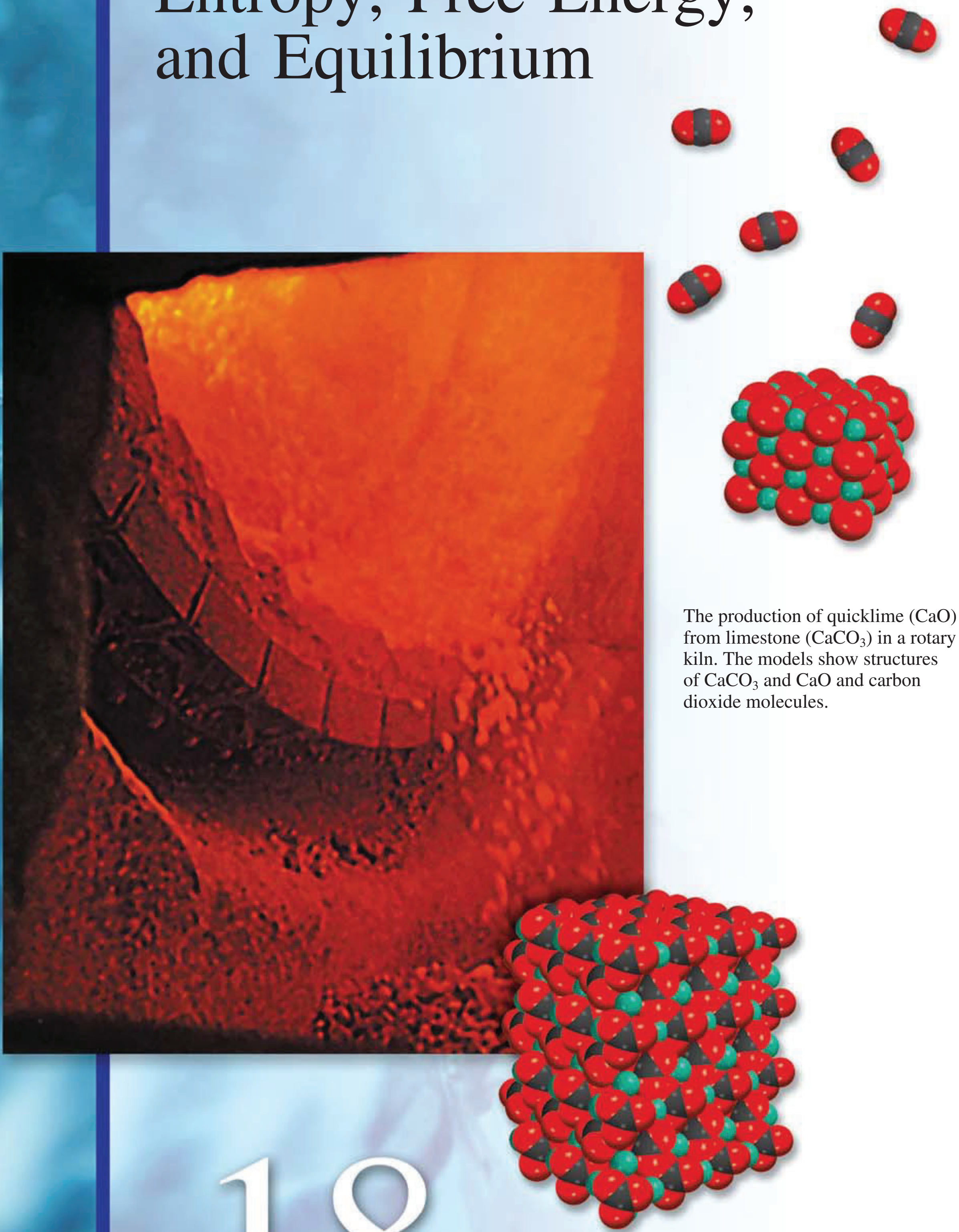
Entropy, Free Energy, and Equilibrium



The production of quicklime (CaO) from limestone ($CaCO_3$) in a rotary kiln. The models show structures of $CaCO_3$ and CaO and carbon dioxide molecules.

18

Chapter Outline

A Look Ahead

- This chapter begins with a discussion of the three laws of thermodynamics and the nature of spontaneous processes. (18.1 and 18.2)
- We then see that entropy is the thermodynamic function for predicting the spontaneity of a reaction. On a molecular level, the entropy of a system can in principle be calculated from the number of microstates associated with the system. We learn that in practice entropy is determined by calorimetric methods and standard entropy values are known for many substances. (18.3)
- The second law of thermodynamics states that the entropy of the universe increases in a spontaneous process and remains unchanged in an equilibrium process. We learn ways to calculate the entropy change of a system and of the surroundings, which together make up for the change in the entropy of the universe. We also discuss the third law of thermodynamics, which enables us to determine the absolute value of entropy of a substance. (18.4)
- We see that a new thermodynamic function called Gibbs free energy is needed to focus on the system. The change in Gibbs free energy can be used to predict spontaneity and equilibrium. For changes carried out under standard-state conditions, the change in Gibbs free energy is related to the equilibrium constant of a reaction. (18.5 and 18.6)
- The chapter concludes with a discussion of how thermodynamics is applied to living systems. We see that the principle of coupled reactions plays a crucial role in many biological processes. (18.7)

Student Interactive Activities

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Chapter Summary

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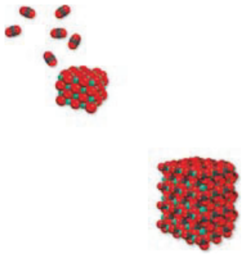
Thermodynamics is an extensive and far-reaching scientific discipline that deals with the interconversion of heat and other forms of energy. Thermodynamics enables us to use information gained from experiments on a system to draw conclusions about other aspects of the same system without further experimentation. For example, we saw in Chapter 6 that it is possible to calculate the enthalpy of reaction from the standard enthalpies of formation of the reactant and product molecules. This chapter introduces the second law of thermodynamics and the Gibbs free-energy function. It also discusses the relationship between Gibbs free energy and chemical equilibrium.



18.1 The Three Laws of Thermodynamics

In Chapter 6 we encountered the first of three laws of thermodynamics, which says that energy can be converted from one form to another, but it cannot be created or destroyed. One measure of these changes is the amount of heat given off or absorbed by a system during a constant-pressure process, which chemists define as a change in enthalpy (ΔH).

The second law of thermodynamics explains why chemical processes tend to favor one direction. The third law is an extension of the second law and will be examined briefly in Section 18.4.

18.2 Spontaneous Processes

A spontaneous reaction does not necessarily mean an instantaneous reaction.

One of the main objectives in studying thermodynamics, as far as chemists are concerned, is to be able to predict whether or not a reaction will occur when reactants are brought together under a specific set of conditions (for example, at a certain temperature, pressure, and concentration). This knowledge is important whether one is synthesizing compounds in a research laboratory, manufacturing chemicals on an industrial scale, or trying to understand the intricate biological processes in a cell. A reaction that *does* occur under the given set of conditions is called a *spontaneous reaction.* If a reaction does not occur under specified conditions, it is said to be nonspontaneous. We observe spontaneous physical and chemical processes every day, including many of the following examples:

- A waterfall runs downhill, but never up, spontaneously.
- A lump of sugar spontaneously dissolves in a cup of coffee, but dissolved sugar does not spontaneously reappear in its original form.
- Water freezes spontaneously below 0°C, and ice melts spontaneously above 0°C (at 1 atm).
- Heat flows from a hotter object to a colder one, but the reverse never happens spontaneously.
- The expansion of a gas into an evacuated bulb is a spontaneous process [Figure 18.1(a)]. The reverse process, that is, the gathering of all the molecules into one bulb, is not spontaneous [Figure 18.1(b)].
- A piece of sodium metal reacts violently with water to form sodium hydroxide and hydrogen gas. However, hydrogen gas does not react with sodium hydroxide to form water and sodium.
- Iron exposed to water and oxygen forms rust, but rust does not spontaneously change back to iron.

A spontaneous and a nonspontaneous process.

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These examples show that processes that occur spontaneously in one direction cannot, under the same conditions, also take place spontaneously in the opposite direction.

If we assume that spontaneous processes occur so as to decrease the energy of a system, we can explain why a ball rolls downhill and why springs in a clock unwind. Similarly, a large number of exothermic reactions are spontaneous. An example is the combustion of methane:

Because of activation energy barrier, an input of energy is needed to get this reaction going at an observable rate.

