrightarrow CuSO_4 \cdot 5\,H_2O(s)$
   (c) $SO_3(g) + H_2(g) \longrightarrow SO_2(g) + H_2O(g)$
   (d) $H_2S(g) + O_2(g) \longrightarrow H_2O(g) + SO_2(g)$ (not balanced)
10. Which substance in each of the following pairs would have the greater entropy? Explain.
    (a) at 75 °C and 1 bar: 1 mol $H_2O(l)$ or 1 mol $H_2O(g)$
    (b) at 5 °C and 1 bar: 50.0 g Fe(s) or 0.80 mol Fe(s)
    (c) 1 mol Br_2 (l, 1 bar, 8 °C) or 1 mol Br_2 (s, 1 bar, −8 °C)
    (d) 0.312 mol SO_2 (g, 0.110 bar, 32.5 °C) or 0.284 mol O_2 (g, 15.0 bar, 22.3 °C)
11. *Without performing any calculations* or using data from Appendix D, predict whether $\Delta_r S°$ for each of the following reactions is positive or negative. If it is not possible to determine the sign $\Delta_r S°$ of from the information given, indicate why.
    (a) $CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(s)$
    (b) $2\,HgO(s) \longrightarrow 2\,Hg(l) + O_2(g)$
    (c) $2\,NaCl(l) \longrightarrow 2\,Na(l) + Cl_2(g)$
    (d) $Fe_2O_3(s) + 3\,CO(g) \longrightarrow 2\,Fe(s) + 3\,CO_2(g)$
    (e) $Si(s) + 2\,Cl_2(g) \longrightarrow SiCl_4(g)$
12. By analogy to $\Delta_f H°$ and $\Delta_f G°$ how would you define standard entropy of formation? Which would have the largest standard entropy of formation: $CH_4(g)$, $CH_3CH_2OH(l)$, or $CS_2(l)$? First make a qualitative prediction; then test your prediction with data from Appendix D.
13. Calculate the entropy change, ΔS, for the following processes. If necessary, look up required data in Appendix D.
    (a) A mole of He(g) undergoes an expansion from V to $2V$ at 298 K.
    (b) The temperature of one mole of $CH_4(g)$ is increased from 298 K to 325 K at a constant pressure of 1 bar.
14. Calculate the entropy change, ΔS, for the following processes. If necessary, look up required data in Appendix D.
    (a) The pressure of one mole of $O_2(g)$ is increased from P to $2P$ at 298 K.
    (b) The temperature of one mole of $CO_2(g)$ is increased from 298 K to 355 K at a constant volume of 20.0 L.
15. In Example 13-3, we dealt with $\Delta_{vap}H°$ and $\Delta_{vap}S°$ for water at 100 °C.
    (a) Use data from Appendix D to determine values for these two quantities at 25 °C.

(b) From your knowledge of the structure of liquid water, explain the differences in $\Delta_{\text{vap}}H°$ values and in $\Delta_{\text{vap}}S°$ values between 25 °C and 100 °C.

16. Pentane is one of the most volatile of the hydrocarbons in gasoline. At 298.15 K, the following enthalpies of formation are given for pentane: $\Delta_f H°[C_5H_{12}(l)] = -173.5\ \text{kJ mol}^{-1}$; $\Delta_f H°[C_5H_{12}(g)] = -146.9\ \text{kJ mol}^{-1}$.
(a) Estimate the normal boiling point of pentane.
(b) Estimate $\Delta_{\text{vap}}G°$ for pentane at 298 K.
(c) Comment on the significance of the sign of $\Delta_{\text{vap}}G°$ for at 298 K.

17. Which of the following substances would obey Trouton's rule most closely: HF, $C_6H_5CH_3$ (toluene), or CH_3OH (methanol)? Explain your reasoning.

18. Estimate the normal boiling point of bromine, Br_2, in the following way: Determine $\Delta_{\text{vap}}H°$ for Br_2 from data in Appendix D. Assume that $\Delta_{\text{vap}}H°$ remains constant and that Trouton's rule is obeyed.

19. In what temperature range can the following equilibrium be established? Explain.

$$H_2O(l, 0.50\ \text{bar}) \rightleftharpoons H_2O(g, 0.50\ \text{bar})$$

20. Refer to Figure 12-28 and equation (13.13). Which has the lowest Gibbs energy at 1 atm and −60 °C: solid, liquid, or gaseous carbon dioxide? Explain.

Gibbs Energy and Spontaneous Change

21. Which of the following changes in a thermodynamic property would you expect to find for the reaction $Br_2(g) \longrightarrow 2\,Br(g)$ *at all temperatures:* **(a)** $\Delta H < 0$; **(b)** $\Delta S > 0$; **(c)** $\Delta G < 0$; **(d)** $\Delta S < 0$? Explain.

22. If a reaction can be carried out only because of an external influence, such as the use of an external source of power, which of the following changes in a thermodynamic property *must* apply: **(a)** $\Delta H > 0$; **(b)** $\Delta S > 0$; **(c)** $\Delta G = \Delta H$; **(d)** $\Delta G > 0$? Explain.

23. Indicate which of the four cases in Table 13.3 applies to each of the following reactions. If you are unable to decide from only the information given, state why.

(a) $PCl_3(g) + Cl_2(g) \longrightarrow PCl_5(g)$ $\quad \Delta_r H° = -87.9\ \text{kJ mol}^{-1}$

(b) $CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(g)$ $\quad \Delta_r H° = +41.2\ \text{kJ mol}^{-1}$

(c) $NH_4CO_2NH_2(s) \longrightarrow 2\,NH_3(g) + CO_2(g)$ $\quad \Delta_r H° = +159.2\ \text{kJ mol}^{-1}$

24. Indicate which of the four cases in Table 13.3 applies to each of the following reactions. If you are unable to decide from only the information given, state why.

(a) $H_2O(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O_2(g)$ $\quad \Delta_r H° = +105.5\ \text{kJ mol}^{-1}$

(b) $C_6H_6(l) + \frac{15}{2}O_2(g) \longrightarrow 6\,CO_2(g) + 3\,H_2O(g)$ $\quad \Delta_r H° = -3135\ \text{kJ mol}^{-1}$

(c) $NO(g) + \frac{1}{2}Cl_2(g) \longrightarrow NOCl(g)$ $\quad \Delta_r H° = -38.54\ \text{kJ mol}^{-1}$

25. For the mixing of ideal gases (see Figure 13-3), explain whether a positive, negative, or zero value is expected for ΔH, ΔS, and ΔG.

26. What values of ΔH, ΔS, and ΔG would you expect for the formation of an ideal solution of liquid components? (Is each value positive, negative, or zero?)

27. Explain why **(a)** some exothermic reactions do not occur spontaneously, and **(b)** some reactions in which the entropy of the system increases do not occur spontaneously.

28. Explain why you would expect a reaction of the type $AB(g) \longrightarrow A(g) + B(g)$ always to be spontaneous at *high* rather than at low temperatures.

Standard Gibbs Energy of Reaction, $\Delta_r G°$

29. From the data given in the following table, determine $\Delta_r S°$ for the reaction $NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$. All data are at 298 K.

