16 Spontaneity of Reaction

The ballerinas in Degas's painting *The Dancers* look like they have depleted their glucose by using it for energy to dance.

Geoffrey Clements/Corbis

Things are always at their best in their beginnings.

—BLAISE PASCAL

Chapter Outline

The goal of this chapter is to answer a basic question: Will a given reaction occur "by itself" at a particular temperature and pressure, without the exertion of any outside force? In that sense, is the reaction *spontaneous*? This is a critical question in just about every area of science and technology. A synthetic organic chemist looking for a source of acetylene, C_2H_2, would like to know whether this compound can be made by heating the elements together. A metallurgist trying to produce titanium metal from TiO_2 would like to know what reaction to use; would hydrogen, carbon, or aluminum be feasible reducing agents?

To develop a general criterion for spontaneity, we will apply the principles of **thermodynamics,** the science that deals with heat and energy effects. Three different thermodynamic functions are of value in analyzing spontaneity.

1. ΔH, the change in enthalpy (Chapter 8); a *negative* value of ΔH tends to make a reaction spontaneous.
2. ΔS, the change in entropy (Section 16-2); a *positive* value of ΔS tends to make a reaction spontaneous.
3. ΔG, the change in free energy (Sections 16-3 and 16-4); a reaction at constant temperature and pressure will be *spontaneous* if ΔG is *negative*, no ifs, ands, or buts.

Besides serving as a general criterion for spontaneity, the free energy change can be used to:

- determine the effect of temperature, pressure, and concentration on reaction spontaneity (Section 16-5).
- calculate the equilibrium constant for a reaction (Section 16-6).
- determine whether coupled reactions will be spontaneous (Section 16-7).

16-1 Spontaneous Processes

All of us are familiar with certain **spontaneous processes.** For example,

- an ice cube melts when added to a glass of water at room temperature

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

- a mixture of hydrogen and oxygen burns if ignited by a spark

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

- an iron (steel) tool exposed to moist air rusts

$$2Fe(s) + \tfrac{3}{2}O_2(g) + 3H_2O(l) \longrightarrow 2Fe(OH)_3(s)$$

A spark is OK, but a continuous input of energy isn't.

In other words, these three reactions are spontaneous at 25°C and 1 atm.

The word "spontaneous" does not imply anything about how rapidly a reaction occurs. Some spontaneous reactions, notably the rusting of iron, are quite slow. Often a reaction that is spontaneous does not occur without some sort of stimulus to get the reaction started. A mixture of hydrogen and oxygen shows no sign of reaction in the absence of a spark or match. Once started, though, a spontaneous reaction continues by itself without further input of energy from the outside.

If a reaction is spontaneous under a given set of conditions, the reverse reaction must be nonspontaneous. For example, water does not spontaneously decompose to the elements by the reverse of the reaction referred to above.

$$2H_2O(l) \longrightarrow 2H_2(g) + O_2(g) \qquad \text{nonspontaneous}$$

However, it is often possible to bring about a nonspontaneous reaction by supplying energy in the form of work. Electrolysis can be used to decompose water to the elements. Electrical energy must be furnished for the decomposition, perhaps from a storage battery.

Perhaps the simplest way to define spontaneity is to say that **a spontaneous process is one that moves the reaction system toward equilibrium.** A nonspontaneous process moves the system away from equilibrium.

The Energy Factor

Many spontaneous processes proceed with a decrease of energy. Boulders roll downhill, not uphill. A storage battery discharges when you leave your car's headlights on. Extrapolating to chemical reactions, one might guess that spontaneous reactions would be exothermic ($\Delta H < 0$). Marcellin Berthelot (1827–1907) in Paris and Julius Thomsen (1826–1909) in Copenhagen proposed this as a general principle, applicable to all reactions.

Instead it turns out that in almost all cases the reverse is true. Nearly all exothermic chemical reactions are spontaneous at 25°C and 1 atm. Consider, for example, the formation of water from the elements and the rusting of iron:

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l) \qquad \Delta H = -571.6 \text{ kJ}$$
$$2Fe(s) + \tfrac{3}{2}O_2(g) + 3H_2O(l) \longrightarrow 2Fe(OH)_3(s) \qquad \Delta H = -788.6 \text{ kJ}$$

For both of these spontaneous reactions, ΔH is a negative quantity.

On the other hand, this simple rule fails for many familiar phase changes. An example of a spontaneous reaction that is not exothermic is the melting of ice. This takes place spontaneously at 1 atm above 0°C, even though it is endothermic:

$$H_2O(s) \longrightarrow H_2O(l) \qquad \Delta H = +6.0 \text{ kJ}$$

There is still another basic objection to using the sign of ΔH as a general criterion for spontaneity. Endothermic reactions that are nonspontaneous at room temperature often become spontaneous when the temperature is raised. Consider,

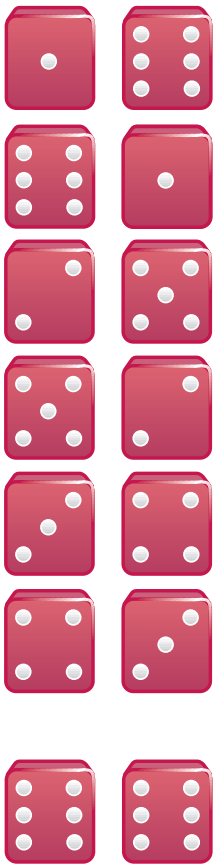


Figure 16.1 Certain "states" are more probable than others. For example, when you toss a pair of dice, a 7 is much more likely to come up than a 12.

for example, the decomposition of limestone:

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g) \qquad \Delta H = +178.3 \text{ kJ}$$

At 25°C and 1 atm, this reaction does not occur. Witness the existence of the white cliffs of Dover and other limestone deposits over eons of time. However, if the temperature is raised to about 1100 K, limestone decomposes to give off carbon dioxide gas at 1 atm. In other words, this endothermic reaction becomes spontaneous at high temperatures. This is true despite the fact that ΔH remains about 178 kJ, nearly independent of temperature.

The Randomness Factor

Clearly, the direction of a spontaneous change is not always determined by the tendency for a system to go to a state of lower energy. There is another natural tendency that must be taken into account to predict the direction of spontaneity. ***Nature tends to move spontaneously from a state of lower probability to one of higher probability.*** Or, as G. N. Lewis put it,

> Each system which is left to its own, will over time, change toward a condition of maximum probability.

To illustrate what these statements mean, consider a pastime far removed from chemistry: tossing dice. If you've ever shot craps (and maybe even if you haven't), you know that when a pair of dice is thrown, a 7 is much more likely to come up than a 12. Figure 16.1 shows why this is the case. There are six different ways to throw a 7 and only one way to throw a 12. Over time, dice will come up 7 six times as often as 12. A 7 is a state of "high" probability; a 12 is a state of "low" probability.

Now let's consider a process a bit closer to chemistry (Figure 16.2). Two different gases, let us say H_2 and N_2, are originally contained in different glass bulbs, separated by a stopcock. When the stopcock is opened, the two different kinds of molecules distribute themselves evenly between the two bulbs. Eventually, half of the H_2 molecules will end up in the left bulb and half in the right; the same holds for the N_2 molecules. Each gas achieves its own most probable distribution, independent of the presence of the other gas.

We could explain the results of this experiment the way we did before; the final distribution is clearly much more probable than the initial distribution. There is, however, another useful way of looking at this process. The system has gone from a highly ordered state (all the H_2 molecules on the left, all the N_2 molecules on the right) to a more disordered, or random, state in which the molecules are distributed evenly between the two bulbs. The same situation holds when marbles rather than molecules are mixed (Figure 16.3). ***In general, nature tends to move spontaneously from more ordered to more random states.***

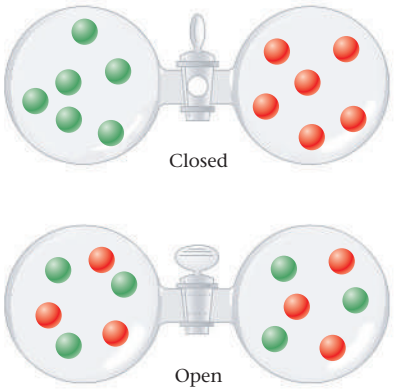


Figure 16.2 Spontaneous change. Different kinds of gas molecules mix spontaneously, going from a more ordered to a more random state.

Charles Steele

Figure 16.3 Probability. Some states are much more probable than others. If you shake red and black marbles with each other, the random distribution at the left is much more probable than the highly ordered distribution at the right.

This statement is quite easy for parents or students to understand. Your room tends to get messy because an ordered room has few options for objects to be moved around (leaving socks on the floor is not an option for an orderly room). The comedian Bill Cosby insists that with an army of 80 two-year-olds he could take over any country in the world, because they have a remarkable ability for disorganization.

16-2 Entropy, *S*

Entropy is often described as a measure of disorder or randomness. While useful, these terms are subjective and should be used cautiously. It is better to think about entropic changes in terms of the change in the number of *microstates* of the system. Microstates are different ways in which molecules can be distributed. An increase in the number of possible microstates (i.e., disorder) results in an increase of entropy. Entropy treats the randomness factor quantitatively. Rudolf Clausius gave it the symbol *S* for no particular reason. In general, the more random the state, the larger the number of its possible microstates, the more probable the state, thus the greater its entropy.

Entropy, like enthalpy (Chapter 8), is a state property. That is, the entropy depends only on the state of a system, not on its history. The **entropy change** is determined by the entropies of the final and initial states, not on the path followed from one state to another.