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H^\circ = -890.4 \text{ kJ/mol}$$

Another example is the acid-base neutralization reaction:

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l) \qquad \Delta H^\circ = -56.2 \text{ kJ/mol}$$

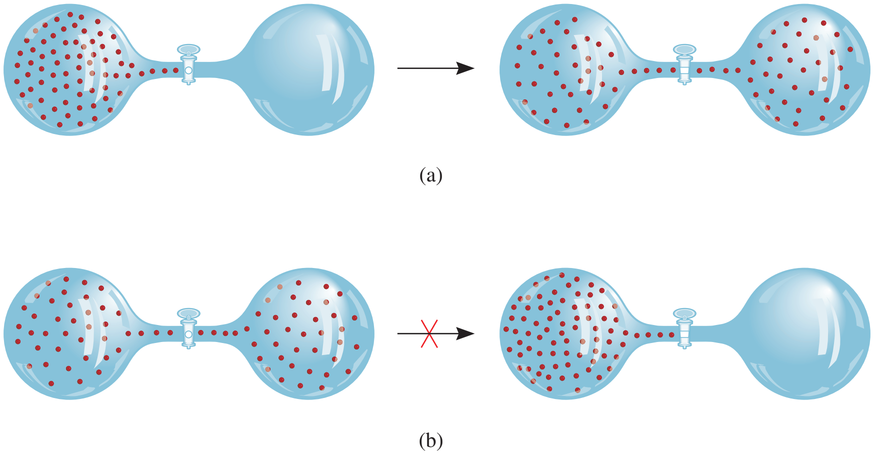


Figure 18.1 *(a) A spontaneous process. After the valve is opened, the molecules distribute evenly between the two bulbs. (b) A nonspontaneous process. After the valve is opened, the molecules preferentially gather in one bulb.*

But consider a solid-to-liquid phase transition such as

$$H_2O(s) \longrightarrow H_2O(l) \qquad \Delta H^\circ = 6.01\ \text{kJ/mol}$$

In this case, the assumption that spontaneous processes always decrease a system's energy fails. Experience tells us that ice melts spontaneously above 0°C even though the process is endothermic. Another example that contradicts our assumption is the dissolution of ammonium nitrate in water:

$$NH_4NO_3(s) \xrightarrow{H_2O} NH_4^+(aq) + NO_3^-(aq) \qquad \Delta H^\circ = 25\ \text{kJ/mol}$$

This process is spontaneous, and yet it is also endothermic. The decomposition of mercury(II) oxide is an endothermic reaction that is nonspontaneous at room temperature, but it becomes spontaneous when the temperature is raised:

$$2HgO(s) \longrightarrow 2Hg(l) + O_2(g) \qquad \Delta H^\circ = 90.7\ \text{kJ/mol}$$

When heated, HgO decomposes to give Hg and O_2.

From a study of the examples mentioned and many more cases, we come to the following conclusion: Exothermicity favors the spontaneity of a reaction but does not guarantee it. Just as it is possible for an endothermic reaction to be spontaneous, it is possible for an exothermic reaction to be nonspontaneous. In other words, we cannot decide whether or not a chemical reaction will occur spontaneously solely on the basis of energy changes in the system. To make this kind of prediction we need another thermodynamic quantity, which turns out to be *entropy.*

18.3 Entropy

In order to predict the spontaneity of a process, we need to introduce a new thermodynamic quantity called entropy. ***Entropy (S)*** is often described as *a measure of how spread out or dispersed the energy of a system is among the different possible ways that system can contain energy.* The greater the dispersal, the greater is the entropy. Most processes are accompanied by a change in entropy. A cup of hot water has a certain amount of entropy due to the dispersal of energy among the various energy states of the water molecules (for example, energy states associated with the translational, rotational, and vibrational motions of the water molecules). If left standing on a table, the water loses heat to the cooler surroundings. Consequently, there is an overall increase in entropy because of the dispersal of energy over a great many energy states of the air molecules.

As another example, consider the situation depicted in Figure 18.1. Before the valve is opened, the system possesses a certain amount of entropy. Upon opening the valve, the gas molecules now have access to the combined volume of both bulbs. A larger volume for movement results in a narrowing of the gap between translational energy levels of the molecules. Consequently, the entropy of the system increases because closely spaced energy levels leads to a greater dispersal among the energy levels.

Quantum mechanical analysis shows that the spacing between translational energy levels is inversely proportional to the volume of the container and the mass of the molecules.

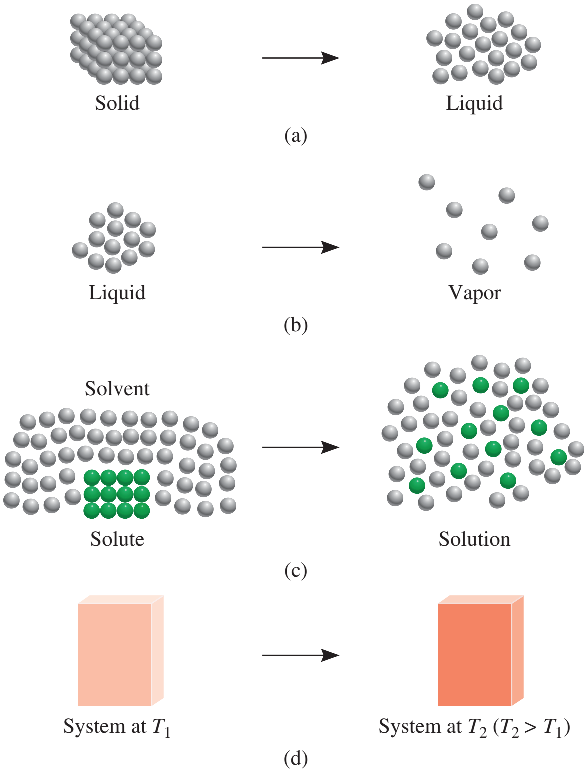
Changes in Entropy

Earlier we described the increase in entropy of a system as a result of the increase in the dispersal of energy. There is a connection between the qualitative description of entropy in terms of dispersal of energy.

Next, we will study several processes that lead to a change in entropy of a system in terms of the change in the number of microstates of the system.

Consider the situations shown in Figure 18.3. In a solid, the atoms or molecules are confined to fixed positions and the number of microstates is small. Upon melting, these atoms or molecules can occupy many more positions as they move away from the lattice points. Consequently, the number of microstates increases because there are now many more ways to arrange the particles. Therefore, we predict this “order ⟶ disorder” phase transition to result in an increase in entropy because the number of microstates has increased. Similarly, we predict the vaporization process will also lead to an increase in the entropy of the system. The increase will be considerably greater than that for melting, however, because molecules in the gas phase occupy much more space, and therefore there are far more microstates than in the liquid phase. The solution process usually leads to an increase in entropy. When a sugar crystal dissolves in water, the highly ordered structure of the solid and part of the ordered structure of

Figure 18.3 *Processes that lead to an increase in entropy of the system: (a) melting:* $S_{liquid} > S_{solid}$; *(b) vaporization:* $S_{vapor} > S_{liquid}$; *(c) dissolving:* $S_{soln} > S_{solute} + S_{solvent}$; *(d) heating:* $S_{T_2} > S_{T_1}$.

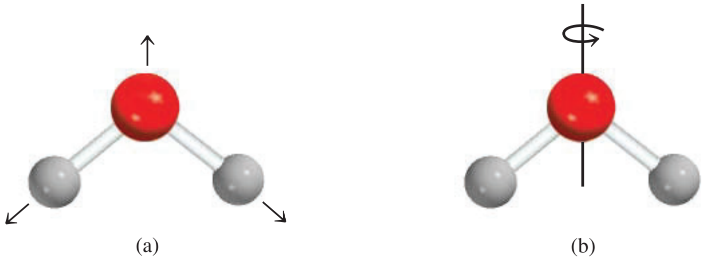


water break down. Thus, the solution has a greater number of microstates than the pure solute and pure solvent combined. When an ionic solid such as NaCl dissolves in water, there are two contributions to entropy increase: the solution process (mixing of solute with solvent) and the dissociation of the compound into ions:

$$NaCl(s) \xrightarrow{H_2O} Na^+(aq) + Cl^-(aq)$$

More particles lead to a greater number of microstates. However, we must also consider hydration, which causes water molecules to become more ordered around the ions. This process decreases entropy because it reduces the number of microstates of the solvent molecules. For small, highly charged ions such as $A1^{3+}$ and Fe^{3+}, the decrease in entropy due to hydration can outweigh the increase in entropy due to mixing and dissociation so that the entropy change for the overall process can actually be negative. Heating also increases the entropy of a system. In addition to translational motion, molecules can also execute rotational motions and vibrational motions (Figure 18.4). As

Figure 18.4 *(a) A vibrational motion in a water molecule. The atoms are displaced as shown by the arrows and then reverse their directions to complete a cycle of vibration. (b) A rotational motion of a water molecule about an axis through the oxygen atom. The molecule can also vibrate and rotate in other ways.*



the temperature is increased, the energies associated with all types of molecular motion increase. This increase in energy is distributed or dispersed among the quantized energy levels. Consequently, more microstates become available at a higher temperature; therefore, the entropy of a system always increases with increasing temperature.

Standard Entropy

Equation (18.1) provides a useful molecular interpretation of entropy, but is normally not used to calculate the entropy of a system because it is difficult to determine the number of microstates for a macroscopic system containing many molecules. Instead, entropy is obtained by calorimetric methods. In fact, as we will see shortly, it is possible to determine the absolute value of entropy of a substance, called absolute entropy, something we cannot do for energy or enthalpy. *Standard entropy* is the absolute entropy of a substance at 1 atm and 25°C. (Recall that the standard state refers only to 1 atm. The reason for specifying 25°C is that many processes are carried out at room temperature.) Table 18.1 lists standard entropies of a few elements and compounds; Appendix 3 provides a more extensive listing.[†] The units of entropy are J/K or J/K · mol for 1 mole of the substance. We use joules rather than kilojoules because entropy values are typically quite small. Entropies of elements and compounds are all positive (that is, $S° > 0$). By contrast, the standard enthalpy of formation (ΔH_f°) for elements in their stable form is arbitrarily set equal to zero, and for compounds, it may be positive or negative.