	$\Delta_f H°$, kJ mol^{-1}	$\Delta_f G°$, kJ mol^{-1}
$NH_3(g)$	−46.11	−16.48
$HCl(g)$	−92.31	−95.30
$NH_4Cl(s)$	−314.4	−202.9

30. Use data from Appendix D to determine values of $\Delta_r G°$ for the following reactions at 25 °C.
(a) $C_2H_2(g) + 2\,H_2(g) \longrightarrow C_2H_6(g)$
(b) $2\,SO_3(g) \longrightarrow 2\,SO_2(g) + O_2(g)$
(c) $Fe_3O_4(s) + 4\,H_2(g) \longrightarrow 3\,Fe(s) + 4\,H_2O(g)$
(d) $2\,Al(s) + 6\,H^+(aq) \longrightarrow 2\,Al^{3+}(aq) + 3\,H_2(g)$

31. At 298 K, for the reaction $2\,PCl_3(g) + O_2(g) \longrightarrow 2\,POCl_3(l)$, $\Delta_r H° = -620.2\ \text{kJ mol}^{-1}$ and the standard molar entropies are $PCl_3(g)$, $311.8\ \text{J K}^{-1}$; $O_2(g)$, $205.1\ \text{J K}^{-1}$; and $POCl_3(l)$, $222.4\ \text{J K}^{-1}$. Determine **(a)** $\Delta_r G°$ at 298 K and **(b)** whether the reaction proceeds spontaneously in the forward or the reverse direction when reactants and products are in their standard states.

32. At 298 K, for the reaction $2\,H^+(aq) + 2\,Br^-(aq) + 2\,NO_2(g) \longrightarrow Br_2(l) + 2\,HNO_2(aq)$, $\Delta_r H° = -61.6\ \text{kJ mol}^{-1}$ and the standard molar entropies are $H^+(aq)$, $0\ \text{J mol}^{-1}\,\text{K}^{-1}$; $Br^-(aq)$, $82.4\ \text{J mol}^{-1}\,\text{K}^{-1}$; $NO_2(g)$, $240.1\ \text{J K}^{-1}$; $Br_2(l)$, $152.2\ \text{J mol}^{-1}\,\text{K}^{-1}$; $HNO_2(aq)$, $135.6\ \text{J mol}^{-1}\,\text{K}^{-1}$. Determine **(a)** $\Delta_r G°$ at 298 K and **(b)** whether the reaction proceeds spontaneously in the forward or the reverse direction when reactants and products are in their standard states.

33. The following $\Delta_r G°$ values are given for 25 °C.

(1) $N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g)$ $\quad \Delta_r G° = -33.0\ \text{kJ mol}^{-1}$

(2) $4\,NH_3(g) + 5\,O_2(g) \longrightarrow 4\,NO(g) + 6\,H_2O(l)$ $\quad \Delta_rG° = -1010.5\ kJ\ mol^{-1}$

(3) $N_2(g) + O_2(g) \longrightarrow 2\,NO(g)$ $\quad \Delta_rG° = +173.1\ kJ\ mol^{-1}$

(4) $N_2(g) + 2\,O_2(g) \longrightarrow 2\,NO_2(g)$ $\quad \Delta_rG° = +102.6\ kJ\ mol^{-1}$

(5) $2\,N_2(g) + O_2(g) \longrightarrow 2\,N_2O(g)$ $\quad \Delta_rG° = +208.4\ kJ\ mol^{-1}$

Combine the preceding equations, as necessary, to obtain $\Delta_rG°$ values for each of the following reactions.

(a) $N_2O(g) + \frac{3}{2}O_2(g) \longrightarrow 2\,NO_2(g)$ $\quad \Delta_rG° = ?$

(b) $2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(l)$ $\quad \Delta_rG° = ?$

(c) $2\,NH_3(g) + 2\,O_2(g) \longrightarrow N_2O(g) + 3\,H_2O(l)$ $\quad \Delta_rG° = ?$

Of reactions (a), (b), and (c), which would tend to go to completion at 25 °C, and which would reach an equilibrium condition with significant amounts of all reactants and products present?

34. The following $\Delta_rG°$ values are given for 25 °C.

(1) $SO_2(g) + 3\,CO(g) \longrightarrow COS(g) + 2\,CO_2(g)$ $\quad \Delta_rG° = -246.4\ kJ\ mol^{-1}$

(2) $CS_2(g) + H_2O(g) \longrightarrow COS(g) + H_2S(g)$ $\quad \Delta_rG° = -41.5\ kJ\ mol^{-1}$

(3) $CO(g) + H_2S(g) \longrightarrow COS(g) + H_2(g)$ $\quad \Delta_rG° = +1.4\ kJ\ mol^{-1}$

(4) $CO(g) + H_2O(g) \longrightarrow CO_2(g) + H_2(g)$ $\quad \Delta_rG° = -28.6\ kJ\ mol^{-1}$

Combine the preceding equations, as necessary, to obtain $\Delta_rG°$ values for the following reactions.

(a) $COS(g) + 2\,H_2O(g) \longrightarrow SO_2(g) + CO(g) + 2\,H_2(g)$ $\quad \Delta_rG° = ?$

(b) $COS(g) + 3\,H_2O(g) \longrightarrow SO_2(g) + CO_2(g) + 3\,H_2(g)$ $\quad \Delta_rG° = ?$

(c) $COS(g) + H_2O(g) \longrightarrow CO_2(g) + H_2S(g)$ $\quad \Delta_rG° = ?$

Of reactions (a), (b), and (c), which is spontaneous in the forward direction when reactants and products are present in their standard states?

35. Write an equation for the combustion of one mole of benzene, $C_6H_6(l)$, and use data from Appendix D to determine $\Delta_rG°$ at 298 K if the products of the combustion are **(a)** $CO_2(g)$ and $H_2O(l)$, and **(b)** $CO_2(g)$ and $H_2O(g)$. Describe how you might determine the *difference* between the values obtained in (a) and (b) without having either to write the combustion equation or to determine $\Delta_rG°$ values for the combustion reactions.

36. Use molar entropies from Appendix D, together with the following data, to estimate the bond-dissociation energy of the F_2 molecule.

$$F_2(g) \longrightarrow 2\,F(g)\ \Delta_rG° = 123.9\ kJ\ mol^{-1}$$

Compare your result with the value listed in Table 10.3.

37. Assess the feasibility of the reaction

$$N_2H_4(g) + 2\,OF_2(g) \longrightarrow N_2F_4(g) + 2\,H_2O(g)$$

by determining each of the following quantities for this reaction at 25 °C.

(a) $\Delta_rS°$ (The standard molar entropy of $N_2F_4(g)$ is $301.2\ J\ mol^{-1}\ K^{-1}$.)

(b) $\Delta_rH°$ (Use data from Table 10.3 and F—O and N—F bond energies of 222 and 301 kJ mol^{-1}, respectively.)

(c) $\Delta_rG°$

Is the reaction feasible? If so, is it favored at high or low temperatures?