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

Several factors influence the amount of entropy that a system has in a particular state. In general,

- ***a liquid has a higher entropy than the solid from which it is formed.*** In a solid the atoms or molecules are confined to fixed positions, so the number of microstates is small. In the liquid, these atoms or molecules can occupy many more positions as they move away from the lattice. Thus, the number of microstates increases and there are then many more ways to arrange the particles. The phase transition is from an "ordered" to a "disordered" system.
- ***a gas has a higher entropy than the liquid from which it is formed.*** When vaporization occurs, the particles acquire greater freedom to move about. They are distributed throughout the entire container instead of being restricted to a small volume. In vaporization, the number of microstates increases.
- ***increasing the temperature of a substance increases its entropy.*** Raising the temperature increases the kinetic energy of the molecules (or atoms or ions) and hence their freedom of motion. In the solid, the molecules vibrate with a greater amplitude at higher temperatures. In a liquid or a gas, they move about more rapidly.

One way or another, heating a substance increases its entropy.

These effects are shown in Figure 16.4, where the entropy of ammonia, NH_3, is plotted versus temperature. Note that the entropy of solid ammonia at 0 K is

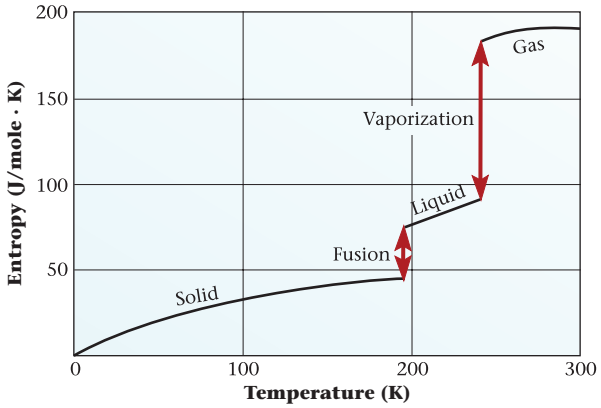


Figure 16.4 Molar entropy of ammonia as a function of temperature. Note the large increases in entropy upon fusion (melting) and vaporization.

zero. This reflects the fact that molecules are completely ordered in the solid state at this temperature; there is no randomness whatsoever. More generally, the **third law of thermodynamics** tells us that *a completely ordered pure crystalline solid has an entropy of zero at 0 K.*

We'll get to the second law shortly.

Notice from the figure that the effect of temperature on entropy is due almost entirely to phase changes. The slope of the curve is small in regions where only one phase is present. In contrast, there is a large jump in entropy when the solid melts and an even larger one when the liquid vaporizes. This behavior is typical of all substances; melting and vaporization are accompanied by relatively large increases in entropy.

EXAMPLE 16.1 CONCEPTUAL

Predict whether ΔS is positive or negative for each of the following processes:

(a) taking dry ice from a freezer where its temperature is −80°C and allowing it to warm to room temperature.

(b) dissolving bromine in hexane.

(c) condensing gaseous bromine to liquid bromine.

STRATEGY

1. Consider the relative disorder of final and intial states.
2. Recall that entropy increases from solid to liquid to gas.

SOLUTION

(a) Dry ice warming	Increase in temperature and a phase change; $\Delta S > 0$
(b) Dissolving bromine	A solution with two different molecules is more random than a solution with only one kind of molecule; $\Delta S > 0$
(c) $Br_2(g) \longrightarrow Br_2(l)$	A phase change from gas to liquid; $\Delta S < 0$

Decomposition of ammonium nitrate. The value of ΔS for this reaction,

$$NH_4NO_3(s) \longrightarrow N_2O(g) + 2H_2O(g)$$

is positive. That can be predicted because a solid decomposes to gases.

Standard Molar Entropies

The entropy of a substance, unlike its enthalpy, can be evaluated directly. The details of how this is done are beyond the level of this text, but Figure 16.4 shows the results for one substance, ammonia. From such a plot you can read off the **standard molar entropy** at 1 atm pressure and any given temperature, most often 25°C. This quantity is given the symbol $S°$ and has the units of joules per mole per kelvin (J/mol·K). From Figure 16.4, it appears that

$$S° \ NH_3(g) \text{ at } 25°C \approx 192 \text{ J/mol·K}$$

Standard molar entropies of elements, compounds, and aqueous ions are listed in Table 16.1. Notice that

- ***elements have nonzero standard entropies.*** This means that in calculating the standard entropy change for a reaction, $\Delta S°$, elements as well as compounds must be taken into account.
- ***standard molar entropies of pure substances*** (elements and compounds) ***are always positive quantities*** ($S° > 0$).
- ***aqueous ions may have negative S° values.*** This is a consequence of the arbitrary way in which ionic entropies are defined, taking

$$S° \ H^+(aq) = 0$$

The fluoride ion has a standard entropy 13.8 units less than that of H^+; hence $S° \ F^-(aq) = -13.8$ J/mol·K.

Table 16.1 Standard Entropies at 25°C (J/mol·K) of Elements and Compounds at 1 atm, Aqueous Ions at 1 *M*

Elements

$Ag(s)$	42.6	$Cl_2(g)$	223.0	$I_2(s)$	116.1	$O_2(g)$	205.0
$Al(s)$	28.3	$Cr(s)$	23.8	$K(s)$	64.2	$Pb(s)$	64.8
$Ba(s)$	62.8	$Cu(s)$	33.2	$Mg(s)$	32.7	$P_4(s)$	164.4
$Br_2(l)$	152.2	$F_2(g)$	202.7	$Mn(s)$	32.0	$S(s)$	31.8
$C(s)$	5.7	$Fe(s)$	27.3	$N_2(g)$	191.5	$Si(s)$	18.8
$Ca(s)$	41.4	$H_2(g)$	130.6	$Na(s)$	51.2	$Sn(s)$	51.6
$Cd(s)$	51.8	$Hg(l)$	76.0	$Ni(s)$	29.9	$Zn(s)$	41.6

Compounds

$AgBr(s)$	107.1	$CaCl_2(s)$	104.6	$H_2O(g)$	188.7	$NH_4NO_3(s)$	151.1
$AgCl(s)$	96.2	$CaCO_3(s)$	92.9	$H_2O(l)$	69.9	$NO(g)$	210.7
$AgI(s)$	115.5	$CaO(s)$	39.8	$H_2O_2(l)$	109.6	$NO_2(g)$	240.0
$AgNO_3(s)$	140.9	$Ca(OH)_2(s)$	83.4	$H_2S(g)$	205.7	$N_2O_4(g)$	304.2
$Ag_2O(s)$	121.3	$CaSO_4(s)$	106.7	$H_2SO_4(l)$	156.9	$NaCl(s)$	72.1
$Al_2O_3(s)$	50.9	$CdCl_2(s)$	115.3	$HgO(s)$	70.3	$NaF(s)$	51.5
$BaCl_2(s)$	123.7	$CdO(s)$	54.8	$KBr(s)$	95.9	$NaOH(s)$	64.5
$BaCO_3(s)$	112.1	$Cr_2O_3(s)$	81.2	$KCl(s)$	82.6	$NiO(s)$	38.0
$BaO(s)$	70.4	$CuO(s)$	42.6	$KClO_3(s)$	143.1	$PbBr_2(s)$	161.5
$BaSO_4(s)$	132.2	$Cu_2O(s)$	93.1	$KClO_4(s)$	151.0	$PbCl_2(s)$	136.0
$CCl_4(l)$	216.4	$CuS(s)$	66.5	$KNO_3(s)$	133.0	$PbO(s)$	66.5
$CHCl_3(l)$	201.7	$Cu_2S(s)$	120.9	$MgCl_2(s)$	89.6	$PbO_2(s)$	68.6
$CH_4(g)$	186.2	$CuSO_4(s)$	107.6	$MgCO_3(s)$	65.7	$PCl_3(g)$	311.7
$C_2H_2(g)$	200.8	$Fe(OH)_3(s)$	106.7	$MgO(s)$	26.9	$PCl_5(g)$	364.5
$C_2H_4(g)$	219.5	$Fe_2O_3(s)$	87.4	$Mg(OH)_2(s)$	63.2	$SiO_2(s)$	41.8
$C_2H_6(g)$	229.5	$Fe_3O_4(s)$	146.4	$MgSO_4(s)$	91.6	$SnO_2(s)$	52.3
$C_3H_8(g)$	269.9	$HBr(g)$	198.6	$MnO(s)$	59.7	$SO_2(g)$	248.1
$CH_3OH(l)$	126.8	$HCl(g)$	186.8	$MnO_2(s)$	53.0	$SO_3(g)$	256.7
$C_2H_5OH(l)$	160.7	$HF(g)$	173.7	$NH_3(g)$	192.3	$ZnI_2(s)$	161.1
$CO(g)$	197.6	$HI(g)$	206.5	$N_2H_4(l)$	121.2	$ZnO(s)$	43.6
$CO_2(g)$	213.6	$HNO_3(l)$	155.6	$NH_4Cl(s)$	94.6	$ZnS(s)$	57.7