Referring to Table 18.1, we see that the standard entropy of water vapor is greater than that of liquid water. Similarly, bromine vapor has a higher standard entropy than liquid bromine, and iodine vapor has a greater standard entropy than solid iodine. For different substances in the same phase, molecular complexity determines which ones have higher entropies. Both diamond and graphite are solids, but diamond has a more ordered structure and hence a smaller number of microstates (see Figure 11.28). Therefore, diamond has a smaller standard entropy than graphite. Consider the natural gases methane and ethane. Ethane has a more complex structure and hence more ways to execute molecular motions, which also increase its microstates. Therefore, ethane has a greater standard entropy than methane. Both helium and neon are monatomic gases, which cannot execute rotational or vibrational motions, but neon has a greater standard entropy than helium because its molar mass is greater. Heavier atoms have more closely spaced energy levels so there is a greater distribution of the atoms' energy among the levels. Consequently, there are more microstates associated with these atoms.

TABLE 18.1

Standard Entropy Values ($S°$) for Some Substances at 25°C

Substance	$S°$ (J/K · mol)
$H_2O(l)$	69.9
$H_2O(g)$	188.7
$Br_2(l)$	152.3
$Br_2(g)$	245.3
$I_2(s)$	116.7
$I_2(g)$	260.6
C (diamond)	2.4
C (graphite)	5.69
CH_4 (methane)	186.2
C_2H_6 (ethane)	229.5
He(g)	126.1
Ne(g)	146.2

The spinning motion of an atom about its own axis does not constitute a rotational motion because it does not displace the position of the nucleus.

EXAMPLE 18.1

Predict whether the entropy change is greater or less than zero for each of the following processes: (a) freezing ethanol, (b) evaporating a beaker of liquid bromine at room temperature, (c) dissolving glucose in water, (d) cooling nitrogen gas from 80°C to 20°C.

(Continued)


Bromine is a fuming liquid at room temperature.

[†] Because the entropy of an individual ion cannot be studied experimentally, chemists arbitrarily assign a zero value of entropy for the hydrogen ion in solution. Based on this scale, one can then determine the entropy of the chloride ion (from measurements on HCl), which in turn enables one to determine the entropy of the sodium ion (from measurements on NaCl), and so on. From Appendix 3 you will note that some ions have positive entropy values, while others have negative values. The signs are determined by the extent of hydration relative to the hydrogen ion. If an ion has a greater extent of hydration than the hydrogen ion, then the entropy of the ion has a negative value. The opposite holds for ions with positive entropies.

Strategy To determine the entropy change in each case, we examine whether the number of microstates of the system increases or decreases. The sign of ΔS will be positive if there is an increase in the number of microstates and negative if the number of microstates decreases.

Solution (a) Upon freezing, the ethanol molecules are held rigid in position. This phase transition reduces the number of microstates and therefore the entropy decreases; that is, $\Delta S < 0$.

(b) Evaporating bromine increases the number of microstates because the Br_2 molecules can occupy many more positions in nearly empty space. Therefore, $\Delta S > 0$.

(c) Glucose is a nonelectrolyte. The solution process leads to a greater dispersal of matter due to the mixing of glucose and water molecules so we expect $\Delta S > 0$.

(d) The cooling process decreases various molecular motions. This leads to a decrease in microstates and so $\Delta S < 0$.

Practice Exercise How does the entropy of a system change for each of the following processes? (a) condensing water vapor, (b) forming sucrose crystals from a supersaturated solution, (c) heating hydrogen gas from 60°C to 80°C, and (d) subliming dry ice.

18.4 The Second Law of Thermodynamics

Just talking about entropy increases its value in the universe.

The connection between entropy and the spontaneity of a reaction is expressed by the ***second law of thermodynamics:*** *The entropy of the universe increases in a spontaneous process and remains unchanged in an equilibrium process*. Because the universe is made up of the system and the surroundings, the entropy change in the universe (ΔS_{univ}) for any process is the *sum* of the entropy changes in the system (ΔS_{sys}) and in the surroundings (ΔS_{surr}). Mathematically, we can express the second law of thermodynamics as follows:

For a spontaneous process:
$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0 \tag{18.4}$$

For an equilibrium process:
$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 0 \tag{18.5}$$

For a spontaneous process, the second law says that ΔS_{univ} must be greater than zero, but it does not place a restriction on either ΔS_{sys} or ΔS_{surr}. Thus, it is possible for either ΔS_{sys} or ΔS_{surr} to be negative, as long as the sum of these two quantities is greater than zero. For an equilibrium process, ΔS_{univ} is zero. In this case, ΔS_{sys} and ΔS_{surr} must be equal in magnitude, but opposite in sign. What if for some hypothetical process we find that ΔS_{univ} is negative? What this means is that the process is not spontaneous in the direction described. Rather, it is spontaneous in the *opposite* direction.

Entropy Changes in the System

To calculate ΔS_{univ}, we need to know both ΔS_{sys} and ΔS_{surr}. Let us focus first on ΔS_{sys}. Suppose that the system is represented by the following reaction:

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

As is the case for the enthalpy of a reaction [see Equation (6.18)], the ***standard entropy of reaction*** ΔS°_{rxn} is given by *the difference in standard entropies between products and reactants:*

$$\Delta S^\circ_{\text{rxn}} = [cS^\circ(\text{C}) + dS^\circ(\text{D})] - [aS^\circ(\text{A}) + bS^\circ(\text{B})] \tag{18.6}$$

or, in general, using Σ to represent summation and m and n for the stoichiometric coefficients in the reaction

$$\Delta S^\circ_{\text{rxn}} = \Sigma nS^\circ(\text{products}) - \Sigma mS^\circ(\text{reactants}) \tag{18.7}$$

The standard entropy values of a large number of compounds have been measured in J/K · mol. To calculate $\Delta S^\circ_{\text{rxn}}$ (which is ΔS_{sys}), we look up their values in Appendix 3 and proceed according to Example 18.2.

EXAMPLE 18.2

From the standard entropy values in Appendix 3, calculate the standard entropy changes for the following reactions at 25°C.

(a) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$
(b) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$
(c) $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$

Strategy To calculate the standard entropy of a reaction, we look up the standard entropies of reactants and products in Appendix 3 and apply Equation (18.7). As in the calculation of enthalpy of reaction [see Equation (6.18)], the stoichiometric coefficients have no units, so $\Delta S^\circ_{\text{rxn}}$ is expressed in units of J/K · mol.

Solution

(a)
$$\begin{aligned}\Delta S^\circ_{\text{rxn}} &= [S^\circ(\text{CaO}) + S^\circ(\text{CO}_2)] - [S^\circ(\text{CaCO}_3)]\\ &= [(39.8\ \text{J/K}\cdot\text{mol}) + (213.6\ \text{J/K}\cdot\text{mol})] - (92.9\ \text{J/K}\cdot\text{mol})\\ &= 160.5\ \text{J/K}\cdot\text{mol}\end{aligned}$$

Thus, when 1 mole of $CaCO_3$ decomposes to form 1 mole of CaO and 1 mole of gaseous CO_2, there is an increase in entropy equal to 160.5 J/K · mol.

(b)
$$\begin{aligned}\Delta S^\circ_{\text{rxn}} &= [2S^\circ(\text{NH}_3)] - [S^\circ(\text{N}_2) + 3S^\circ(\text{H}_2)]\\ &= (2)(193\ \text{J/K}\cdot\text{mol}) - [(192\ \text{J/K}\cdot\text{mol}) + (3)(131\ \text{J/K}\cdot\text{mol})]\\ &= -199\ \text{J/K}\cdot\text{mol}\end{aligned}$$

This result shows that when 1 mole of gaseous nitrogen reacts with 3 moles of gaseous hydrogen to form 2 moles of gaseous ammonia, there is a decrease in entropy equal to −199 J/K · mol.

(c)
$$\begin{aligned}\Delta S^\circ_{\text{rxn}} &= [2S^\circ(\text{HCl})] - [S^\circ(\text{H}_2) + S^\circ(\text{Cl}_2)]\\ &= (2)(187\ \text{J/K}\cdot\text{mol}) - [(131\ \text{J/K}\cdot\text{mol}) + (223\ \text{J/K}\cdot\text{mol})]\\ &= 20\ \text{J/K}\cdot\text{mol}\end{aligned}$$

Thus, the formation of 2 moles of gaseous HCl from 1 mole of gaseous H_2 and 1 mole of gaseous Cl_2 results in a small increase in entropy equal to 20 J/K · mol.

Comment The $\Delta S^\circ_{\text{rxn}}$ values all apply to the system.

Similar problems: 18.11, 18.12.