38. Solid ammonium nitrate can decompose to dinitrogen oxide gas and liquid water. What is $\Delta_rG°$ at 298 K? Is the decomposition reaction favored at temperatures above or below 298 K?

The Thermodynamic Equilibrium Constant

39. For each of the following reactions, write down the relationship between K and either K_p or K_c, as appropriate.

(a) $2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$

(b) $HI(g) \rightleftharpoons \frac{1}{2}H_2(g) + \frac{1}{2}I_2(g)$

(c) $NH_4HCO_3(s) \rightleftharpoons NH_3(g) + CO_2(g) + H_2O(l)$

40. $H_2(g)$ can be prepared by passing steam over hot iron: $3\,Fe(s) + 4\,H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4\,H_2(g)$.

(a) Write an expression for the thermodynamic equilibrium constant for this reaction.

(b) Explain why the partial pressure of $H_2(g)$ is independent of the amounts of Fe(s) and $Fe_3O_4(s)$ present.

(c) Can we conclude that the production of $H_2(g)$ from $H_2O(g)$ could be accomplished regardless of the proportions of Fe(s) and $Fe_3O_4(s)$ present? Explain.

41. In the synthesis of gaseous methanol from carbon monoxide gas and hydrogen gas, the following equilibrium concentrations were determined at 483 K: $[CO(g)] = 0.0911\ M$, $[H_2(g)] = 0.0822\ M$, and $[CH_3OH(g)] = 0.00892\ M$. Calculate the equilibrium constant and $\Delta_rG°$ for the reaction $CO(g) + 2\,H_2(g) \longrightarrow CH_3OH(g)$.

42. Calculate the equilibrium constant and $\Delta_rG°$ for the reaction $CO(g) + 2\,H_2(g) \longrightarrow CH_3OH(g)$ at 483 K by using the data tables from Appendix D. [*Hint:* The value you obtain for K will be slightly different from the value you calculated in Exercise 41.]

Relationships Involving Δ_rG, $\Delta_rG°$, Q, and K

43. Use data from Appendix D to determine K at 298 K for the reaction $N_2O(g) + \frac{1}{2}O_2(g) \rightleftharpoons 2\,NO(g)$.

44. Use data from Appendix D to establish for the reaction $2\,N_2O_4(g) + O_2(g) \rightleftharpoons 2\,N_2O_5(g)$:

(a) $\Delta_rG°$ at 298 K for the reaction as written;

(b) K at 298 K.

45. Use data from Appendix D to determine values at 298 K of $\Delta_rG°$ and K for the following reactions. (*Note:* The equations are not balanced.)

(a) $HCl(g) + O_2(g) \rightleftharpoons H_2O(g) + Cl_2(g)$

(b) $Fe_2O_3(s) + H_2(g) \rightleftharpoons Fe_3O_4(s) + H_2O(g)$

(c) $Ag^+(aq) + SO_4^{2-}(aq) \rightleftharpoons Ag_2SO_4(s)$

46. In Example 13-2, we were unable to conclude by inspection whether $\Delta_r S°$ for the reaction $CO(g) + H_2O(g) \longrightarrow CO_2(g) + H_2(g)$ should be positive or negative. Use data from Appendix D to obtain $\Delta_r S°$ at 298 K.

47. Use thermodynamic data at 298 K to decide in which direction the reaction

$$2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$$

is spontaneous when the partial pressures of SO_2, O_2, and SO_3 are 1.0×10^{-4}, 0.20, and 0.10 bar, respectively.

48. Use thermodynamic data at 298 K to decide in which direction the reaction

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

is spontaneous when the partial pressures of H_2, Cl_2, and HCl are all 0.5 bar.

49. For the reaction below, $\Delta_r G° = 27.07\ \text{kJ mol}^{-1}$ at 298 K.

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons CH_3CO_2^-(aq) + H_3O^+(aq)$$

Use this thermodynamic quantity to decide in which direction the reaction is spontaneous when the concentrations of $CH_3CO_2H(aq)$, $CH_3CO_2^-(aq)$, and $H_3O^+(aq)$ are 0.10 M, 1.0×10^{-3} M, and 1.0×10^{-3} M, respectively.

50. For the reaction below, $\Delta_r G° = 29.05\ \text{kJ mol}^{-1}$ at 298 K.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Use this thermodynamic quantity to decide in which direction the reaction is spontaneous when the concentrations of $NH_3(aq)$, $NH_4^+(aq)$, and $OH^-(aq)$ are 0.10 M, 1.0×10^{-3} M, and 1.0×10^{-3} M, respectively.

51. For the reaction $2\,NO(g) + O_2(g) \longrightarrow 2\,NO_2(g)$ all but one of the following equations is correct. Which is *incorrect*, and why? **(a)** $K = K_p$; **(b)** $\Delta_r S° = (\Delta_r H° - \Delta_r G°)/T$; **(c)** $K = e^{-\Delta_r G°/RT}$; **(d)** $\Delta_r G = \Delta_r G° + RT \ln Q$.

52. Why is $\Delta_r G°$ such an important property of a chemical reaction, even though the reaction is generally carried out under *nonstandard* conditions?

53. At 1000 K, an equilibrium mixture in the reaction $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$ contains 0.276 mol H_2, 0.276 mol CO_2, 0.224 mol CO, and 0.224 mol H_2O.

(a) What is K at 1000 K?

(b) Calculate $\Delta_r G°$ at 1000 K.

(c) In which direction would a spontaneous reaction occur if the following were brought together at 1000 K: 0.0750 mol CO_2, 0.095 mol H_2, 0.0340 mol CO, and 0.0650 mol H_2O?

54. For the reaction $2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$, $K_c = 2.8 \times 10^2\ \text{M}^{-1}$ at 1000 K.

(a) What is $\Delta_r G°$ at 1000 K? [*Hint:* What is K?]

(b) If 0.40 mol SO_2, 0.18 mol O_2, and 0.72 mol SO_3 are mixed in a 2.50 L flask at 1000 K, in what direction will a net reaction occur?

55. For the following equilibrium reactions, calculate $\Delta_r G°$ at the indicated temperature. [*Hint:* How is each equilibrium constant related to a thermodynamic equilibrium constant, K?]

(a) $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g) \quad K_c = 50.2$ at 445 °C

(b) $N_2O(g) + \frac{1}{2}O_2(g) \rightleftharpoons 2\,NO(g) \quad K_c = 1.7 \times 10^{-13}$ at 25 °C

(c) $N_2O_4(g) \rightleftharpoons 2\,NO_2(g) \quad K_c = 4.61 \times 10^{-3}$ at 25 °C

(d) $2\,Fe^{3+}(aq) + Hg_2{}^{2+}(aq) \rightleftharpoons 2\,Fe^{2+}(aq) + 2\,Hg^{2+}(aq) \quad K_c = 9.14 \times 10^{-6}$ at 25 °C

56. Two equations can be written for the dissolution of $Mg(OH)_2(s)$ in acidic solution.

$$Mg(OH)_2(s) + 2\,H^+(aq) \rightleftharpoons Mg^{2+}(aq) + 2\,H_2O(l) \qquad \Delta_r G° = -95.5\ \text{kJ mol}^{-1}$$

$$\frac{1}{2}Mg(OH)_2(s) + H^+(aq) \rightleftharpoons \frac{1}{2}Mg^{2+}(aq) + H_2O(l) \qquad \Delta_r G° = -47.8\ \text{kJ mol}^{-1}$$

(a) Explain why these two equations have different $\Delta_r G°$ values.