Cations

				Anions			
$Ag^+(aq)$	72.7	$Hg^{2+}(aq)$	−32.2	$Br^-(aq)$	82.4	$HPO_4^{2-}(aq)$	−33.5
$Al^{3+}(aq)$	−321.7	$K^+(aq)$	102.5	$CO_3^{2-}(aq)$	−56.9	$HSO_4^-(aq)$	131.8
$Ba^{2+}(aq)$	9.6	$Mg^{2+}(aq)$	−138.1	$Cl^-(aq)$	56.5	$I^-(aq)$	111.3
$Ca^{2+}(aq)$	−53.1	$Mn^{2+}(aq)$	−73.6	$ClO_3^-(aq)$	162.3	$MnO_4^-(aq)$	191.2
$Cd^{2+}(aq)$	−73.2	$Na^+(aq)$	59.0	$ClO_4^-(aq)$	182.0	$NO_2^-(aq)$	123.0
$Cu^+(aq)$	40.6	$NH_4^+(aq)$	113.4	$CrO_4^{2-}(aq)$	50.2	$NO_3^-(aq)$	146.4
$Cu^{2+}(aq)$	−99.6	$Ni^{2+}(aq)$	−128.9	$Cr_2O_7^{2-}(aq)$	261.9	$OH^-(aq)$	−10.8
$Fe^{2+}(aq)$	−137.7	$Pb^{2+}(aq)$	10.5	$F^-(aq)$	−13.8	$PO_4^{3-}(aq)$	−222
$Fe^{3+}(aq)$	−315.9	$Sn^{2+}(aq)$	−17.4	$HCO_3^-(aq)$	91.2	$S^{2-}(aq)$	−14.6
$H^+(aq)$	0.0	$Zn^{2+}(aq)$	−112.1	$H_2PO_4^-(aq)$	90.4	$SO_4^{2-}(aq)$	20.1

As a group, gases have higher entropies than liquids or solids. Moreover, among substances of similar structure and physical state, entropy usually increases with molar mass. Compare, for example, the hydrocarbons

$$CH_4(g) \qquad S° = 186.2 \text{ J/mol·K}$$
$$C_2H_6(g) \qquad S° = 229.5 \text{ J/mol·K}$$
$$C_3H_8(g) \qquad S° = 269.9 \text{ J/mol·K}$$

As the molecule becomes more complex, there are more ways for the atoms to move about with respect to one another, leading to a higher entropy.

$\Delta S°$ for Reactions

Table 16.1 can be used to calculate the **standard entropy change,** $\Delta S°$, for reactions, from the relation

$$\Delta S° = \sum S°_{\text{products}} - \sum S°_{\text{reactants}} \qquad (16.1)$$

In taking these sums, the standard molar entropies are multiplied by the number of moles specified in the balanced chemical equation.

To show how this relation is used, consider the reaction

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

$$\Delta S° = S° CaO(s) + S° CO_2(g) - S° CaCO_3(s)$$

$$\Delta S° = 1 \text{ mol}\left(39.8 \frac{\text{J}}{\text{mol} \cdot \text{K}}\right) + 1 \text{ mol}\left(213.6 \frac{\text{J}}{\text{mol} \cdot \text{K}}\right) - 1 \text{ mol}\left(92.9 \frac{\text{J}}{\text{mol} \cdot \text{K}}\right)$$

$$= 39.8 \text{ J/K} + 213.6 \text{ J/K} - 92.9 \text{ J/K} = +160.5 \text{ J/K}$$

The units of $S°$ are J/mol·K: Those of $\Delta S°$ are J/K. Why the difference?

Observe that $\Delta S°$ for the decomposition of calcium carbonate is a positive quantity. This is reasonable because the gas formed, CO_2, has a much higher molar entropy than either of the solids, CaO or $CaCO_3$. As a matter of fact, ***a reaction that results in an increase in the number of moles of gas is almost always accompanied by an increase in entropy. Conversely, if the number of moles of gas decreases, $\Delta S°$ is a negative quantity.*** Consider, for example, the reaction

If there is no change to the number of moles of gas, ΔS is usually small.

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

$$\Delta S° = 2S° H_2O(l) - 2S° H_2(g) - S° O_2(g)$$

$$= 139.8 \text{ J/K} - 261.2 \text{ J/K} - 205.0 \text{ J/K} = -326.4 \text{ J/K}$$

EXAMPLE 16.2

Consider calcium hydroxide, commonly called slaked lime. It is used as the lye substitute in "no-lye" hair relaxers. It is also found in most depilatory creams.

a Calculate $\Delta S°$ for dissolving one mole of calcium hydroxide in water.

STRATEGY

1. Write a balanced equation for dissolving $Ca(OH)_2$.
2. Find $\Delta S°$ by substituting $S°$ values found in Table 16.1 into Equation 16.1.

SOLUTION

1. Equation

$$Ca(OH)_2(s) \longrightarrow Ca^{2+}(aq) + 2OH^-(aq)$$

2. $\Delta S°$

$$\Delta S° = S° Ca^{2+}(aq) + 2S° OH^-(aq) - S° Ca(OH)_2(s)$$

$$= 1 \text{ mol}\left(\frac{-53.1 \text{ J}}{\text{mol} \cdot \text{K}}\right) + 2 \text{ mol}\left(\frac{-10.8 \text{ J}}{\text{mol} \cdot \text{K}}\right) - 1 \text{ mol}\left(\frac{+83.4 \text{ J}}{\text{mol} \cdot \text{K}}\right) = -158.1 \text{ J/K}$$

b Calculate $\Delta S°$ for the formation of one gram of $Ca(OH)_2$ by reacting lime (CaO) with water.

STRATEGY

1. Write a balanced equation for the reaction.
2. Find $\Delta S°$ by substituting $S°$ values from Table 16.1 into Equation 16.1.
   Note that the value you obtained is for the difference in entropy for *one mole*.
3. Use $\Delta S°$ for one mole as a conversion factor to obtain $\Delta S°$ for one gram of $Ca(OH)_2$.

continued

SOLUTION

1. Equation

$$CaO(s) + H_2O \longrightarrow Ca(OH)_2(s)$$

2. $\Delta S°$ for one mole

$$\Delta S° = S° \, Ca(OH)_2 - [S° \, CaO + S° \, H_2O]$$

$$\Delta S° = 1 \text{ mol}\left(\frac{+83.4 \text{ J}}{\text{mol} \cdot \text{K}}\right) - \left[1 \text{ mol}\left(\frac{+39.8 \text{ J}}{\text{mol} \cdot \text{K}}\right) + 1 \text{ mol}\left(\frac{+69.9 \text{ J}}{\text{mol} \cdot \text{K}}\right)\right]$$

$$= -26.3 \text{ J/K}$$

3. $\Delta S°$ for one gram

$$\frac{-26.3 \text{ J/K}}{1 \text{ mol } Ca(OH)_2} \times \frac{1 \text{ mol } Ca(OH)_2}{74.10 \text{ g}} = -0.355 \text{ J/K}$$

The Second Law of Thermodynamics

The relationship between entropy change and spontaneity can be expressed through a basic principle of nature known as the **second law of thermodynamics**. One way to state this law is to say that ***in a spontaneous process, there is a net increase in entropy, taking into account both system and surroundings.*** That is,

$$\Delta S_{universe} = (\Delta S_{system} + \Delta S_{surroundings}) > 0 \qquad \text{spontaneous process}$$

In this sense, the universe is running down.

(Recall from Chapter 8 that the system is that portion of the universe on which attention is focused; the surroundings include everything else.)

Notice that the second law refers to the total entropy change, involving both system and surroundings. For many spontaneous processes, the entropy change for the system is a *negative* quantity. Consider, for example, the rusting of iron, a spontaneous process:

$$2Fe(s) + \tfrac{3}{2}O_2(g) + 3H_2O(l) \longrightarrow 2Fe(OH)_3(s)$$

$\Delta S°$ for this system at 25°C and 1 atm can be calculated from a table of standard entropies; it is found to be −358.4 J/K. The negative sign of $\Delta S°$ is entirely consistent with the second law. All the law requires is that the entropy change of the surroundings be greater than 358.4 J/K, so that $\Delta S_{universe} > 0$.

In principle, the second law can be used to determine whether a reaction is spontaneous. To do that, however, requires calculating the entropy change for the surroundings, which is not easy. We follow a conceptually simpler approach (Section 16-3), which deals only with the thermodynamic properties of chemical *systems*.

16-3 Free Energy, *G*

As pointed out earlier, two thermodynamic quantities affect reaction spontaneity. One of these is the enthalpy, *H;* the other is the entropy, *S*. The problem is to put these two quantities together in such a way as to arrive at a single function whose sign will determine whether a reaction is spontaneous. This problem was first solved more than a century ago by J. Willard Gibbs, who introduced a new quantity, now called the *Gibbs free energy* and given the symbol *G*. Gibbs showed that for a reaction taking place at constant pressure and temperature, the **free energy of formation**, ΔG represents that portion of the total energy change that is available (i.e., "free") to do useful work. If, for example, ΔG for a reaction is −270 kJ, it is possible to obtain 270 kJ of useful work from the reaction. Conversely, if ΔG is +270 kJ, at least that much energy in the form of work must be supplied to make the reaction take place.

A spontaneous process is capable of producing useful work.