(Continued)

Practice Exercise Calculate the standard entropy change for the following reactions at 25°C:

(a) $2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$
(b) $3O_2(g) \longrightarrow 2O_3(g)$
(c) $2NaHCO_3(s) \longrightarrow Na_2CO_3(s) + H_2O(l) + CO_2(g)$

The results of Example 18.2 are consistent with those observed for many other reactions. Taken together, they support the following general rules:

We omit the subscript rxn for simplicity.

- If a reaction produces more gas molecules than it consumes [Example 18.2(a)], $\Delta S°$ is positive.
- If the total number of gas molecules diminishes [Example 18.2(b)], $\Delta S°$ is negative.
- If there is no net change in the total number of gas molecules [Example 18.2(c)], then $\Delta S°$ may be positive or negative, but will be relatively small numerically.

These conclusions make sense, given that gases invariably have greater entropy than liquids and solids. For reactions involving only liquids and solids, predicting the sign of $\Delta S°$ is more difficult, but in many such cases an increase in the total number of molecules and/or ions is accompanied by an increase in entropy.

Example 18.3 shows how knowing the nature of reactants and products makes it possible to predict entropy changes.

EXAMPLE 18.3

Predict whether the entropy change of the system in each of the following reactions is positive or negative.

(a) $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$
(b) $NH_4Cl(s) \longrightarrow NH_3(g) + HCl(g)$
(c) $H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$

Strategy We are asked to predict, not calculate, the sign of entropy change in the reactions. The factors that lead to an increase in entropy are: (1) a transition from a condensed phase to the vapor phase and (2) a reaction that produces more product molecules than reactant molecules in the same phase. It is also important to compare the relative complexity of the product and reactant molecules. In general, the more complex the molecular structure, the greater the entropy of the compound.

Solution (a) Two reactant molecules combine to form one product molecule. Even though H_2O is a more complex molecule than either H_2 and O_2, the fact that there is a net decrease of one molecule and gases are converted to liquid ensures that the number of microstates will be diminished and hence $\Delta S°$ is negative.

(b) A solid is converted to two gaseous products. Therefore, $\Delta S°$ is positive.

(c) The same number of molecules is involved in the reactants as in the product. Furthermore, all molecules are diatomic and therefore of similar complexity. As a result, we cannot predict the sign of $\Delta S°$, but we know that the change must be quite small in magnitude.

Practice Exercise Discuss qualitatively the sign of the entropy change expected for each of the following processes:

(a) $I_2(s) \longrightarrow 2I(g)$
(b) $2Zn(s) + O_2(g) \longrightarrow 2ZnO(s)$
(c) $N_2(g) + O_2(g) \longrightarrow 2NO(g)$

It is important to keep in mind that just because a reaction is spontaneous does not mean that it will occur at an observable rate. The synthesis of ammonia is, in fact, extremely slow at room temperature. Thermodynamics can tell us whether a reaction will occur spontaneously under specific conditions, but it does not say how fast it will occur. Reaction rates are the subject of chemical kinetics (see Chapter 13).

The Third Law of Thermodynamics and Absolute Entropy

According to the ***third law of thermodynamics,*** *the entropy of a perfect crystalline substance is zero at the absolute zero of temperature*. As the temperature increases, the freedom of motion increases and hence also the number of microstates. Thus, the entropy of any substance at a temperature above 0 K is greater than zero. Note also hat if the crystal is impure or if it has defects, then its entropy is greater than zero even at 0 K, because it would not be perfectly ordered and the number of microstates would be greater than one

The important point about the third law of thermodynamics is that it enables us to determine the absolute entropies of substances.

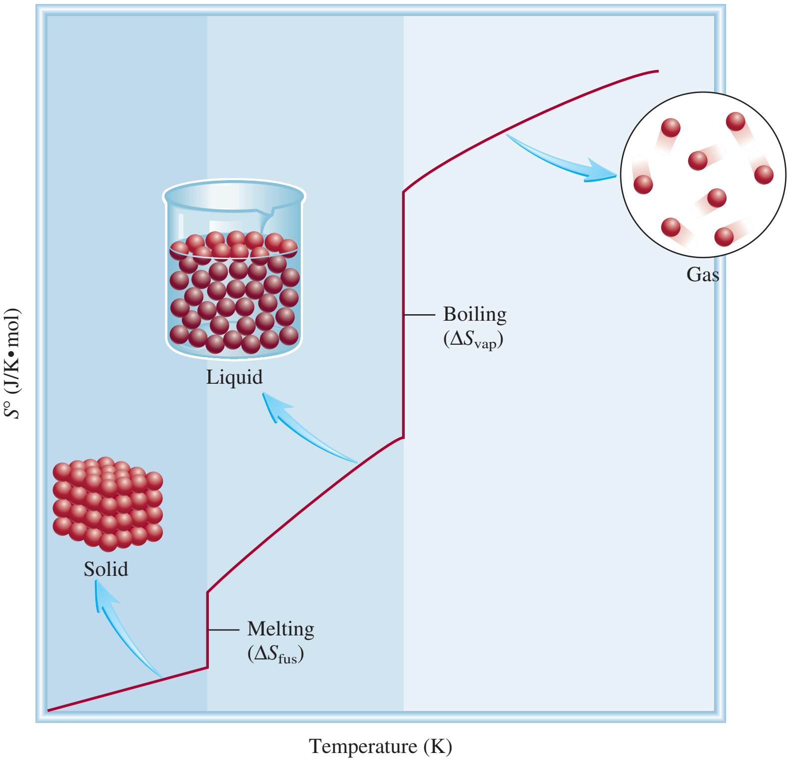


Figure 18.6 *Entropy increase of a substance as the temperature rises from absolute zero.*

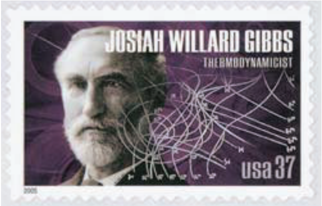
Gibbs Free Energy

The second law of thermodynamics tells us that a spontaneous reaction increases the entropy of the universe; that is, $\Delta S_{\text{univ}} > 0$. In order to determine the sign of ΔS_{univ} for a reaction, however, we would need to calculate both ΔS_{sys} and ΔS_{surr}. In general, we are usually concerned only with what happens in a particular system. Therefore, we need another thermodynamic function to help us determine whether a reaction will occur spontaneously if we consider only the system itself.

The change in free energy (ΔG) of a system for a *constant-temperature* process is

$$\boxed{\Delta G = \Delta H - T\Delta S} \qquad (18.10)$$

The change in unequal sign when we multiply the equation by -1 follows from the fact that $1 > 0$ and $-1 < 0$.



A 2005 commemorative stamp honoring Gibbs.

[†] Josiah Willard Gibbs (1839–1903). American physicist. One of the founders of thermodynamics, Gibbs was a modest and private individual who spent almost all of his professional life at Yale University. Because he published most of his works in obscure journals, Gibbs never gained the eminence that his contemporary and admirer James Maxwell did. Even today, very few people outside of chemistry and physics have ever heard of Gibbs.

The word "free" in the term "free energy" does not mean without cost.

In this context, free energy is *the energy available to do work*. Thus, if a particular reaction is accompanied by a release of usable energy (that is, if ΔG is negative), this fact alone guarantees that it is spontaneous, and there is no need to worry about what happens to the rest of the universe.

Note that we have merely organized the expression for the entropy change of the universe and equating the free-energy change of the system (ΔG) with $-T\Delta S_{\text{univ}}$, so that we can focus on changes in the system. We can now summarize the conditions for spontaneity and equilibrium at constant temperature and pressure in terms of ΔG as follows:

$\Delta G < 0$ The reaction is spontaneous in the forward direction.
$\Delta G > 0$ The reaction is nonspontaneous. The reaction is spontaneous in the opposite direction.
$\Delta G = 0$ The system is at equilibrium. There is no net change.

TABLE 18.2

Conventions for Standard States

State of Matter	Standard State
Gas	1 atm pressure
Liquid	Pure liquid
Solid	Pure solid
Elements*	$\Delta G^\circ_f = 0$
Solution	1 molar concentration

*The most stable allotropic form at 25°C and 1 atm.