(b) Will K for these two equations be the same or different? Explain.

57. At 298 K, $\Delta_f G°[CO(g)] = -137.2\ \text{kJ mol}^{-1}$ and $K = 6.5 \times 10^{11}$ for the reaction $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$. Use these data to determine $\Delta_f G°[COCl_2(g)]$, and compare your result with the value in Appendix D.

58. Use thermodynamic data from Appendix D to calculate values of K for the reaction describing the dissolution of the following sparingly soluble solutes: **(a)** AgBr; **(b)** $CaSO_4$; **(c)** $Fe(OH)_3$. [*Hint:* The dissolution process is the reverse of the precipitation reaction. Precipitation reactions were discussed in Chapter 5.]

59. To establish the law of conservation of mass, Lavoisier carefully studied the decomposition of mercury(II) oxide:

$$HgO(s) \longrightarrow Hg(l) + \frac{1}{2}O_2(g)$$

At 25 °C, $\Delta_r H° = +90.83\ \text{kJ mol}^{-1}$ and $\Delta_r G° = +58.54\ \text{kJ mol}^{-1}$.

(a) Show that the partial pressure of $O_2(g)$ in equilibrium with HgO(s) and Hg(l) at 25 °C is extremely low.

(b) What conditions do you suppose Lavoisier used to obtain significant quantities of oxygen?

60. Currently, CO_2 is being studied as a source of carbon atoms for synthesizing organic compounds. One possible reaction involves the conversion of CO_2 to methanol, CH_3OH.

$$CO_2(g) + 3\,H_2(g) \longrightarrow CH_3OH(g) + H_2O(g)$$

With the aid of data from Appendix D, determine

(a) if this reaction proceeds to any significant extent at 25 °C;

(b) if the production of $CH_3OH(g)$ is favored by raising or lowering the temperature from 25 °C;

(c) K for this reaction at 500 K;

$\Delta_r G°$ and K as Functions of Temperature

61. Use data from Appendix D to establish at 298 K for the reaction:

$$2\,\text{NaHCO}_3(\text{s}) \longrightarrow \text{Na}_2\text{CO}_3(\text{s}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$$

(a) $\Delta_r S°$; **(b)** $\Delta_r H°$; **(c)** $\Delta_r G°$; **(d)** K.

62. A possible reaction for converting methanol to ethanol is

$$\text{CO}(\text{g}) + 2\,\text{H}_2(\text{g}) + \text{CH}_3\text{OH}(\text{g}) \longrightarrow \text{C}_2\text{H}_5\text{OH}(\text{g}) + \text{H}_2\text{O}(\text{g})$$

(a) Use data from Appendix D to calculate $\Delta_r H°$ $\Delta_r S°$, and $\Delta_r G°$; for this reaction at 25 °C.
(b) Is this reaction thermodynamically favored at high or low temperatures? At high or low pressures? Explain.
(c) Estimate K for the reaction at 750 K.

63. What must be the temperature if the following reaction has $\Delta_r G° = -45.5\ \text{kJ mol}^{-1}$, $\Delta_r H° = -24.8\ \text{kJ mol}^{-1}$, and $\Delta_r S° = 15.2\ \text{J mol}^{-1}\ \text{K}^{-1}$?

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

64. Estimate K at 100 °C for the reaction $2\,\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\,\text{SO}_3(\text{g})$. Use data from Table 13.8 and Figure 13-10.

65. The synthesis of ammonia by the Haber process occurs by the reaction $\text{N}_2(\text{g}) + 3\,\text{H}_2(\text{g}) \rightleftharpoons 2\,\text{NH}_3(\text{g})$ at 400 °C. Using data from Appendix D and assuming that $\Delta_r H°$ and $\Delta_r S°$ are essentially unchanged in the temperature interval from 25 to 400 °C, estimate K at 400 °C.

66. Use data from Appendix D to determine **(a)** $\Delta_r H°$, $\Delta_r S°$, and $\Delta_r G°$ at 298 K and **(b)** K at 875 K for the water gas shift reaction, used commercially to produce $\text{H}_2(\text{g})$: $\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{H}_2(\text{g})$. [*Hint:* Assume that $\Delta_r H°$ and $\Delta_r S°$ are essentially unchanged in this temperature interval.]

67. In Example 13-12, we used the van't Hoff equation to determine the temperature at which $K = 1.0 \times 10^6$ for the reaction $2\,\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\,\text{SO}_3(\text{g})$. Obtain another estimate of this temperature with data from Appendix D and equations (13.13) and (13.17). Compare your result with that obtained in Example 13-12.

68. The following equilibrium constants have been determined for the reaction $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\,\text{HI}(\text{g})$: $K = 50.0$ at 448 °C and 66.9 at 350 °C. Use these data to estimate $\Delta_r H°$ for the reaction.

69. For the reaction $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\,\text{NO}_2(\text{g})$, $\Delta_r H° = +57.2\ \text{kJ mol}^{-1}$ and $K = 0.113$ at 298 K.
(a) What is K at 0 °C?
(b) At what temperature will $K = 1.00$?

70. Use data from Appendix D and the van't Hoff equation (13.25) to estimate a value of K at 100 °C for the reaction $2\,\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\,\text{NO}_2(\text{g})$. [*Hint:* First determine K at 25 °C. What is $\Delta_r H°$ for the reaction?]

71. For the reaction

$$\text{CO}(\text{g}) + 3\,\text{H}_2(\text{g}) \rightleftharpoons \text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}),$$
$$K = 2.15 \times 10^{11} \text{ at } 200\ °\text{C}$$
$$K = 4.56 \times 10^{8} \text{ at } 260\ °\text{C}$$

determine $\Delta_r H°$ by using the van't Hoff equation (13.25) and by using tabulated data in Appendix D. Compare the two results, and comment on how good the assumption is that $\Delta_r H°$ is essentially independent of temperature in this case.

72. Sodium carbonate, an important chemical used in the production of glass, is made from sodium hydrogen carbonate by the reaction

$$2\,\text{NaHCO}_3(\text{s}) \rightleftharpoons \text{Na}_2\text{CO}_3(\text{s}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$$

Data for the temperature variation of K for this reaction are $K = 1.66 \times 10^{-5}$ at 30 °C; 3.90×10^{-4} at 50 °C; 6.27×10^{-3} at 70 °C; and 2.31×10^{-1} at 100 °C.
(a) Plot a graph similar to Figure 13-10, and determine $\Delta_r H°$for the reaction.
(b) Calculate the temperature at which the total gas pressure above a mixture of $\text{NaHCO}_3(\text{s})$ and $\text{Na}_2\text{CO}_3(\text{s})$ is 2.00 bar.