The basic definition of the Gibbs free energy is

$$G = H - TS$$

where *T* is the absolute (Kelvin) temperature. The **free energy** of a substance, like its enthalpy and entropy, is a state property; its value is determined only by the

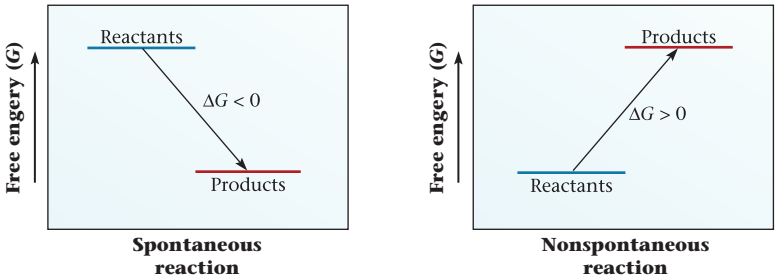


Figure 16.5 Sign of free energy and spontaneity. For a spontaneous reaction, the free energy of the products is less than that of the reactants: $\Delta G < 0$. For a nonspontaneous reaction, the reverse is true, $\Delta G > 0$.

state of a system, not by how it got there. Putting it another way, the **free energy change**, ΔG for a reaction depends only on the nature of products and reactants and the conditions (temperature, pressure, and concentration). It does *not* depend on the path by which the reaction is carried out.

The sign of the free energy change can be used to determine the spontaneity of a reaction carried out at constant temperature and pressure.

1. ***If ΔG is negative, the reaction is spontaneous.***
2. ***If ΔG is positive, the reaction will not take place spontaneously.*** Instead, the reverse reaction will be spontaneous.
3. ***If ΔG is 0, the system is at equilibrium;*** there is no tendency for reaction to occur in either direction.

A system has its minimum free energy at equilibrium.

In other words, ΔG is a measure of the driving force of a reaction. ***Reactions, at constant pressure and temperature, go in such a direction as to decrease the free energy of the system.*** This means that the direction in which a reaction takes place is determined by the relative free energies of products and reactants. If the products at the specified conditions of temperature, pressure, and concentration have a lower free energy than the reactants ($G_{products} < G_{reactants}$), the forward reaction will occur (Figure 16.5). If the reverse is true ($G_{reactants} < G_{products}$), the reverse reaction is spontaneous. Finally, if $G_{products} = G_{reactants}$, there is no driving force to make the reaction go in either direction.

Relation Among ΔG, ΔH, and ΔS

From the defining equation for free energy, it follows that at constant temperature

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

where ΔG, ΔH, and ΔS are the changes in free energy, enthalpy, and entropy, respectively, for a reaction. This relation, known as the **Gibbs-Helmholtz equation**, is perhaps the most important equation in chemical thermodynamics. As you can see, two factors tend to make ΔG negative and hence lead to a spontaneous reaction:

1. ***A negative value of ΔH.*** Exothermic reactions ($\Delta H < 0$) tend to be spontaneous, inasmuch as they contribute to a negative value of ΔG. On the molecular level, this means that there will be a tendency to form "strong" bonds at the expense of "weak" ones.
2. ***A positive value of ΔS.*** If the entropy change is positive ($\Delta S > 0$), the term $-T\Delta S$ will make a negative contribution to ΔG. Hence there will be a tendency for a reaction to be spontaneous if the products are less ordered than the reactants.

In many physical changes, the entropy increase is the major driving force. This situation applies when two liquids with similar intermolecular forces, such as benzene (C_6H_6) and toluene (C_7H_8), are mixed. There is no change in enthalpy, but the entropy increases because the molecules of benzene and toluene are mixed randomly in solution.*

*The formation of a *water* solution is often accompanied by a *decrease* in entropy because hydrogen bonding or hydration effects lead to a highly ordered solution structure. Recall from Example 16.2 that when one mole of $Ca(OH)_2$ dissolves in water, $\Delta S^\circ = -158.1$ J/K.

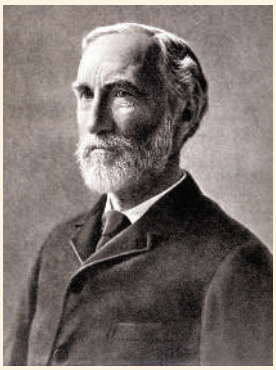
CHEMISTRY THE **HUMAN** SIDE

Two theoreticians working in the latter half of the nineteenth century changed the very nature of chemistry by deriving the mathematical laws that govern the behavior of matter undergoing physical or chemical change. One of these was James Clerk Maxwell, whose contributions to kinetic theory were discussed in Chapter 5. The other was J. Willard Gibbs, Professor of Mathematical Physics at Yale from 1871 until his death in 1903.

In 1876, Gibbs published the first portion of a remarkable paper in the *Transactions of the Connecticut Academy of Sciences* titled, "On the Equilibrium of Heterogeneous Substances." When the paper was completed in 1878 (it was 323 pages long), the foundation was laid for the science of chemical thermodynamics. For the first time, the concept of free energy appeared. Included as well were the basic principles of chemical equilibrium (Chapter 12), phase equilibrium (Chapter 9), and the relations governing energy changes in electrical cells (Chapter 17).

If Gibbs had never published another paper, this single contribution would have placed him among the greatest theoreticians in the history of science. Generations of experimental scientists have established their reputations by demonstrating in the laboratory the validity of the relationships that Gibbs derived at his desk. Many of these relationships were rediscovered by others; an example is the Gibbs-Helmholtz equation developed in 1882 by Hermann von Helmholtz (1821–1894), a prestigious German physiologist and physicist who was completely unaware of Gibbs's work.

Gibbs is often cited as an example of the "prophet without honor in his own country." His colleagues in New Haven and elsewhere in the United States seem not to have realized the significance of his work until late in his life. During his first ten years as a professor at Yale he received no salary. They started paying him when he got an offer from Johns Hopkins. In 1920, when he was first proposed for the Hall of Fame of Distinguished Americans at New York University, he received 9 votes out of a possible 100. Not until 1950 was he elected to that body. Even today the name of Gibbs is generally unknown among educated Americans outside of those interested in the natural sciences.



Interfoto/Personalities/Alamy

J. Willard Gibbs
(1839–1903)

Admittedly, Gibbs himself was largely responsible for the fact that for many years his work did not attract the attention it deserved. He made little effort to publicize it; the *Transactions of the Connecticut Academy of Sciences* was hardly the leading scientific journal of its day. Gibbs was one of those rare individuals who seem to have no inner need for recognition by contemporaries. His satisfaction came from solving a problem in his mind; having done so, he was ready to proceed to other problems. His papers are not easy to read; he seldom cites examples to illustrate his abstract reasoning. Frequently, the implications of the laws that he derives are left for the readers to grasp on their own. One of his colleagues at Yale confessed many years later that none of the members of the Connecticut Academy of Sciences understood his paper on thermodynamics; as he put it, "We knew Gibbs and took his contributions on faith."

In certain reactions, ΔS is nearly zero, and ΔH is the only important component of the driving force for spontaneity. An example is the synthesis of hydrogen fluoride from the elements

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}F_2(g) \longrightarrow HF(g)$$

For this reaction, ΔH is a large negative number, -271.1 kJ, showing that the bonds in HF are stronger than those in the H_2 and F_2 molecules. As you might expect for a gaseous reaction in which there is no change in the number of moles, ΔS is very small, about 0.0070 kJ/K. The free energy change, ΔG, at 1 atm is -273.2 kJ at 25°C, almost identical to ΔH. Even at very high temperatures, the difference between ΔG and ΔH is small, amounting to only about 14 kJ at 2000 K.

16-4 Standard Free Energy Change, $\Delta G°$

Although the Gibbs-Helmholtz equation is valid under all conditions we will apply it only under *standard conditions,* where

- gases are at one atmosphere partial pressure.
- ions or molecules in solution are at one molar concentration.

"Standard conditions" has quite a different meaning from "STP."

In other words, we will use the equation in the form

$$\Delta G° = \Delta H° - T\Delta S° \qquad (16.2)$$

Figure 16.6 Precipitation of silver chloride. A spontaneous reaction for which ΔG° is negative.

where ΔG° is the **standard free energy change** (1 atm, 1 *M*); ΔH° is the standard enthalpy change, which can be calculated from heats of formation, ΔH_f° (listed in Table 8.3, Chapter 8); and ΔS° is the standard entropy change (Table 16.1).

Recall that the sign of ΔG correlates with the spontaneity of reaction. We can do the same thing with ΔG° provided we restrict our attention to standard conditions (1 atm, 1 *M*).

1. ***If ΔG° is negative, the reaction is spontaneous at standard conditions.*** For example, the following reaction is spontaneous at 25°C:

$$CaO(s) + CO_2(g, 1\text{ atm}) \longrightarrow CaCO_3(s) \quad \Delta G^\circ \text{ at } 25^\circ C = -130.4\text{ kJ}$$

2. ***If ΔG° is positive, the reaction is nonspontaneous at standard conditions.*** The reaction

$$AgCl(s) \longrightarrow Ag^+(aq, 1\ M) + Cl^-(aq, 1\ M) \quad \Delta G^\circ \text{ at } 25^\circ C = +55.7\text{ kJ}$$

is nonspontaneous at 25°C. The reverse reaction is spontaneous; when solutions of $AgNO_3$ and HCl are mixed in such a way that $[Ag^+] = [Cl^-] = 1\ M$, silver chloride precipitates (Figure 16.6).

3. ***If ΔG° is 0, the system is at equilibrium at standard conditions;*** there is no tendency for the reaction to occur in either direction. An example is the vaporization of water at 100°C and 1 atm:

$$H_2O(l) \longrightarrow H_2O(g, 1\text{ atm}) \qquad \Delta G^\circ = 0$$

under these conditions (i.e., at the normal boiling point), the molar free energies of liquid and gaseous water are identical. Hence $\Delta G^\circ = 0$ and the system is at equilibrium.