Standard Free-Energy Changes

The ***standard free-energy of reaction*** (ΔG°_{rxn}) is *the free-energy change for a reaction when it occurs under standard-state conditions, when reactants in their standard states are converted to products in their standard states*. Table 18.2 summarizes the conventions used by chemists to define the standard states of pure substances as well as solutions. To calculate $\Delta G^\circ_{\text{rxn}}$ we start with the equation

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

The standard free-energy change for this reaction is given by

$$\Delta G^\circ_{\text{rxn}} = [c\Delta G^\circ_{\text{f}}(\text{C}) + d\Delta G^\circ_{\text{f}}(\text{D})] - [a\Delta G^\circ_{\text{f}}(\text{A}) + b\Delta G^\circ_{\text{f}}(\text{B})] \tag{18.11}$$

or, in general,

$$\Delta G^\circ_{\text{rxn}} = \Sigma n\Delta G^\circ_{\text{f}}(\text{products}) - \Sigma m\Delta G^\circ_{\text{f}}(\text{reactants}) \tag{18.12}$$

where m and n are stoichiometric coefficients. The term ΔG°_f is the ***standard free-energy of formation*** of a compound, that is, *the free-energy change that occurs when 1 mole of the compound is synthesized from its elements in their standard states*. For the combustion of graphite:

$$\text{C(graphite)} + \text{O}_2(g) \longrightarrow \text{CO}_2(g)$$

the standard free-energy change [from Equation (18.12)] is

$$\Delta G^\circ_{\text{rxn}} = \Delta G^\circ_{\text{f}}(\text{CO}_2) - [\Delta G^\circ_{\text{f}}(\text{C, graphite}) + \Delta G^\circ_{\text{f}}(\text{O}_2)]$$

As in the case of the standard enthalpy of formation (p. 252), we define the standard free-energy of formation of any element in its stable allotropic form at 1 atm and 25°C as zero. Thus,

$$\Delta G^\circ_{\text{f}}(\text{C, graphite}) = 0 \quad \text{and} \quad \Delta G^\circ_{\text{f}}(\text{O}_2) = 0$$

Therefore, the standard free-energy change for the reaction in this case is equal to the standard free energy of formation of CO_2:

$$\Delta G^\circ_{\text{rxn}} = \Delta G^\circ_{\text{f}}(\text{CO}_2)$$

Appendix 3 lists the values of $\Delta G^\circ_{\text{f}}$ for a number of compounds.

Calculations of standard free-energy changes are handled as shown in Example 18.4.

EXAMPLE 18.4

Calculate the standard free-energy changes for the following reactions at 25°C.

(a) $\text{CH}_4(g) + 2\text{O}_2(g) \longrightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l)$

(b) $2\text{MgO}(s) \longrightarrow 2\text{Mg}(s) + \text{O}_2(g)$

Strategy To calculate the standard free-energy change of a reaction, we look up the standard free energies of formation of reactants and products in Appendix 3 and apply Equation (18.12). Note that all the stoichiometric coefficients have no units so $\Delta G^\circ_{\text{rxn}}$ is expressed in units of kJ/mol, and $\Delta G^\circ_{\text{f}}$ for O_2 is zero because it is the stable allotropic element at 1 atm and 25°C.

Solution (a) According to Equation (18.12), we write

$$\Delta G^\circ_{\text{rxn}} = [\Delta G^\circ_{\text{f}}(\text{CO}_2) + 2\Delta G^\circ_{\text{f}}(\text{H}_2\text{O})] - [\Delta G^\circ_{\text{f}}(\text{CH}_4) + 2\Delta G^\circ_{\text{f}}(\text{O}_2)]$$

We insert the appropriate values from Appendix 3:

$$\begin{aligned}\Delta G^\circ_{\text{rxn}} &= [(-394.4\ \text{kJ/mol}) + (2)(-237.2\ \text{kJ/mol})] - [(-50.8\ \text{kJ/mol}) + (2)(0\ \text{kJ/mol})] \\ &= -818.0\ \text{kJ/mol}\end{aligned}$$

(b) The equation is

$$\Delta G^\circ_{\text{rxn}} = [2\Delta G^\circ_{\text{f}}(\text{Mg}) + \Delta G^\circ_{\text{f}}(\text{O}_2)] - [2\Delta G^\circ_{\text{f}}(\text{MgO})]$$

From data in Appendix 3 we write

$$\begin{aligned}\Delta G^\circ_{\text{rxn}} &= [(2)(0\ \text{kJ/mol}) + (0\ \text{kJ/mol})] - [(2)(-569.6\ \text{kJ/mol})] \\ &= 1139\ \text{kJ/mol}\end{aligned}$$

Similar problems: 18.17, 18.18.

Practice Exercise Calculate the standard free-energy changes for the following reactions at 25°C:

(a) $\text{H}_2(g) + \text{Br}_2(l) \longrightarrow 2\text{HBr}(g)$

(b) $2\text{C}_2\text{H}_6(g) + 7\text{O}_2(g) \longrightarrow 4\text{CO}_2(g) + 6\text{H}_2\text{O}(l)$

Applications of Equation (18.10)

In order to predict the sign of ΔG, according to Equation (18.10), we need to know both ΔH and ΔS. A negative ΔH (an exothermic reaction) and a positive ΔS (a reaction that results in an increase in the microstates of the system) tend to make ΔG negative, although temperature may also influence the *direction* of a spontaneous reaction. The four possible outcomes of this relationship are

- If both ΔH and ΔS are positive, then ΔG will be negative only when the $T\Delta S$ term is greater in magnitude than ΔH. This condition is met when T is large.
- If ΔH is positive and ΔS is negative, ΔG will always be positive, regardless of temperature.

TABLE 18.3 Factors Affecting the Sign of ΔG in the Relationship $\Delta G = \Delta H - T\Delta S$

ΔH	ΔS	ΔG	Example
+	+	Reaction proceeds spontaneously at high temperatures. At low temperatures, reaction is spontaneous in the reverse direction.	$2HgO(s) \longrightarrow 2Hg(l) + O_2(g)$
+	−	ΔG is always positive. Reaction is spontaneous in the reverse direction at all temperatures.	$3O_2(g) \longrightarrow 2O_3(g)$
−	+	ΔG is always negative. Reaction proceeds spontaneously at all temperatures.	$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$
−	−	Reaction proceeds spontaneously at low temperatures. At high temperatures, the reverse reaction becomes spontaneous.	$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$

- If ΔH is negative and ΔS is positive, then ΔG will always be negative regardless of temperature.
- If ΔH is negative and ΔS is negative, then ΔG will be negative only when $T\Delta S$ is smaller in magnitude than ΔH. This condition is met when T is small.

The temperatures that will cause ΔG to be negative for the first and last cases depend on the actual values of ΔH and ΔS of the system. Table 18.3 summarizes the effects of the possibilities just described.

In Section 18.6 we will see an equation relating $\Delta G°$ to the equilibrium constant K.

Before we apply the change in free energy to predict reaction spontaneity, it is useful to distinguish between ΔG and $\Delta G°$. Suppose we carry out a reaction in solution with all the reactants in their standard states (that is, all at 1 *M* concentration). As soon as the reaction starts, the standard-state condition no longer exists for the reactants or the products because their concentrations are different from 1 *M*. Under nonstandard state conditions, we must use the sign of ΔG rather than that of $\Delta G°$ to predict the direction of the reaction. The sign of $\Delta G°$, on the other hand, tells us whether the products or the reactants are favored when the reacting system reaches equilibrium. Thus, a negative value of $\Delta G°$ indicates that the reaction favors product formation whereas a positive value of $\Delta G°$ indicates that there will be more reactants than products at equilibrium.

We will now consider two specific applications of Equation (18.10).

Temperature and Chemical Reactions

Calcium oxide (CaO), also called quicklime, is an extremely valuable inorganic substance used in steelmaking, production of calcium metal, the paper industry, water treatment, and pollution control. It is prepared by decomposing limestone ($CaCO_3$) in a kiln at a high temperature (see p. 800):

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

Le Châtelier's principle predicts that the forward, endothermic reaction is favored by heating.

The reaction is reversible, and CaO readily combines with CO_2 to form $CaCO_3$. The pressure of CO_2 in equilibrium with $CaCO_3$ and CaO increases with temperature. In the industrial preparation of quicklime, the system is never maintained at equilibrium;

rather, CO_2 is constantly removed from the kiln to shift the equilibrium from left to right, promoting the formation of calcium oxide.

The important information for the practical chemist is the temperature at which the decomposition of $CaCO_3$ becomes appreciable (that is, the temperature at which the reaction begins to favor products). We can make a reliable estimate of that temperature as follows. First we calculate ΔH° and ΔS° for the reaction at 25°C, using the data in Appendix 3. To determine ΔH° we apply Equation (6.18):

$$\begin{aligned}\Delta H^\circ &= [\Delta H_f^\circ(\mathrm{CaO}) + \Delta H_f^\circ(\mathrm{CO_2})] - [\Delta H_f^\circ(\mathrm{CaCO_3})]\\ &= [(-635.6\ \mathrm{kJ/mol}) + (-393.5\ \mathrm{kJ/mol})] - (-1206.9\ \mathrm{kJ/mol})\\ &= 177.8\ \mathrm{kJ/mol}\end{aligned}$$

Next we apply Equation (18.6) to find ΔS°:

$$\begin{aligned}\Delta S^\circ &= [S^\circ(\mathrm{CaO}) + S^\circ(\mathrm{CO_2})] - S^\circ(\mathrm{CaCO_3})\\ &= [(39.8\ \mathrm{J/K\cdot mol}) + (213.6\ \mathrm{J/K\cdot mol})] - (92.9\ \mathrm{J/K\cdot mol})\\ &= 160.5\ \mathrm{J/K\cdot mol}\end{aligned}$$

From Equation (18.10),

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

we obtain

$$\begin{aligned}\Delta G^\circ &= 177.8\ \mathrm{kJ/mol} - (298\ \mathrm{K})(160.5\ \mathrm{J/K\cdot mol})\left(\frac{1\ \mathrm{kJ}}{1000\ \mathrm{J}}\right)\\ &= 130.0\ \mathrm{kJ/mol}\end{aligned}$$