Coupled Reactions

73. Titanium is obtained by the reduction of $\text{TiCl}_4(\text{l})$, which in turn is produced from the mineral rutile (TiO_2).
(a) With data from Appendix D, determine $\Delta_r G°$ at 298 K for this reaction.

$$\text{TiO}_2(\text{s}) + 2\,\text{Cl}_2(\text{g}) \longrightarrow \text{TiCl}_4(\text{l}) + \text{O}_2(\text{g})$$

(b) Show that the conversion of $\text{TiO}_2(\text{s})$ to $\text{TiCl}_4(\text{l})$, with reactants and products in their standard states, is spontaneous at 298 K if the reaction in (a) is coupled with the reaction

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

74. Following are some standard Gibbs energies of formation, $\Delta_f G°$, at 1000 K: NiO, $-115\ \text{kJ mol}^{-1}$; MnO, $-280\ \text{kJ mol}^{-1}$; TiO_2, $-630\ \text{kJ mol}^{-1}$. The standard Gibbs energy of formation of CO at 1000 K is $-250\ \text{kJ mol}^{-1}$. Use the method of coupled reactions (page 622) to determine which of these metal oxides can be reduced to the metal by a spontaneous reaction with carbon at 1000 K and with all reactants and products in their standard states.

75. In biochemical reactions the phosphorylation of amino acids is an important step. Consider the following two reactions and determine whether the phosphorylation of arginine with ATP is spontaneous.

$$\text{ATP} + \text{H}_2\text{O} \longrightarrow \text{ADP} + \text{P} \qquad \Delta_r G°' = -31.5\ \text{kJ mol}^{-1}$$
$$\text{arginine} + \text{P} \longrightarrow \text{phosphorarginine} + \text{H}_2\text{O}$$
$$\Delta_r G°' = 33.2\ \text{kJ mol}^{-1}$$

76. The synthesis of glutamine from glutamic acid is given by $\text{Glu}^- + \text{NH}_4^+ \longrightarrow \text{Gln} + \text{H}_2\text{O}$. The standard Gibbs energy for this reaction at pH = 7 and $T = 310$ K is $\Delta_r G°' = 14.8\ \text{kJ mol}^{-1}$. Will this reaction be spontaneous if coupled with the hydrolysis of ATP?

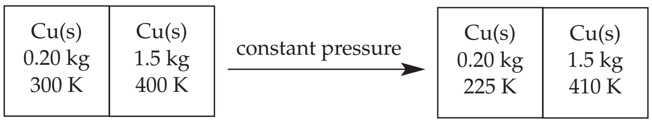
$$\text{ATP} + \text{H}_2\text{O} \longrightarrow \text{ADP} + \text{P}$$
$$\Delta_r G°' = -31.5\ \text{kJ mol}^{-1}$$

Integrative and Advanced Exercises

77. In an *adiabatic* process, there is no exchange of heat between the system and its surroundings. Of the quantities ΔS, ΔS_{surr}, and ΔS_{univ}, which one(s) must always be equal to zero for a spontaneous adiabatic process? Under what condition(s) will an adiabatic process have $\Delta S = \Delta S_{\text{surr}} = \Delta S_{\text{univ}} = 0$?

78. Calculate ΔS and ΔS_{univ} when 1.00 mol of $H_2O(l)$, initially at 10 °C, is converted to $H_2O(g)$ at 125 °C at a constant pressure of 1.00 bar. The molar heat capacities of $H_2O(l)$ and $H_2O(g)$ are, respectively, 75.3 J mol^{-1} K^{-1} and 33.6 J mol^{-1} K^{-1}. The standard enthalpy of vaporization of water is 40.66 kJ mol^{-1} at 100 °C.

79. Consider the following hypothetical process in which heat flows from a low to a high temperature. For copper, the heat capacity at constant pressure is 0.385 J mol^{-1} K^{-1}. (For simplicity, you may assume that no heat is lost to the surroundings and that the volume changes are negligible.)



(a) Show that the process conserves energy (i.e., show that the heat absorbed by warmer block of metal is equal to the heat released from the colder block).
(b) Calculate ΔS_{univ} for the process to show that the process is nonspontaneous.

80. One mole of argon gas, Ar(g), undergoes a change in state from 25.6 L and 0.877 bar to 15.1 L and 2.42 bar. What are ΔH and ΔS for the argon gas? For Ar(g), the molar heat capacity at constant pressure is 20.79 J mol^{-1} K^{-1}.

81. Use data from Appendix D to estimate **(a)** the normal boiling point of mercury and **(b)** the vapor pressure of mercury at 25 °C.

82. Consider the vaporization of water: $H_2O(l) \longrightarrow H_2O(g)$ at 100 °C, with $H_2O(l)$ in its standard state, but with the partial pressure of $H_2O(g)$ at 2.0 atm. Which of the following statements about this vaporization at 100 °C are true? **(a)** $\Delta_r G° = 0$, **(b)** $\Delta_r G = 0$, **(c)** $\Delta_r G° > 0$, **(d)** $\Delta_r G > 0$? Explain.

83. At 298 K, 1.00 mol BrCl(g) is introduced into a 10.0 L vessel, and equilibrium is established in the reaction $BrCl(g) \rightleftharpoons \frac{1}{2}Br_2(g) + \frac{1}{2}Cl_2(g)$. Calculate the amounts of each of the three gases present when equilibrium is established. [*Hint:* First, use data from Appendix D, as necessary, to calculate the equilibrium constant K for the reaction. Then, relate the equilibrium amounts of the gases to their initial amounts through the extent of reaction, ξ. You might find it helpful to use a tabular approach, as was done on page 626. Finally, use the equilibrium condition $Q = K$ to solve for ξ.]

84. Use data from Appendix D and other information from this chapter to estimate the temperature at which the dissociation of $I_2(g)$ becomes appreciable [for example, with the $I_2(g)$ 50% dissociated into I(g) at 1 atm total pressure].

85. The following table shows the enthalpies and Gibbs energies of formation of three metal oxides at 25 °C.
(a) Which of these oxides can be most readily decomposed to the free metal and $O_2(g)$?
(b) For the oxide that is most easily decomposed, to what temperature must it be heated to produce $O_2(g)$ at 1.00 atm pressure?

	$\Delta_f H°$, kJ mol^{-1}	$\Delta_f G°$, kJ mol^{-1}
PbO(red)	−219.0	−188.9
Ag_2O	−31.05	−11.20
ZnO	−348.3	−318.3

86. The following data are given for the two solid forms of HgI_2 at 298 K.

	$\Delta_r H°$, kJ mol^{-1}	$\Delta_f G°$, kJ mol^{-1}	$S°$, J mol^{-1} K^{-1}
HgI_2(red)	−105.4	−101.7	180
HgI_2(yellow)	−102.9	(?)	(?)

Estimate values for the two missing entries. To do this, assume that for the transition $HgI_2(\text{red}) \longrightarrow HgI_2(\text{yellow})$, the values of $\Delta_r H°$ and $\Delta_r S°$ at 25 °C have the same values that they do at the equilibrium temperature of 127 °C.