EXAMPLE 16.3

Calcium sulfate, $CaSO_4$, is used as a drying agent and sold under the trade name Drierite. The reaction for dissolving calcium sulfate is

$$CaSO_4(s) \longrightarrow Ca^{2+}(aq) + SO_4^{2-}(aq)$$

a Find ΔH° for the reaction.

ANALYSIS

Information given:	equation for the reaction ($CaSO_4(s) \longrightarrow Ca^{2+}(aq) + SO_4^{2-}(aq)$)
Information implied:	Table 8.3 (ΔH_f° values)
Asked for:	ΔH°

STRATEGY

1. Recall Equation 8.4 to determine ΔH°.

$$\Delta H^\circ = \Sigma \Delta H_f^\circ{}_{\text{products}} - \Sigma \Delta H_f^\circ{}_{\text{reactants}}$$

2. Obtain ΔH_f° values from Table 8.3 and substitute into Equation 8.4.

SOLUTION

ΔH°

$$\Delta H^\circ = \Delta H_f^\circ Ca^{2+}(aq) + \Delta H_f^\circ SO_4^{2-}(aq) - \Delta H_f^\circ CaSO_4(s)$$
$$= -542.8\text{ kJ} - 909.3\text{ kJ} - (-1434.1\text{ kJ}) = -18.0\text{ kJ}$$

b Find ΔS° for the reaction.

ANALYSIS

Information given:	equation for the reaction ($CaSO_4 \longrightarrow Ca^{2+}(aq) + SO_4^{2-}(aq)$)
Information implied:	Table 16.1 (S° values)
Asked for:	ΔS°

continued

STRATEGY

Obtain $S°$ values from Table 16.1 and substitute into Equation 16.1.

SOLUTION

$\Delta S°$	$\Delta S° = S°\ Ca^{2+}(aq) + S°\ SO_4^{2-}(aq) - S°\ CaSO_4(s)$ $= -53.1\ J/K + 20.1\ J/K - 106.7\ J/K = -139.7\ J/K$

C Find $\Delta G°$ at 25°C for the reaction.

ANALYSIS

Information given:	From part (a): $\Delta H°(-18.0\ kJ)$ From part (b): $\Delta S°(-139.7\ J/K)$
Asked for:	$\Delta G°$

STRATEGY

1. Convert $\Delta S°$ into kJ and °C to K.
2. Substitute into the Gibbs-Helmholtz equation (Equation 16.2).

SOLUTION

1. $\Delta S°$ in kJ; T in K	$\Delta S° = -139.7\ J/K = -0.1397\ kJ/K$; $25°C = 298\ K$
2. $\Delta G°$	$\Delta G° = \Delta H° - T\Delta S° = -18.0\ kJ - 298\ K(-0.1397\ kJ/K) = 23.6\ kJ$

END POINT

$\Delta G°$ is positive, so this reaction at standard conditions

$$CaSO_4(s) \longrightarrow Ca^{2+}(aq, 1\ M) + SO_4^{2-}(aq, 1\ M)$$

should not be spontaneous. In other words, calcium sulfate should not dissolve in water to give a 1 *M* solution. This is indeed the case. The solubility of $CaSO_4$ at 25°C is considerably less than 1 mol/L.

Calculation of $\Delta G°$ at 25°C; Free Energies of Formation

To illustrate the use of the Gibbs-Helmholtz equation (16.2), we apply it first to find $\Delta G°$ for a reaction at 25°C (Example 16.3). To do this, the units of $\Delta H°$ and $\Delta S°$ must be consistent. Using $\Delta H°$ in kilojoules, it is necessary to convert $\Delta S°$ from joules per kelvin to *kilojoules per kelvin*.

The Gibbs-Helmholtz equation can be used to calculate the **standard free energy of formation** of a compound. This quantity, $\Delta G_f°$, is analogous to the enthalpy of formation, $\Delta H_f°$.◂ It is defined as the free energy change per mole when a compound is formed from the elements in their stable states at 1 atm.

ℹ $\Delta G_f°$ for an element, like $\Delta H_f°$, is zero.

Tables of standard free energies of formation at 25°C of compounds and ions in solution are given in Appendix 1 (along with standard heats of formation and standard entropies). Notice that, for most compounds, $\Delta G_f°$ is a negative quantity, which means that the compound can be formed spontaneously from the elements. This is true for water:

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta G_f°\ H_2O(l) = -237.2\ kJ/mol$$

and, at least in principle, for methane:

$$C(s) + 2H_2(g) \longrightarrow CH_4(g) \qquad \Delta G_f°\ CH_4(g) = -50.7\ kJ/mol$$

A few compounds, including acetylene, have positive free energies of formation ($\Delta G_f°\ C_2H_2(g) = +209.2\ kJ/mol$). These compounds cannot be made from the elements at ordinary temperatures and pressures; indeed, they are potentially unstable with respect to the elements. In the case of acetylene, the reaction

$$C_2H_2(g) \longrightarrow 2C(s) + H_2(g) \qquad \Delta G° \text{ at } 25°C = -209.2\ kJ$$

occurs with explosive violence unless special precautions are taken.

Values of ΔG_f° can be used to calculate free energy changes for reactions. The relationship is entirely analogous to that for enthalpies in Chapter 8:

$$\Delta G^\circ_{\text{reaction}} = \sum \Delta G_f^\circ{}_{\text{products}} - \sum \Delta G_f^\circ{}_{\text{reactants}} \qquad (16.3)$$

If you calculate ΔG° in this way, you should keep in mind an important limitation. $\Delta G^\circ_{\text{reaction}}$ ***is valid only at the temperature at which ΔG_f° data are tabulated, in this case 25°C.*** ΔG° varies considerably with temperature, so this approach is not even approximately valid at other temperatures.

To find ΔG° at temperatures other than 25°C, use the Gibbs-Helmholtz equation.

EXAMPLE 16.4

Using ΔG_f° values from Appendix 1, calculate the standard free energy change at 25°C for the reaction referred to in Example 16.3.

ANALYSIS

Information given:	equation for the reaction ($CaSO_4(s) \longrightarrow Ca^{2+}(aq) + SO_4^{2-}(aq)$)
Information implied:	ΔG_f° values (Appendix 1)
Asked for:	ΔG°

STRATEGY

Obtain ΔG_f° values from Appendix 1 and substitute into Equation 16.3.

SOLUTION

ΔG°

$$\Delta G^\circ = \Delta G_f^\circ\ Ca^{2+}(aq) + \Delta G_f^\circ\ SO_4^{2-}(aq) - \Delta G_f^\circ\ CaSO_4(s)$$
$$= -553.6\ \text{kJ} - 744.5\ \text{kJ} + 1321.8\ \text{kJ} = +23.7\ \text{kJ}$$

END POINT

Notice that the value of ΔG° at 25°C is essentially identical to that obtained in Example 16.3, which is reassuring.

Calculation of ΔG° at Other Temperatures

To a good degree of approximation, the temperature variation of ΔH° and ΔS° can be neglected.* This means that to apply the Gibbs-Helmholtz equation

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

at temperatures other than 25°C, you need only change the value of T. The quantities ΔH° and ΔS° can be calculated in the usual way from tables of standard enthalpies and entropies.

*As far as the Gibbs-Helmholtz equation is concerned, there is another reason for ignoring the temperature dependence of ΔH and ΔS. These two quantities always change in the same direction as the temperature changes (i.e., if ΔH becomes more positive, so does ΔS). Hence the two effects tend to cancel each other.

EXAMPLE 16.5

Iron, a large component of steel, is obtained by reducing iron(III) oxide (present in hematite ore) with hydrogen in a blast furnace. Steam is a byproduct of the reaction. Calculate ΔG° at 230°C for the reduction of one mole of Fe_2O_3.

ANALYSIS

Information given:	n Fe_2O_3 (one mole); temperature (230°C)
Information implied:	Table 8.3 (ΔH_f° values) Table 16.1 (S° values)
Asked for:	ΔG°

continued

STRATEGY

1. Write a balanced equation for the reaction.
2. Find ΔH_f° values in Table 8.3 (or Appendix 1) and substitute into Equation 8.3 to obtain ΔH°.
3. Find S° values in Table 16.1 (or Appendix 1) and substitute into Equation 16.1 to obtain ΔS°. (Remember to convert J/K to kJ/K.)
4. Change °C to K and substitute the values for ΔH° and ΔS° into the Gibbs-Helmholtz equation (Equation 16.2) to obtain ΔG°.

SOLUTION

1. Equation	$Fe_2O_3(s) + 3H_2(g) \longrightarrow 2Fe(s) + 3H_2O(g)$
2. ΔH°	$\Delta H^\circ = 3\Delta H_f^\circ\ H_2O(g) - \Delta H_f^\circ\ Fe_2O_3(s) = -725.4\ kJ + 824.2\ kJ = +98.8\ kJ$
3. ΔS°	$\Delta S^\circ = 3S^\circ\ H_2O(g) + 2S^\circ\ Fe(s) - 3S^\circ\ H_2(g) - S^\circ\ Fe_2O_3(s)$
	$= 566.1\ J/K + 54.6\ J/K - 391.8\ J/K - 87.4\ J/K = +141.5\ J/K = +0.1415\ kJ/K$
4. ΔG°	$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 98.8\ kJ - (273 + 230)K\ (0.1415\ kJ/K) = +27.6\ kJ$

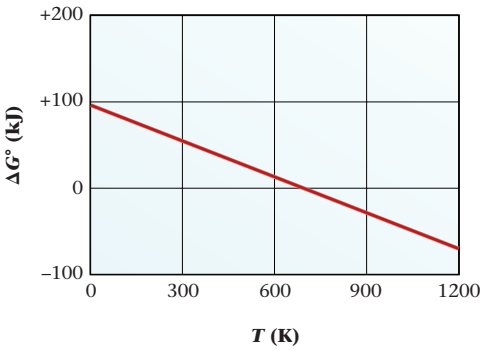


Figure 16.7 Variation of ΔG° with T.
For the reaction:

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

ΔG° decreases from +98.8 kJ at 0 K (the value of ΔH°), to +27.6 kJ at 503 K, 0.0 kJ at 698 K, and −71.0 kJ at 1200 K.