Because ΔG° is a large positive quantity, we conclude that the reaction is not favored for product formation at 25°C (or 298 K). Indeed, the pressure of CO_2 is so low at room temperature that it cannot be measured. In order to make ΔG° negative, we first have to find the temperature at which ΔG° is zero; that is,

$$0 = \Delta H^\circ - T\Delta S^\circ$$

or

$$\begin{aligned}T &= \frac{\Delta H^\circ}{\Delta S^\circ}\\ &= \frac{(177.8\ \mathrm{kJ/mol})(1000\ \mathrm{J/1\ kJ})}{160.5\ \mathrm{J/K\cdot mol}}\\ &= 1108\ \mathrm{K\ or\ 835^\circ C}\end{aligned}$$

At a temperature higher than 835°C, ΔG° becomes negative, indicating that the reaction now favors the formation of CaO and CO_2. For example, at 840°C, or 1113 K,

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ\\ &= 177.8\ \mathrm{kJ/mol} - (1113\ \mathrm{K})(160.5\ \mathrm{J/K\cdot mol})\left(\frac{1\ \mathrm{kJ}}{1000\ \mathrm{J}}\right)\\ &= -0.8\ \mathrm{kJ/mol}\end{aligned}$$

Two points are worth making about such a calculation. First, we used the ΔH° and ΔS° values at 25°C to calculate changes that occur at a much higher temperature. Because both ΔH° and ΔS° change with temperature, this approach will not give us an accurate value of ΔG°, but it is good enough for "ballpark" estimates. Second, we should not be misled into thinking that nothing happens below 835°C and that at 835°C $CaCO_3$ suddenly begins to decompose. Far from it. The fact that ΔG° is a positive value at some temperature below 835°C does not mean that no CO_2 is produced, but rather that the pressure of the CO_2 gas formed at that temperature will be below 1 atm (its standard-state value; see Table 18.2). As Figure 18.7 shows, the pressure of CO_2 at first increases very slowly with temperature; it becomes easily measurable above 700°C. The significance of 835°C is that this is the temperature at which the equilibrium pressure of CO_2 reaches 1 atm. Above 835°C, the equilibrium pressure of CO_2 exceeds 1 atm.

The equilibrium constant of this reaction is $K_P = P_{CO_2}$.

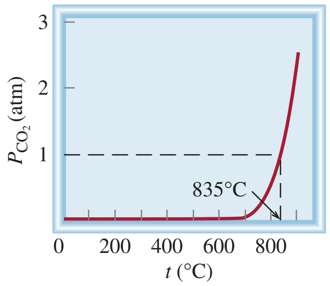


Figure 18.7 *Equilibrium pressure of CO_2 from the decomposition of $CaCO_3$, as a function of temperature. This curve is calculated by assuming that $\Delta H°$ and $\Delta S°$ of the reaction do not change with temperature.*

The melting of ice is an endothermic process (ΔH is positive), and the freezing of water is exothermic (ΔH is negative).

18.6 Free Energy and Chemical Equilibrium

As mentioned earlier, during the course of a chemical reaction not all the reactants and products will be at their standard states. Under this condition, the relationship between ΔG and $\Delta G°$, which can be derived from thermodynamics, is

$$\Delta G = \Delta G° + RT \ln Q \tag{18.13}$$

Note that the units of ΔG and $\Delta G°$ are kJ/mol, where the "per mole" unit cancels that in R.

where R is the gas constant (8.314 J/K · mol), T is the absolute temperature of the reaction, and Q is the reaction quotient (see p. 632). We see that ΔG depends on two quantities: $\Delta G°$ and $RT \ln Q$. For a given reaction at temperature T the value of $\Delta G°$

is fixed but that of $RT \ln Q$ is not, because Q varies according to the composition of the reaction mixture. Let us consider two special cases:

Case 1: A large negative value of $\Delta G°$ will tend to make ΔG also negative. Thus, the net reaction will proceed from left to right until a significant amount of product has been formed. At that point, the $RT \ln Q$ term will become positive enough to match the negative $\Delta G°$ term in magnitude.

Case 2: A large positive $\Delta G°$ term will tend to make ΔG also positive. Thus, the net reaction will proceed from right to left until a significant amount of reactant has been formed. At that point the $RT \ln Q$ term will become negative enough to match the positive $\Delta G°$ term in magnitude.

Sooner or later a reversible reaction will reach equilibrium.

At equilibrium, by definition, $\Delta G = 0$ and $Q = K$, where K is the equilibrium constant. Thus,

$$0 = \Delta G° + RT \ln K$$

or

$$\Delta G° = -RT \ln K \qquad (18.14)$$

In this equation, K_P is used for gases and K_c for reactions in solution. Note that the larger the K is, the more negative $\Delta G°$ is. For chemists, Equation (18.14) is one of the most important equations in thermodynamics because it enables us to find the equilibrium constant of a reaction if we know the change in standard free energy and vice versa.

It is significant that Equation (18.14) relates the equilibrium constant to the *standard* free-energy change $\Delta G°$ rather than to the *actual* free-energy change ΔG. The actual free-energy change of the system varies as the reaction progresses and becomes zero at equilibrium. On the other hand, $\Delta G°$ is a constant for a particular reaction at a given temperature. Figure 18.8 shows plots of the free energy of a reacting system versus the extent of the reaction for two types of reactions. As you can see, if $\Delta G° < 0$, the products are favored over reactants at equilibrium. Conversely, if $\Delta G° > 0$, there will be more reactants than products at equilibrium. Table 18.4

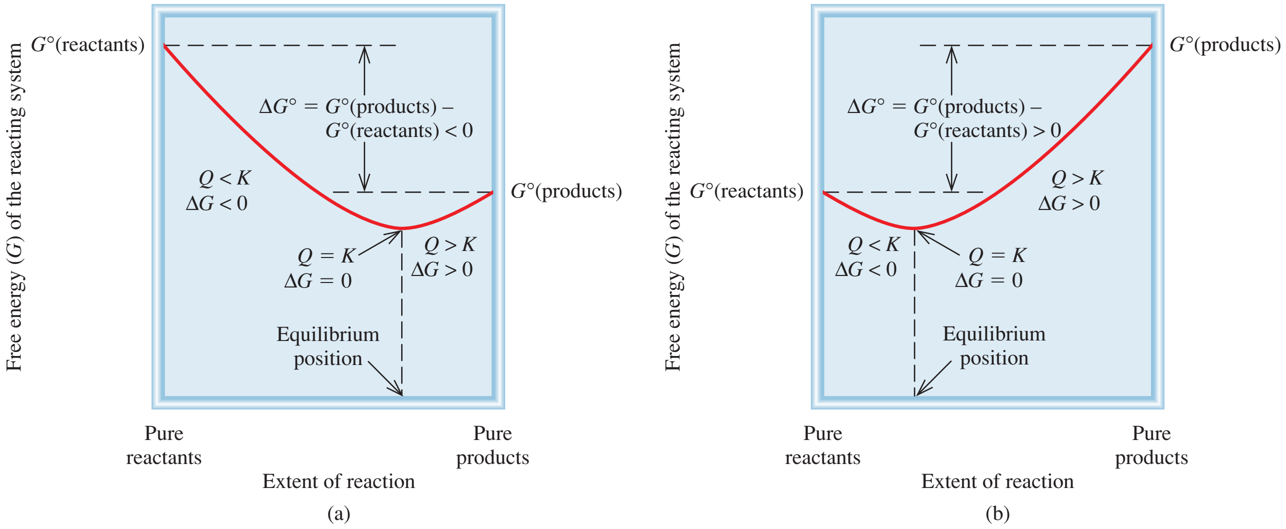


Figure 18.8 *(a) $\Delta G° < 0$. At equilibrium, there is a significant conversion of reactants to products. (b) $\Delta G° > 0$. At equilibrium, reactants are favored over products. In both cases, the net reaction toward equilibrium is from left to right (reactants to products) if $Q < K$ and right to left (products to reactants) if $Q > K$. At equilibrium, $Q = K$.*

TABLE 18.4 Relation Between ΔG° and K as Predicted by the Equation $\Delta G^\circ = -RT \ln K$

K	$\ln K$	ΔG°	Comments
> 1	Positive	Negative	Products are favored over reactants at equilibrium.
$= 1$	0	0	Products and reactants are equally favored at equilibrium.
< 1	Negative	Positive	Reactants are favored over products at equilibrium.

summarizes the three possible relations between ΔG° and K, as predicted by Equation (18.14). Remember this important distinction: It is the sign of ΔG and not that of ΔG° that determines the direction of reaction spontaneity. The sign of ΔG° only tells us the relative amounts of products and reactants when equilibrium is reached, not the direction of the net reaction.