87. Oxides of nitrogen are produced in high-temperature combustion processes. The essential reaction is $N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$. At what approximate temperature will an *equimolar* mixture of $N_2(g)$ and $O_2(g)$ be 1.0% converted to NO(g)? [*Hint:* Use data from Appendix D as necessary.]

88. Use the following data together with other data from the text to determine the temperature at which the equilibrium pressure of water vapor above the two solids in the following reaction is 75 Torr.

$$CuSO_4 \cdot 3\,H_2O(s) \rightleftharpoons CuSO_4 \cdot H_2O(s) + 2\,H_2O(g)$$

	$\Delta_f H°$, kJ mol^{-1}	$\Delta_f G°$, kJ mol^{-1}	$S°$, J mol^{-1} K^{-1}
$CuSO_4 \cdot 3\,H_2O(s)$	−1684.3	−1400.0	221.3
$CuSO_4 \cdot H_2O(s)$	−1085.8	−918.1	146.0

89. From the data given in Exercise 72, estimate a value of $\Delta_r S°$ at 298 K for the reaction

$$2\,NaHCO_3(s) \longrightarrow Na_2CO_3(s) + H_2O(g) + CO_2(g)$$

90. The normal boiling point of cyclohexane, C_6H_{12}, is 80.7 °C. Estimate the temperature at which the vapor pressure of cyclohexane is 100.0 mmHg.

91. The term *thermodynamic stability* refers to the sign of $\Delta_f G°$. If $\Delta_f G°$ is negative, the compound is stable with respect to decomposition into its elements. Use the data in Appendix D to determine whether $Ag_2O(s)$ is thermodynamically stable at **(a)** 25 °C and **(b)** 200 °C.

92. At 0 °C, ice has a density of $0.917\ \mathrm{g\ mL^{-1}}$ and an absolute entropy of $37.95\ \mathrm{J\ mol^{-1}\ K^{-1}}$. At this temperature, liquid water has a density of $1.000\ \mathrm{g\ mL^{-1}}$ and an absolute entropy of $59.94\ \mathrm{J\ mol^{-1}\ K^{-1}}$. The pressure corresponding to these values is 1 bar. Calculate ΔG, $\Delta S°$ and $\Delta H°$ for the melting of two moles of ice at its normal melting point.

93. The decomposition of the poisonous gas phosgene is represented by the equation $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$. Values of K for this reaction are $K = 6.7 \times 10^{-9}$ at 99.8 °C and $K = 4.44 \times 10^{-2}$ at 395 °C. At what temperature is $COCl_2$ 15% dissociated when the total gas pressure is maintained at 1.00 atm?

94. Assume that the constant pressure heat capacity, C_p, of a solid is a linear function of temperature of the form $C_p = aT$, where a is a constant. Starting from the expressions below for $S°$ and $\Delta H°$, show that $S°/\Delta H° = 2/(298.15\ \mathrm{K}) = 0.00671\ \mathrm{K^{-1}}$, a claim made in Are You Wondering? 13-3.

$$S° = \int_{0\ \mathrm{K}}^{298.15\ \mathrm{K}} \frac{C_p}{T}\, dT \qquad\qquad \Delta H° = \int_{0\ \mathrm{K}}^{298.15\ \mathrm{K}} C_p dT$$

95. The standard molar entropy of solid hydrazine at its melting point of 1.53 °C is $67.15\ \mathrm{J\ mol^{-1}\ K^{-1}}$. The enthalpy of fusion is $12.66\ \mathrm{kJ\ mol^{-1}}$. For $N_2H_4(l)$ in the interval from 1.53 °C to 298.15 K, the molar heat capacity at constant pressure is given by the expression $C_p = 97.78 + 0.0586(T - 280)$. Determine the standard molar entropy of $N_2H_4(l)$ at 298.15 K. [*Hint:* The heat absorbed to produce an infinitesimal change in the temperature of a substance is $\delta q = C_p\, dT$.

96. Use the following data to estimate the standard molar entropy of gaseous benzene at 298.15 K; that is, $S°[C_6H_6(g, 1\ \mathrm{atm})]$. For C_6H_6 (s, 1 atm) at its melting point of 5.53 °C, $S°$ is $128.82\ \mathrm{J\ mol^{-1}\ K^{-1}}$. The enthalpy of fusion is $9.866\ \mathrm{kJ\ mol^{-1}}$. From the melting point to 298.15 K, the average heat capacity of liquid benzene is $134.0\ \mathrm{J\ mol^{-1}\ K^{-1}}$. The enthalpy of vaporization of $C_6H_6(l)$ at 298.15 K is $33.85\ \mathrm{kJ\ mol^{-1}}$, and in the vaporization, $C_6H_6(g)$ is produced at a pressure of 95.13 Torr. Imagine that this vapor could be compressed to 1 atm pressure without condensing and while behaving as an ideal gas. Calculate $S°[C_6H_6(g, 1\ \mathrm{atm})]$. [*Hint:* Refer to the preceding exercise, and note the following: For infinitesimal quantities, $dS = \delta q/dT$; for the isothermal compression of an ideal gas, $\delta q = -dw$; and for pressure–volume work, $\delta_w = -P\,dV$.

97. Consider a system that has four energy levels, with energy $\varepsilon = 0, 1, 2,$ and 3 energy units, and three particles labeled A, B, and C. The total energy of the system, in energy units, is 3. How many microstates can be generated?

98. In Figure 13-5 the temperature dependence of the standard molar entropy for chloroform is plotted. **(a)** Explain why the slope for the standard molar entropy of the solid is greater than the slope for the standard molar entropy of the liquid, which is greater than the slope for the standard molar entropy of the gas. **(b)** Explain why the change in the standard molar entropy from solid to liquid is smaller than that for the liquid to gas.

99. The following data are from a laboratory experiment that examines the relationship between solubility and thermodynamics. In this experiment $KNO_3(s)$ is placed in a test tube containing some water. The solution is heated until all the $KNO_3(s)$ is dissolved and then allowed to cool. The temperature at which crystals appear is then measured. From this experiment we can determine the equilibrium constant, Gibbs energy, enthalpy, and entropy for the reaction. Use the following data to calculate $\Delta_r G$, $\Delta_r H$, and $\Delta_r S$ for the dissolution of $KNO_3(s)$. (Assume the initial mass of $KNO_3(s)$ was 20.2 g.)

Total Volume, mL	Temperature Crystals Formed, K
25.0	340
29.2	329
33.4	320
37.6	313
41.8	310
46.0	306
51.0	303

Data reported by J. O. Schreck, *J. Chem. Educ.*, **73**, 426 (1996).

Feature Problems

100. A tabulation of more precise thermodynamic data than are presented in Appendix D lists the following values for $H_2O(l)$ and $H_2O(g)$ at 298.15 K, at a standard state pressure of 1 bar.