From Example 16.5 and the preceding discussion, it should be clear that ΔG°, unlike ΔH° and ΔS°, is strongly dependent on temperature. This comes about, of course, because of the T in the Gibbs-Helmholtz equation:

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

Comparing this equation with that of a straight line,

$$y = b + mx$$

it is clear that a plot of ΔG° versus T should be linear, with a slope of $-\Delta S^\circ$ and a y-intercept (at 0 K) of ΔH° (Figure 16.7).

16-5 Effect of Temperature, Pressure, and Concentration on Reaction Spontaneity

A change in reaction conditions can, and often does, change the direction in which a reaction occurs spontaneously. The Gibbs-Helmholtz equation in the form

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

is readily applied to deduce the effect of temperature on reaction spontaneity. To consider the effect of pressure or concentration, we need an analogous expression for the dependence of ΔG on these factors.

Temperature

When the temperature of a reaction system is increased, the sign of $\Delta G°$, and hence the direction in which the reaction proceeds spontaneously, may or may not change. Whether it does or does not depends on the signs of $\Delta H°$ and $\Delta S°$. The four possible situations, deduced from the Gibbs-Helmholtz equation, are summarized in Table 16.2.

If $\Delta H°$ and $\Delta S°$ have opposite signs (Table 16.2, I and II), it is impossible to reverse the direction of spontaneity by a change in temperature alone. The two terms $\Delta H°$ and $-T\Delta S°$ reinforce one another. Hence $\Delta G°$ has the same sign at all temperatures. Reactions of this type are rather uncommon. One such reaction is

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

Here $\Delta H°$ is +84.5 kJ and $\Delta S°$ is −0.0487 kJ/K. Hence

$$\begin{aligned}\Delta G° &= \Delta H° - T\Delta S° \\ &= +84.5 \text{ kJ} + T(0.0487 \text{ kJ/K})\end{aligned}$$

Clearly $\Delta G°$ is positive at all temperatures. The reaction cannot take place spontaneously at 1 atm regardless of temperature.

Copper metal doesn't react with water vapor, period.

It is more common to find that $\Delta H°$ and $\Delta S°$ have the same sign (Table 16.2, III and IV). When this happens, the enthalpy and entropy factors oppose each other. $\Delta G°$ changes sign as temperature increases, and the direction of spontaneity reverses. At low temperatures, $\Delta H°$ predominates, and the exothermic reaction, which may be either the forward or the reverse reaction, occurs. As the temperature rises, the quantity $T\Delta S°$ increases in magnitude and eventually exceeds $\Delta H°$. At high temperatures, the reaction that leads to an increase in entropy occurs. In most cases, 25°C is a "low" temperature, at least at a pressure of 1 atm. This explains why exothermic reactions are usually spontaneous at room temperature and atmospheric pressure.

An example of a reaction for which $\Delta H°$ and $\Delta S°$ have the same sign is the decomposition of calcium carbonate:

CaO is made commercially by heating $CaCO_3$.

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

Here $\Delta H° = +178.3$ kJ and $\Delta S° = +160.5$ J/K. Hence

$$\Delta G° = +178.3 \text{ kJ} - T(0.1605 \text{ kJ/K})$$

For this reaction at "low" temperatures, such as 298 K,

$$\Delta G° = +178.3 \text{ kJ} - 47.8 \text{ kJ} = +130.5 \text{ kJ}$$

the $\Delta H°$ term predominates, $\Delta G°$ is positive, and the reaction is nonspontaneous at 1 atm. Conversely, at "high" temperatures, such as 2000 K,

$$\Delta G° = +178.3 \text{ kJ} - 321.0 \text{ kJ} = -142.7 \text{ kJ}$$

the $T\Delta S°$ term predominates, $\Delta G°$ is negative, and the reaction is spontaneous at 1 atm.

Table 16.2 Effect of Temperature on Reaction Spontaneity

	$\Delta H°$	$\Delta S°$	$\Delta G° = \Delta H° - T\Delta S°$	Remarks
I	−	+	Always −	Spontaneous at all T; reverse reaction always nonspontaneous
II	+	−	Always +	Nonspontaneous at all T; reverse reaction occurs
III	+	+	+ at low T − at high T	Nonspontaneous at low T; becomes spontaneous as T is raised
IV	−	−	− at low T + at high T	Spontaneous at low T; at high T, reverse reaction becomes spontaneous

EXAMPLE 16.6

At what temperature does $\Delta G°$ become zero for the reaction considered in Example 16.5?

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

ANALYSIS	
Information given:	equation for the reaction ($Fe_2O_3(s) + 3H_2(g) \longrightarrow 2Fe(s) + 3H_2O(g)$) $\Delta G°$ (0)
Information implied:	from Example 16.5 ($\Delta H°$ and $\Delta S°$)
Asked for:	T

STRATEGY

Substitute $\Delta H°$ and $\Delta S°$ values from Example 16.5 into the Gibbs-Helmholtz equation.

SOLUTION

$\Delta H°$; $\Delta S°$: $\Delta H° = 98.8$ kJ; $\Delta S° = 0.1415$ kJ/K

T: $\Delta G° = \Delta H° - T\Delta S°$; $0 = 98.8 \text{ kJ} - T(0.1415 \text{ kJ/K})$; $T = \dfrac{98.8 \text{ kJ}}{0.1415 \text{ kJ/K}} = 698 \text{ K}$

The development presented in Example 16.6 is an important one from a practical standpoint. It tells us the temperature at which the direction of spontaneity changes. In the reduction of Fe_2O_3 by hydrogen, this temperature is approximately 700 K. At lower temperatures, the reaction does not occur at standard conditions; recall from Example 16.5 that $\Delta G°$ at 500 K is +27.6 kJ. At temperatures above 700 K, $\Delta G°$ has a negative sign and the reaction

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

is spontaneous.

From a slightly different point of view, we can say that the equation $T = \Delta H°/\Delta S°$ allows us to calculate the temperature at which a chemical or physical change is at equilibrium at 1 atm pressure. Consider, for example, the vaporization of water:

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

where $\Delta H° = +40.7$ kJ, $\Delta S° = +0.109$ kJ/K. The temperature at which $\Delta G°$ is zero is

$$T = \frac{40.7}{0.109} \qquad T = 373 \quad K = 100°C$$

This is, of course, the normal boiling point of water (the temperature at which liquid water is at equilibrium with vapor at 1 atm).

P and *T* affect ΔG but not ΔH; *P* affects ΔS.

Pressure and Concentration

All of the free energy calculations to this point have involved the standard free energy change, $\Delta G°$. It is possible, however, to write a general relation for the free energy change, ΔG, valid under any conditions. This relation is a relatively simple one, but we will not attempt to derive it. It says that

$$\Delta G = \Delta G° + RT \ln Q \qquad (16.4)$$

If $Q < 1$, $\Delta G < \Delta G°$. Explain.

The quantity Q that appears in this equation is the "reaction quotient" referred to in Chapter 12. It has the same mathematical form as the equilibrium constant, K;

the difference is that the terms that appear in Q are arbitrary, initial pressures or concentrations rather than equilibrium values.

To use this general expression for ΔG, you need to express T in K, R in kilojoules per kelvin (8.31×10^{-3} kJ/K). As far as Q is concerned, the general rules are as follows:

- gases enter as their partial pressures in atmospheres.
- species in aqueous solution enter as their molar concentrations.
- pure liquids or solids do not appear; neither does the solvent in a dilute solution.

As an example, consider the reaction of zinc with strong acid:

$$Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$$

Here Equation 16.4 would take the following form:

$$\Delta G = \Delta G^\circ + RT \ln \frac{[Zn^{2+}](P_{H_2})}{[H^+]^2}$$

EXAMPLE 16.7 GRADED

When zinc is dissolved in a strong acid at 25°C, zinc ions and hydrogen gas are produced. The equation for the reaction is

$$Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$$

a Calculate ΔG° at the temperature of the reaction.

ANALYSIS

Information given:	equation for the reaction ($Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$) T(25°C)
Information implied:	ΔG_f° values at 25°C (Appendix 1)
Asked for:	ΔG°

STRATEGY

1. Find ΔG° by substituting ΔG_f° values into Equation 16.3.
2. Recall that ΔG_f° for elements in their native state at 25°C and H^+ (aq) is zero.

SOLUTION

ΔG°

$$\Delta G^\circ = \Delta G_f^\circ\ Zn^{2+}(aq) + \Delta G_f^\circ\ H_2(g) - [\Delta G_f\ Zn(s) + 2(\Delta G_f^\circ\ H^+(aq))]$$
$$= -147.1 \text{ kJ} + 0 - [0 + 2(0)] = -147.1 \text{ kJ}$$

b Calculate ΔG when $P_{H_2} = 750$ mm Hg, $[Zn^{2+}] = 0.10\ M$, $[H^+] = 1.0 \times 10^{-4}\ M$.