For reactions having very large or very small equilibrium constants, it is generally very difficult, if not impossible, to measure the K values by monitoring the concentrations of all the reacting species. Consider, for example, the formation of nitric oxide from molecular nitrogen and molecular oxygen:

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

At 25°C, the equilibrium constant K_P is

$$K_P = \frac{P_{NO}^2}{P_{N_2}P_{O_2}} = 4.0 \times 10^{-31}$$

The very small value of K_P means that the concentration of NO at equilibrium will be exceedingly low. In such a case the equilibrium constant is more conveniently obtained from ΔG°. (As we have seen, ΔG° can be calculated from ΔH° and ΔS°.) On the other hand, the equilibrium constant for the formation of hydrogen iodide from molecular hydrogen and molecular iodine is near unity at room temperature:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

For this reaction, it is easier to measure K_P and then calculate ΔG° using Equation (18.14) than to measure ΔH° and ΔS° and use Equation (18.10).

Examples 18.6–18.8 illustrate the use of Equations (18.13) and (18.14).

EXAMPLE 18.6

Using data listed in Appendix 3, calculate the equilibrium constant (K_P) for the following reaction at 25°C:

$$2H_2O(l) \rightleftharpoons 2H_2(g) + O_2(g)$$

Strategy According to Equation (18.14), the equilibrium constant for the reaction is related to the standard free-energy change; that is, $\Delta G^\circ = -RT \ln K$. Therefore, we first need to calculate ΔG° by following the procedure in Example 18.4. Then we can calculate K_P. What temperature unit should be used?

(Continued)

Solution According to Equation (18.12),

$$\begin{aligned}\Delta G^\circ_{\text{rxn}} &= [2\Delta G^\circ_f(H_2) + \Delta G^\circ_f(O_2)] - [2\Delta G^\circ_f(H_2O)]\\ &= [(2)(0\text{ kJ/mol}) + (0\text{ kJ/mol})] - [(2)(-237.2\text{ kJ/mol})]\\ &= 474.4\text{ kJ/mol}\end{aligned}$$

Using Equation (18.14)

$$\begin{aligned}\Delta G^\circ_{\text{rxn}} &= -RT\ln K_P\\ 474.4\text{ kJ/mol} \times \frac{1000\text{ J}}{1\text{ kJ}} &= -(8.314\text{ J/K}\cdot\text{mol})(298\text{ K})\ln K_P\\ \ln K_P &= -191.5\\ K_P &= e^{-191.5} = 7 \times 10^{-84}\end{aligned}$$

To calculate K_P, enter −191.5 on your calculator and then press the key labeled "e" or "inv(erse) ln *x*."

Comment This extremely small equilibrium constant is consistent with the fact that water does not spontaneously decompose into hydrogen and oxygen gases at 25°C. Thus, a large positive ΔG° favors reactants over products at equilibrium.

EXAMPLE 18.7

In Chapter 16 we discussed the solubility product of slightly soluble substances. Using the solubility product of silver chloride at 25°C (1.6×10^{-10}), calculate ΔG° for the process

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

Strategy According to Equation (18.14), the equilibrium constant for the reaction is related to standard free-energy change; that is, $\Delta G^\circ = -RT\ln K$. Because this is a heterogeneous equilibrium, the solubility product (K_{sp}) is the equilibrium constant. We calculate the standard free-energy change from the K_{sp} value of AgCl. What temperature unit should be used?

Solution The solubility equilibrium for AgCl is

$$\begin{aligned}&AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)\\ &K_{sp} = [Ag^+][Cl^-] = 1.6 \times 10^{-10}\end{aligned}$$

Using Equation (18.14) we obtain

$$\begin{aligned}\Delta G^\circ &= -(8.314\text{ J/K}\cdot\text{mol})(298\text{ K})\ln(1.6 \times 10^{-10})\\ &= 5.6 \times 10^4\text{ J/mol}\\ &= 56\text{ kJ/mol}\end{aligned}$$

Check The large, positive ΔG° indicates that AgCl is slightly soluble and that the equilibrium lies mostly to the left.

Practice Exercise Calculate ΔG° for the following process at 25°C:

$$BaF_2(s) \rightleftharpoons Ba^{2+}(aq) + 2F^-(aq)$$

The K_{sp} of BaF_2 is 1.7×10^{-6}.

EXAMPLE 18.8

The equilibrium constant (K_P) for the reaction

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

is 0.113 at 298 K, which corresponds to a standard free-energy change of 5.40 kJ/mol. In a certain experiment, the initial pressures are $P_{NO_2} = 0.122$ atm and $P_{N_2O_4} = 0.453$ atm. Calculate ΔG for the reaction at these pressures and predict the direction of the net reaction toward equilibrium.

Strategy From the information given we see that neither the reactant nor the product is at its standard state of 1 atm. To determine the direction of the net reaction, we need to calculate the free-energy change under nonstandard-state conditions (ΔG) using Equation (18.13) and the given $\Delta G°$ value. Note that the partial pressures are expressed as dimensionless quantities in the reaction quotient Q_P because they are divided by the standard-state value of 1 atm (see p. 621 and Table 18.2).

Solution Equation (18.13) can be written as

$$\begin{aligned}\Delta G &= \Delta G° + RT \ln Q_P \\ &= \Delta G° + RT \ln \frac{P^2_{NO_2}}{P_{N_2O_4}} \\ &= 5.40 \times 10^3 \text{ J/mol} + (8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K}) \times \ln \frac{(0.122)^2}{0.453} \\ &= 5.40 \times 10^3 \text{ J/mol} - 8.46 \times 10^3 \text{ J/mol} \\ &= -3.06 \times 10^3 \text{ J/mol} = -3.06 \text{ kJ/mol}\end{aligned}$$

Because $\Delta G < 0$, the net reaction proceeds from left to right to reach equilibrium.

Check Note that although $\Delta G° > 0$, the reaction can be made to favor product formation initially by having a small concentration (pressure) of the product compared to that of the reactant. Confirm the prediction by showing that $Q_P < K_P$.

Practice Exercise The $\Delta G°$ for the reaction

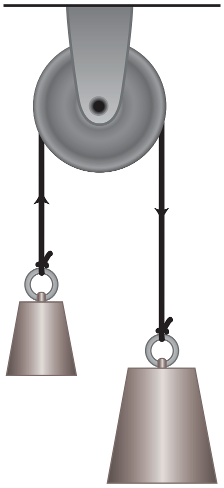
$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

is 2.60 kJ/mol at 25°C. In one experiment, the initial pressures are $P_{H_2} = 4.26$ atm, $P_{I_2} = 0.024$ atm, and $P_{HI} = 0.23$ atm. Calculate ΔG for the reaction and predict the direction of the net reaction.

18.7 Thermodynamics in Living Systems

Many biochemical reactions have a positive $\Delta G°$ value, yet they are essential to the maintenance of life. In living systems these reactions are coupled to an energetically favorable process, one that has a negative $\Delta G°$ value. The principle of *coupled reactions* is based on a simple concept: We can use a thermodynamically favorable reaction to drive an unfavorable one. Consider an industrial process. Suppose we wish to extract zinc from the ore sphalerite (ZnS). The following reaction will not work because it has a large positive $\Delta G°$ value:

$$ZnS(s) \longrightarrow Zn(s) + S(s) \qquad \Delta G° = 198.3 \text{ kJ/mol}$$



A mechanical analog for coupled reactions. We can make the smaller weight move upward (a nonspontaneous process) by coupling it with the falling of a larger weight.

CHEMISTRY in Action

The Thermodynamics of a Rubber Band

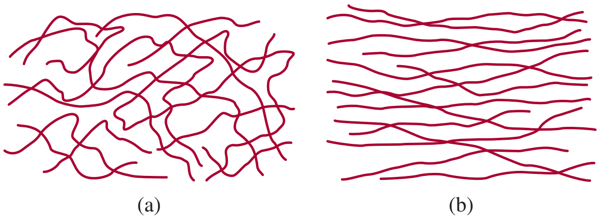
We all know how useful a rubber band can be. But not everyone is aware that a rubber band has some very interesting thermodynamic properties based on its structure.

You can easily perform the following experiments with a rubber band that is at least 0.5 cm wide. Quickly stretch the rubber band and then press it against your lips. You will feel a slight warming effect. Next, reverse the process. Stretch a rubber band and hold it in position for a few seconds. Then quickly release the tension and press the rubber band against your lips. This time you will feel a slight cooling effect. A thermodynamic analysis of these two experiments can tell us something about the molecular structure of rubber.

Rearranging Equation (18.10) ($\Delta G = \Delta H - T\Delta S$) gives

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

The warming effect (an exothermic process) due to stretching means that $\Delta H < 0$, and since stretching is nonspontaneous (that is, $\Delta G > 0$ and $-\Delta G < 0$) $T\Delta S$ must be negative. Because T, the absolute temperature, is always positive, we conclude that ΔS due to stretching must be negative, and therefore rubber in its natural state is more entangled (has more microstates) than when it is under tension.


(a) (b)

(a) Rubber molecules in their normal state. Note the high degree of entanglement (large number of microstates and a high entropy). (b) Under tension, the molecules line up and the arrangement becomes much more ordered (a small number of microstates and a low entropy).

When the tension is removed, the stretched rubber band spontaneously snaps back to its original shape; that is, ΔG is negative and $-\Delta G$ is positive. The cooling effect means that it is an endothermic process ($\Delta H > 0$), so that $T\Delta S$ is positive. Thus, the entropy of the rubber band increases when it goes from the stretched state to the natural state.