	$\Delta_f H°$, $\mathrm{kJ\ mol^{-1}}$	$\Delta_f G°$, $\mathrm{kJ\ mol^{-1}}$	$S°$, $\mathrm{J\ mol^{-1}\ K^{-1}}$
$H_2O(l)$	−285.830	−237.129	69.91
$H_2O(g)$	−241.818	−228.572	188.825

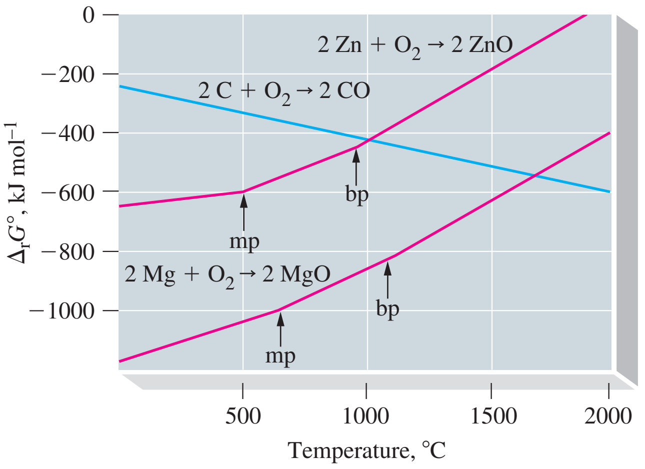
(a) Use these data to determine, in two different ways, $\Delta_r G°$ at 298.15 K for the vaporization: $H_2O\ (l, 1\ \mathrm{bar}) \rightleftharpoons H_2O(g, 1\ \mathrm{bar})$.

(b) Use the result of part (a) to obtain the value of K for this vaporization and, hence, the vapor pressure of water at 298.15 K.

(c) The vapor pressure in part (b) is in the unit bar. Convert the pressure to millimeters of mercury.

(d) Start with the value $\Delta_r G° = 8.590\ \mathrm{kJ\ mol^{-1}}$, and calculate the vapor pressure of water at 298.15 K in a fashion similar to that in parts (b) and (c). In this way, demonstrate that the results obtained in a thermodynamic calculation do not depend on the convention we choose for the standard state pressure, as long as we use standard state thermodynamic data consistent with that choice.

101. The graph shows how $\Delta_r G°$ varies with temperature for three different oxidation reactions: the oxidations of C(graphite), Zn, and Mg to CO, ZnO, and MgO, respectively. Such graphs as these can be used to show the temperatures at which carbon is an effective reducing agent to reduce metal oxides to the free metals. As a result, such graphs are important to metallurgists. Use these graphs to answer the following questions.
(a) Why can Mg be used to reduce ZnO to Zn at all temperatures, but Zn cannot be used to reduce MgO to Mg at any temperature?
(b) Why can C be used to reduce ZnO to Zn at some temperatures but not at others? At what temperatures can carbon be used to reduce zinc oxide?
(c) Is it possible to produce Zn from ZnO by its direct decomposition without requiring a coupled reaction? If so, at what approximate temperatures might this occur?
(d) Is it possible to decompose CO to C and O_2 in a spontaneous reaction? Explain.



▲ $\Delta_r G°$ for three reactions as a function of temperature. The reactions are indicated by the equations written above the graphs. The points noted by arrows are the melting points (mp) and boiling points (bp) of zinc and magnesium.

(e) To the set of graphs, add straight lines representing the reactions

$$\text{C(graphite)} + O_2(g) \longrightarrow CO_2(g)$$
$$2\,CO(g) + O_2(g) \longrightarrow 2\,CO_2(g)$$

given that the three lines representing the formation of oxides of carbon intersect at about 800 °C. [*Hint:* At what other temperature can you relate $\Delta_r G°$ and temperature?]

The slopes of the three lines described above differ sharply. Explain why this is so—that is, explain the slope of each line in terms of principles governing Gibbs energy change.
(f) The graphs for the formation of oxides of other metals are similar to the ones shown for Zn and Mg; that is, they all have positive slopes. Explain why carbon is such a good reducing agent for the reduction of metal oxides.

102. In a heat engine, heat (q_h) is absorbed by a working substance (such as water) at a high temperature (T_h). Part of this heat is converted to work (w), and the rest (q_l) is released to the surroundings at the lower temperature (T_l). The *efficiency* of a heat engine is the ratio w/q_h. The second law of thermodynamics establishes the following equation for the maximum efficiency of a heat engine, expressed on a percentage basis.

$$\text{efficiency} = \frac{w}{q_h} \times 100\% = \frac{T_h - T_l}{T_h} \times 100\%$$

In a particular electric power plant, the steam leaving a steam turbine is condensed to liquid water at 41 °C(T_l) and the water is returned to the boiler to be regenerated as steam. If the system operates at 36% efficiency,
(a) What is the minimum temperature of the steam [$H_2O(g)$] used in the plant?
(b) Why is the actual steam temperature probably higher than that calculated in part (a)?
(c) Assume that at T_h the $H_2O(g)$ is in equilibrium with $H_2O(l)$. Estimate the steam pressure at the temperature calculated in part (a).
(d) Is it possible to devise a heat engine with greater than 100 percent efficiency? With 100 percent efficiency? Explain.

103. The Gibbs energy available from the complete combustion of 1 mol of glucose to carbon dioxide and water is

$$C_6H_{12}O_6(aq) + 6\,O_2(g) \longrightarrow 6\,CO_2(g) + 6\,H_2O(l)$$
$$\Delta_r G° = -2870 \text{ kJ mol}^{-1}$$

(a) Under biological standard conditions, compute the maximum number of moles of ATP that could form from ADP and phosphate if all the energy of combustion of 1 mol of glucose could be utilized.
(b) The actual number of moles of ATP formed by a cell under aerobic conditions (that is, in the presence of oxygen) is about 38. Calculate the efficiency of energy conversion of the cell.
(c) Consider these typical physiological conditions.

$P_{CO_2} = 0.050$ bar; $P_{O_2} = 0.132$ bar;
[glucose] = 1.0 mg/mL; pH = 7.0;
[ATP] = [ADP] = [P_i] = 0.00010 M.

Calculate $\Delta_r G°$ for the conversion of 1 mol ADP to ATP and $\Delta_r G°$ for the oxidation of 1 mol glucose under these conditions.
(d) Calculate the efficiency of energy conversion for the cell under the conditions given in part (c). Compare this efficiency with that of a diesel engine that attains 78% of the theoretical efficiency operating with $T_h = 1923$ K and $T_l = 873$ K. Suggest a reason for your result. [*Hint:* See the preceding exercise.]

104. The entropy of materials at $T = 0$ K should be zero; however, for some substances, this is not true. The difference between the measured value and expected value of zero is known as residual entropy. This residual entropy arises because the molecules can have a number of different orientations in the crystal and can be estimated by applying Boltzmann's formula (equation 13.1) with an appropriate value for W.

(a) Given that a CO molecule can have one of two possible orientations in a crystal (CO or OC), calculate the residual entropy for a crystal consisting of one mole of CO at $T = 0$ K.