ANALYSIS

Information given:	P_{H_2} (750 mm Hg); $[Zn^{2+}](0.10\ M)$; $[H^+](1.0 \times 10^{-4}\ M)$; T(25°C) from part (a): $\Delta G^\circ(-147.1$ kJ)
Information implied:	R value in energy units
Asked for:	ΔG

STRATEGY

1. Write the expression for Q and find its value. Recall that solids and pure liquids are not included. Make sure that concentrations are expressed in molarity and that pressure is in atm.
2. Substitute into Equation 16.4. Remember that R must be in kJ/K and T must be in K.

continued

SOLUTION

1. Q

$$Q = \frac{[Zn^{2+}]P_{H_2}}{[H^+]^2} = \frac{(0.10)(750/760)}{(1.0 \times 10^{-4})^2} = 9.9 \times 10^6$$

2. ΔG

$$\Delta G = \Delta G^\circ + RT \ln Q = -147.1 \text{ kJ} + (0.00831 \text{ kJ/K})(298 \text{ K}) \ln (9.9 \times 10^6)$$
$$= -147.1 \text{ kJ} + 39.9 \text{ kJ} = -107.2 \text{ kJ}$$

C What is the pH when $\Delta G = -100.0$ kJ, $P_{H_2} = 0.933$ atm, $[Zn^{2+}] = 0.220\ M$ and the mass of Zn is 155 g?

ANALYSIS

Information given:	P_{H_2}(0.933 atm); $[Zn^{2+}]$(0.220 M); mass Zn(155 g); T(25°C) ΔG(−100.0 kJ) From part (a): ΔG°(−147.1 kJ)
Information implied:	R value in energy units
Asked for:	pH

STRATEGY

1. Find Q by substituting into Equation 16.4.
2. Write the equation for Q.
3. Solve for $[H^+]$ by substituting into the Q expression. Change $[H^+]$ into pH.

SOLUTION

1. Q

$$-100.0 \text{ kJ} = -147.1 \text{ kJ} + (0.00831 \text{ kJ/K})(298 \text{ K}) \ln Q$$

$$\ln Q = \frac{47.1}{(0.00831)(298)} = 19.0 \longrightarrow Q = e^{19.0} = 1.82 \times 10^8$$

2. Q expression

$$Q = \frac{[Zn^{2+}](P_{H_2})}{[H^+]^2}; \quad 1.82 \times 10^8 = \frac{(0.220)(0.933)}{[H^+]^2}$$

3. $[H^+]$; pH

$$[H^+] = \left(\frac{(0.220)(0.933)}{1.82 \times 10^8}\right)^{1/2} = 3.35 \times 10^{-5}\ M; \quad \text{pH} = -\log_{10} 3.35 \times 10^{-5} = 4.47$$

As Example 16.7 implies, changes in pressure and/or concentration can have a considerable effect on ΔG. Sometimes, when ΔG° is close to zero, changing the pressure from 1 atm to some other value can change the direction of spontaneity. Consider, for example, the reaction at 300°C:

$$NH_4Cl(s) \longrightarrow NH_3(g) + HCl(g) \qquad \Delta G^\circ = +13.0 \text{ kJ}$$

The positive sign of ΔG° implies that ammonium chloride will not decompose at 300°C to give NH_3 and HCl, both at 1 atm pressure. However, notice what happens if $P_{NH_3} = P_{HCl} = 0.10$ atm, in which case $Q = (0.10)^2$:

$$\Delta G = \Delta G^\circ + RT \ln(0.10)^2$$
$$= +13.0 \text{ kJ} + (8.31 \times 10^{-3})\ (573 \text{ kJ})\ (\ln 0.010)$$
$$= +13.0 \text{ kJ} - 21.9 \text{ kJ} = -8.9 \text{ kJ}$$

This means that NH_3 and HCl *can* be formed, each at 0.10 atm pressure, by heating ammonium chloride to 300°C.

Another example of how a change in concentration can change the direction of spontaneity involves the reaction

$$SrCrO_4(s) \longrightarrow Sr^{2+}(aq) + CrO_4^{2-}(aq) \qquad \Delta G^\circ = +25.3 \text{ kJ at } 25°C$$

Because ΔG° is a positive quantity, $SrCrO_4$ does not dissolve spontaneously to form a 1 M solution at 25°C (Figure 16.8). Suppose, however, the concentrations

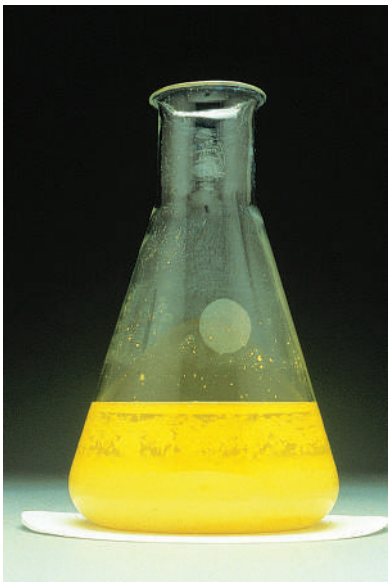


Figure 16.8 A saturated solution of strontium chromate. The solution of $SrCrO_4$ contains 0.006 mol/L of Sr^{2+} and CrO_4^{2-}. For the reaction at 25°C: $SrCrO_4(s) \rightleftharpoons Sr^{2+}(aq, 0.006\ M) + CrO_4^{2-}(aq, 0.006\ M)$, $\Delta G = 0$.

of Sr^{2+} and CrO_4^{2-} are reduced to 0.0010 *M*:

$$\begin{aligned}\Delta G &= \Delta G^\circ + RT \ln [Sr^{2+}][CrO_4^{2-}] \\ &= +25.3 \text{ kJ} + [(8.31 \times 10^{-3})(298)] \text{ kJ } [\ln (1.0 \times 10^{-3})^2] \\ &= +25.3 \text{ kJ} - 34.2 \text{ kJ} = -8.9 \text{ kJ}\end{aligned}$$

Strontium chromate should, and does, dissolve spontaneously to form a 0.0010 *M* water solution. As you might expect, its solubility at 25°C lies between 1 *M* and 0.0010 *M*, at about 0.0060 *M*.

$$\Delta G \text{ at } 0.0060\ M = +25.3 \text{ kJ} + RT \ln (0.0060)^2 = 0$$

16-6 The Free Energy Change and the Equilibrium Constant

Throughout this chapter we have stressed the relation between the free energy change and reaction spontaneity. For a reaction to be spontaneous at standard conditions (1 atm, 1 *M*), ΔG° must be negative. Another indicator of reaction spontaneity is the equilibrium constant, *K;* if *K* is greater than 1, the reaction is spontaneous at standard conditions. As you might suppose, the two quantities ΔG° and *K* are related. The nature of that relationship is readily deduced by starting with the general equation

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

Suppose now that reaction takes place until equilibrium is established, at which point $Q = K$ and $\Delta G = 0$.

Remember, when $\Delta G = 0$, the system is at equilibrium.

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

hence

$$\Delta G^\circ = -RT \ln K \qquad (16.5)$$

Equation 16.5 is generally applicable to any system. The equilibrium constant may be the *K* referred to in our discussion of gaseous equilibrium (Chapter 12), or any of the solution equilibrium constants (K_w, K_a, K_b, K_{sp}, . . .) discussed in subsequent chapters. Notice that ΔG° is the *standard* free energy change (gases at 1 atm, species in solution at 1 *M*). That is why, in the expression for *K*, gases enter as their partial pressures in *atmospheres* and ions or molecules in solution as their *molarities*.

EXAMPLE 16.8

Using ΔG_f° tables in Appendix 1, calculate the solubility product constant, K_{sp}, for $PbCl_2$ at 25°C.

ANALYSIS

Information given:	*T*(25°C)
Information implied:	Equation for dissolving $PbCl_2$ ΔG_f° values (Appendix 1) *R* value
Asked for:	K_{sp}

STRATEGY

1. Obtain ΔG_f° values from Appendix 1 and substitute into Equation 16.3.
2. Substitute into Equation 16.5 to find K_{sp}, which is *K*.

$$\Delta G^\circ = -RT \ln K_{sp}$$

continued

SOLUTION

$\Delta G°$

$$\Delta G° = \Delta G_f° \, Pb^{2+}(aq) + 2\Delta G_f° \, Cl^-(aq) - \Delta G_f° \, PbCl_2(s)$$
$$= -24.4 \text{ kJ} + 2(-131.2 \text{ kJ}) + 314.1 \text{ kJ} = +27.3 \text{ kJ}$$

K_{sp}

$$\Delta G° = -RT \ln K_{sp}; \; 27.3 \text{ kJ} = -(0.00831 \text{ kJ/K})(298 \text{ K}) \ln K_{sp}$$
$$\ln K_{sp} = -11.0 \longrightarrow K_{sp} = e^{-11.0} = 1.7 \times 10^{-5}$$

END POINT

This is the value listed in Chapter 15 for K_{sp} of $PbCl_2$.