On the other hand, the combustion of sulfur to form sulfur dioxide is favored because of its large negative $\Delta G°$ value:

$$\mathrm{S}(s) + \mathrm{O}_2(g) \longrightarrow \mathrm{SO}_2(g) \qquad \Delta G° = -300.1\ \mathrm{kJ/mol}$$

By coupling the two processes we can bring about the separation of zinc from zinc sulfide. In practice, this means heating ZnS in air so that the tendency of S to form SO_2 will promote the decomposition of ZnS:

The price we pay for this procedure is acid rain.

$$\begin{array}{rcll} \mathrm{ZnS}(s) & \longrightarrow & \mathrm{Zn}(s) + \mathrm{S}(s) & \Delta G° = 198.3\ \mathrm{kJ/mol} \\ \mathrm{S}(s) + \mathrm{O}_2(g) & \longrightarrow & \mathrm{SO}_2(g) & \Delta G° = -300.1\ \mathrm{kJ/mol} \\ \hline \mathrm{ZnS}(s) + \mathrm{O}_2(g) & \longrightarrow & \mathrm{Zn}(s) + \mathrm{SO}_2(g) & \Delta G° = -101.8\ \mathrm{kJ/mol} \end{array}$$

Coupled reactions play a crucial role in our survival. In biological systems, enzymes facilitate a wide variety of nonspontaneous reactions. For example, in the human body, food molecules, represented by glucose ($C_6H_{12}O_6$), are converted to carbon dioxide and water during metabolism with a substantial release of free energy:

$$\mathrm{C_6H_{12}O_6}(s) + 6\mathrm{O}_2(g) \longrightarrow 6\mathrm{CO}_2(g) + 6\mathrm{H_2O}(l) \qquad \Delta G° = -2880\ \mathrm{kJ/mol}$$

In a living cell, this reaction does not take place in a single step (as burning glucose in a flame would); rather, the glucose molecule is broken down with the aid of enzymes in a series of steps. Much of the free energy released along the way is used

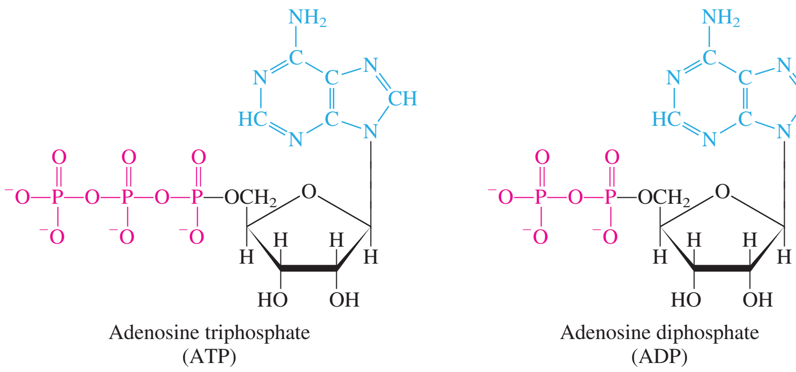


Figure 18.9 *Structure of ATP and ADP in ionized forms. The adenine group is in blue, the ribose group in black, and the phosphate group in red. Note that ADP has one fewer phosphate group than ATP.*

to synthesize adenosine triphosphate (ATP) from adenosine diphosphate (ADP) and phosphoric acid (Figure 18.9):

$$\text{ADP} + \text{H}_3\text{PO}_4 \longrightarrow \text{ATP} + \text{H}_2\text{O} \qquad \Delta G^\circ = +31\ \text{kJ/mol}$$

The function of ATP is to store free energy until it is needed by cells. Under appropriate conditions, ATP undergoes hydrolysis to give ADP and phosphoric acid, with a release of 31 kJ/mol of free energy, which can be used to drive energetically unfavorable reactions, such as protein synthesis.

Proteins are polymers made of amino acids. The stepwise synthesis of a protein molecule involves the joining of individual amino acids. Consider the formation of the dipeptide (a two-amino-acid unit) alanylglycine from alanine and glycine. This reaction represents the first step in the synthesis of a protein molecule:

$$\text{Alanine} + \text{Glycine} \longrightarrow \text{Alanylglycine} \quad \Delta G^\circ = +29\ \text{kJ/mol}$$

As you can see, this reaction does not favor the formation of product, and so only a little of the dipeptide would be formed at equilibrium. However, with the aid of an enzyme, the reaction is coupled to the hydrolysis of ATP as follows:

$$\text{ATP} + \text{H}_2\text{O} + \text{Alanine} + \text{Glycine} \longrightarrow \text{ADP} + \text{H}_3\text{PO}_4 + \text{Alanylglycine}$$

The overall free-energy change is given by $\Delta G^\circ = -31\ \text{kJ/mol} + 29\ \text{kJ/mol} = -2\ \text{kJ/mol}$, which means that the coupled reaction now favors the formation of product, and an appreciable amount of alanylglycine will be formed under this condition. Figure 18.10 shows the ATP-ADP interconversions that act as energy storage (from metabolism) and free-energy release (from ATP hydrolysis) to drive essential reactions.

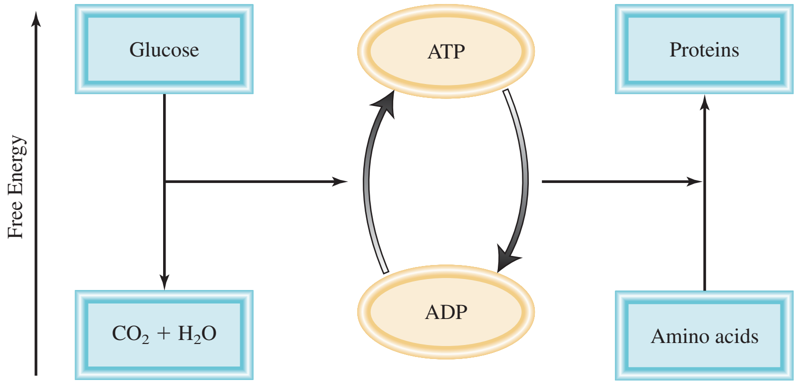


Figure 18.10 *Schematic representation of ATP synthesis and coupled reactions in living systems. The conversion of glucose to carbon dioxide and water during metabolism releases free energy. The released free energy is used to convert ADP into ATP. The ATP molecules are then used as an energy source to drive unfavorable reactions, such as protein synthesis from amino acids.*

Key Equations

$\Delta S^\circ_{\text{rxn}} = \Sigma nS^\circ(\text{products}) - \Sigma mS^\circ(\text{reactants})$	(18.7)	Standard entropy change of a reaction.
$G = H - TS$	(18.9)	Definition of Gibbs free energy.
$\Delta G = \Delta H - T\Delta S$	(18.10)	Free-energy change at constant temperature.
$\Delta G^\circ_{\text{rxn}} = \Sigma n\Delta G^\circ_{\text{f}}(\text{products}) - \Sigma m\Delta G^\circ_{\text{f}}(\text{reactants})$	(18.12)	Standard free-energy change of a reaction.
$\Delta G = \Delta G^\circ + RT \ln Q$	(18.13)	Relationship between free-energy change and standard free-energy change and reaction quotient.
$\Delta G^\circ = -RT \ln K$	(18.14)	Relationship between standard free-energy change and the equilibrium constant.

Summary of Facts and Concepts

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Chapter Summary

1. Entropy is described as a measure of the different ways a system can disperse its energy. Any spontaneous process must lead to a net increase in entropy in the universe (second law of thermodynamics).
2. The standard entropy of a chemical reaction can be calculated from the absolute entropies of reactants and products.
3. The third law of thermodynamics states that the entropy of a perfect crystalline substance is zero at 0 K. This law enables us to measure the absolute entropies of substances.
4. Under conditions of constant temperature and pressure, the free-energy change ΔG is less than zero for a spontaneous process and greater than zero for a nonspontaneous process. For an equilibrium process, $\Delta G = 0$.
5. For a chemical or physical process at constant temperature and pressure, $\Delta G = \Delta H - T\Delta S$. This equation can be used to predict the spontaneity of a process.
6. The standard free-energy change for a reaction, ΔG°, can be calculated from the standard free energies of formation of reactants and products.
7. The equilibrium constant of a reaction and the standard free-energy change of the reaction are related by the equation $\Delta G^\circ = -RT \ln K$.
8. Many biological reactions are nonspontaneous. They are driven by the hydrolysis of ATP, for which ΔG° is negative.

Answers to Practice Exercises

18.1 (a) Entropy decreases, (b) entropy decreases, (c) entropy increases, (d) entropy increases. **18.2** (a) -173.6 J/K · mol, (b) -139.8 J/K · mol, (c) 215.3 J/K · mol.
18.3 (a) $\Delta S > 0$, (b) $\Delta S < 0$, (c) $\Delta S \approx 0$.
18.4 (a) -106.4 kJ/mol, (b) -2935.0 kJ/mol.
18.5 $\Delta S_{\text{fus}} = 16$ J/K · mol; $\Delta S_{\text{vap}} = 72$ J/K · mol.
18.6 2×10^{57}. **18.7** 33 kJ/mol. **18.8** $\Delta G = 0.97$ kJ/mol; direction is from right to left.