(b) Ice consists of water molecules arranged in a tetrahedral pattern. In this configuration the question is whether a given hydrogen atom is halfway between two oxygen atoms or closer to one oxygen atom than the other. Starting with a series of basic assumptions, Linus Pauling used the agreement of his calculated residual entropy and the experimental value to determine that a given hydrogen atom is closer to one oxygen atom. An approach used by Pauling to calculate the residual entropy can be summarized as follows.

i) Place four oxygen atoms in a tetrahedral arrangement around a central water molecule.

ii) Determine the number of orientations of the central water molecule, assuming that it forms two hydrogen bonds with the surrounding oxygen atoms.

iii) Using this approach, plus the additional observation made by Pauling that only one-quarter of the orientations identified in (ii) are accessible, calculate the residual entropy of one mole of H_2O.

Self-Assessment Exercises

105. In your own words, define the following symbols: **(a)** ΔS_{univ}; **(b)** $\Delta_f G°$; **(c)** K; **(d)** $S°$; **(e)** $\Delta_r G°$.

106. Briefly describe each of the following ideas, methods, or phenomena: **(a)** absolute molar entropy; **(b)** coupled reactions; **(c)** Trouton's rule; **(d)** evaluation of an equilibrium constant from tabulated thermodynamic data.

107. Explain the important distinctions between each of the following pairs: **(a)** spontaneous and nonspontaneous processes; **(b)** the second and third laws of thermodynamics; **(c)** $\Delta_r G°$ and $\Delta_r G°$; **(d)** ΔG and $\Delta_r G$.

108. For a process to occur spontaneously, **(a)** the entropy of the system must increase; **(b)** the entropy of the surroundings must increase; **(c)** both the entropy of the system and the entropy of the surroundings must increase; **(d)** the net change in entropy of the system and surroundings considered together must be a positive quantity; **(e)** the entropy of the universe must remain constant.

109. The Gibbs energy of a reaction can be used to assess which of the following? **(a)** how much heat is absorbed from the surroundings; **(b)** how much work the system does on the surroundings; **(c)** the net direction in which the reaction occurs to reach equilibrium; **(d)** the proportion of the heat evolved in an exothermic reaction that can be converted to various forms of work.

110. The reaction, $2\,Cl_2O(g) \longrightarrow 2\,Cl_2(g) + O_2(g)$ $\Delta_r H° = -161\ \text{kJ mol}^{-1}$, is expected to be **(a)** spontaneous at all temperatures; **(b)** spontaneous at low temperatures, but nonspontaneous at high temperatures; **(c)** nonspontaneous at all temperatures; **(d)** spontaneous at high temperatures only.

111. If $\Delta_r G° = 0$ for a reaction, it must also be true that **(a)** $K = 0$; **(b)** $K = 1$; **(c)** $\Delta_r H° = 0$; **(d)** $\Delta_r S° = 0$; **(e)** the equilibrium activities of the reactants and products do not depend on the initial conditions.

112. Two correct statements about the reversible reaction $N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$ are **(a)** $K = K_p$; **(b)** the equilibrium amount of NO increases with an increased total gas pressure; **(c)** the equilibrium amount of NO increases if an equilibrium mixture is transferred from a 10.0 L container to a 20.0 L container; **(d)** $K = K_c$; **(e)** the composition of an equilibrium mixture of the gases is independent of the temperature.

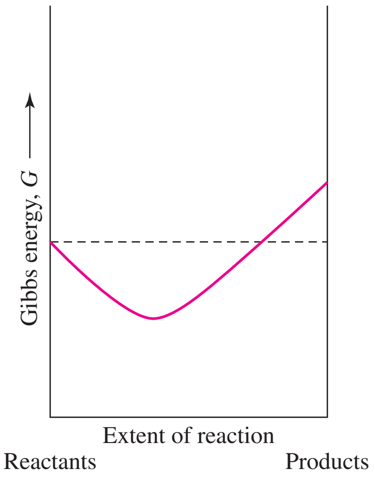
113. *Without performing detailed calculations,* indicate whether any of the following reactions would occur to a measurable extent at 298 K.

(a) Conversion of dioxygen to ozone:

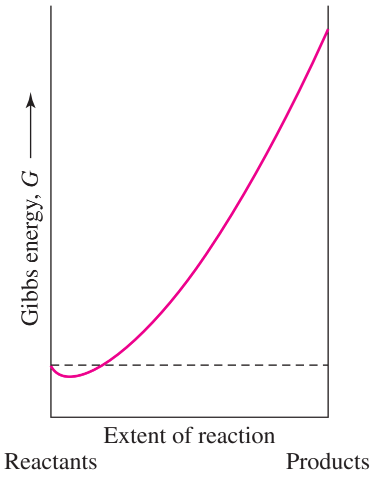
$$3\,O_2(g) \longrightarrow 2\,O_3(g)$$

(b) Dissociation of N_2O_4 to NO_2:

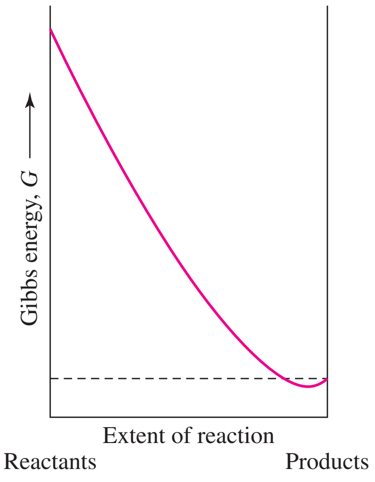
$$N_2O_4(g) \longrightarrow 2\,NO_2(g)$$



(a)



(b)



(c)

(c) Formation of BrCl:

$$Br_2(l) + Cl_2(g) \longrightarrow 2\,BrCl(g)$$

114. Explain briefly why
(a) the change in entropy in a system is not always a suitable criterion for spontaneous change;
(b) $\Delta_r G°$ is so important in dealing with the question of spontaneous change, even though the conditions employed in a reaction are very often nonstandard.

115. A handbook lists the following standard enthalpies of formation at 298 K for cyclopentane, C_5H_{10}: $\Delta_f H°[C_5H_{10}(l)] = -105.9$ kJ mol^{-1} and $\Delta_f H°[C_5H_{10}(g)] = -77.2$ kJ mol^{-1}.
(a) Estimate the normal boiling point of cyclopentane.
(b) Estimate $\Delta_r G°$ for the vaporization of cyclopentane at 298 K.
(c) Comment on the significance of the sign of $\Delta_r G°$ at 298 K.

116. Consider the reaction $NH_4NO_3(s) \longrightarrow N_2O(g) + 2\,H_2O(l)$ at 298 K.
(a) Is the forward reaction endothermic or exothermic?
(b) What is the value of $\Delta_r G°$ at 298 K?
(c) What is the value of K at 298 K?
(d) Does the reaction tend to occur spontaneously at temperatures above 298 K, below 298 K, both, or neither?

117. Which of the following graphs of Gibbs energy versus the extent of reaction represents an equilibrium constant closest to 1?

118. At room temperature and normal atmospheric pressure, is the entropy of the universe positive, negative, or zero for the transition of carbon dioxide solid to liquid?