The relationship $\Delta G° = -RT \ln K$ allows us to relate the standard free energy change to the extent of reaction. Consider, for example, the simple equilibrium system

$$A(g) \rightleftharpoons B(g)$$

at 25°C. Figure 16.9 shows how the extent of reaction varies with the value of $\Delta G°$ for this system. Notice that

- if $\Delta G°$ is greater than about +20 kJ, the equilibrium constant is so small that virtually no A is converted to B. We would say that, for all practical purposes, the reaction does not occur.
- if $\Delta G°$ is less than about −20 kJ, the equilibrium constant is so large that virtually all of A is converted to B. In essence, the reaction goes to completion.
- only if $\Delta G°$ lies between +20 kJ and −20 kJ will the equilibrium mixture contain appreciable amounts of both A and B. In particular, if $\Delta G° = 0$, $K = 1$ and the equilibrium system contains equal amounts of A and B.

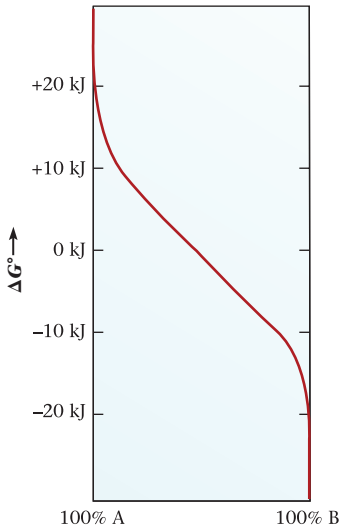


Figure 16.9 Dependence of extent of reaction on the value of $\Delta G°$ for the general system $A(g) \rightleftharpoons B(g)$.

16-7 Additivity of Free Energy Changes; Coupled Reactions

Free energy changes for reactions, like enthalpy or entropy changes, are additive. That is,

$$\text{if Reaction 3} = \text{Reaction 1} + \text{Reaction 2}$$
$$\text{then } \Delta G_3 = \Delta G_1 + \Delta G_2$$

This relation can be regarded as the free energy equivalent of Hess's law (Chapter 8). To illustrate its application, consider the synthesis of $CuCl_2$ from the elements

$$Cu(s) + \tfrac{1}{2}Cl_2(g) \longrightarrow CuCl(s) \qquad \Delta G° \text{ at } 25°C = -119.9 \text{ kJ}$$
$$CuCl(s) + \tfrac{1}{2}Cl_2(g) \longrightarrow CuCl_2(s) \qquad \Delta G° \text{ at } 25°C = -55.8 \text{ kJ}$$
$$Cu(s) + Cl_2(g) \longrightarrow CuCl_2(s)$$

For the overall reaction, $\Delta G°$ at 25°C = −119.9 kJ + (−55.8 kJ) = −175.7 kJ.

Because free energy changes are additive, it is often possible to bring about a nonspontaneous reaction by coupling it with a reaction for which $\Delta G°$ is a large negative number. As an example, consider the preparation of iron metal from hematite ore. The reaction

$$Fe_2O_3(s) \longrightarrow 2Fe(s) + \tfrac{3}{2}O_2(g) \qquad \Delta G° \text{ at } 25°C = +742.2 \text{ kJ}$$

is clearly nonspontaneous; even at temperatures as high as 2000°C, $\Delta G°$ is a positive quantity. Suppose, though, that this reaction is "coupled" with the spontaneous oxidation of carbon monoxide:

$$CO(g) + \tfrac{1}{2}O_2(g) \longrightarrow CO_2(g) \qquad \Delta G° \text{ at } 25°C = -257.2 \text{ kJ}$$

The overall reaction is spontaneous:

$$\begin{aligned} Fe_2O_3(s) &\longrightarrow 2Fe(s) + \tfrac{3}{2}O_2(g) \\ 3CO(g) + \tfrac{3}{2}O_2(g) &\longrightarrow 3CO_2(g) \\ \hline Fe_2O_3(s) + 3CO(g) &\longrightarrow 2Fe(s) + 3CO_2(g) \end{aligned}$$

For the coupled reaction at 25°C,

$$\Delta G^\circ = +742.2\text{ kJ} + 3(-257.2\text{ kJ}) = -29.4\text{ kJ}$$

The negative sign of ΔG° implies that although Fe_2O_3 does not spontaneously decompose, it can be converted to iron by reaction with carbon monoxide. This is in fact the reaction used in the blast furnace when iron ore consisting mainly of Fe_2O_3 is reduced to iron (Chapter 20).

Many industrial processes involve coupled reactions.

Coupled reactions are common in human metabolism. Spontaneous processes, such as the oxidation of glucose,

$$C_6H_{12}O_6(aq) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O \qquad \Delta G^\circ = -2870\text{ kJ at }25^\circ\text{C}$$

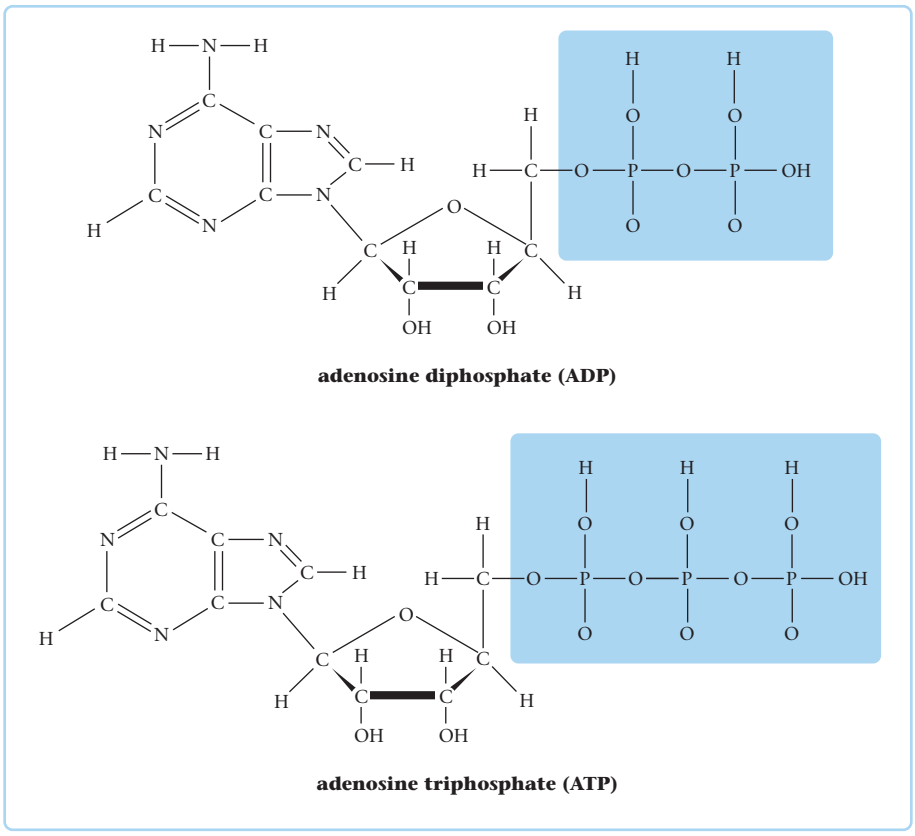
ordinarily do not serve directly as a source of energy. Instead these reactions are used to bring about a nonspontaneous reaction:

$$ADP(aq) + HPO_4^{2-}(aq) + 2H^+(aq) \longrightarrow ATP(aq) + H_2O \qquad (16.6)$$
$$\Delta G^\circ = +31\text{ kJ at }25^\circ\text{C}$$

ADP (adenosine diphosphate) and ATP (adenosine triphosphate) are complex organic molecules (Figure 16.10) that, in essence, differ only by the presence of an extra phosphate group in ATP. In the coupled reaction with glucose, about 38 mol of ATP are synthesized for every mole of glucose consumed. This gives an overall free energy change for the coupled reaction of

$$-2870\text{ kJ} + 38(+31\text{ kJ}) \approx -1700\text{ kJ}$$

Figure 16.10 Structures of ADP and ATP.



In a very real sense, your body "stores" energy available from the metabolism of foods in the form of ATP. This molecule in turn supplies the energy required for all sorts of biochemical reactions taking place in the body. It does this by reverting to ADP, that is, by reversing reaction 16.6. The amount of ATP consumed is amazingly large; a competitive sprinter may hydrolyze as much as 500 g (about 1 lb) of ATP per minute.

Conversion of ATP to ADP gives you energy in a hurry.

EXAMPLE 16.9

The lactic acid ($C_3H_6O_3(aq)$, $\Delta G_f^\circ = -559$ kJ) produced in muscle cells by vigorous exercise eventually is absorbed into the bloodstream, where it is metabolized back to glucose ($\Delta G_f^\circ = -919$ kJ) in the liver. The reaction is

$$2C_3H_6O_3(aq) \longrightarrow C_6H_{12}O_6(aq)$$

(a) Calculate ΔG° at 25°C for this reaction, using free energies of formation.

(b) If the hydrolysis of ATP to ADP is coupled with this reaction, how many moles of ATP must react to make the process spontaneous?

ANALYSIS

Information given:	equation for the reaction ($2C_3H_6O_3(aq) \longrightarrow C_6H_{12}O_6(aq)$) ΔG_f° values: $C_3H_6O_3(aq)$ (−559 kJ); $C_6H_{12}O_6(aq)$(−919 kJ) T(25°C) energy from ATP/mol (31 kJ)
Asked for:	(a) ΔG° (b) mol ATP for spontaneity

STRATEGY

1. Find ΔG° using the ΔG_f° values given in Appendix 1.

$$\Delta G^\circ = \Sigma \Delta G_{f\,\text{products}}^\circ - \Sigma \Delta G_{f\,\text{reactants}}^\circ$$

2. Convert the energy obtaned in (1) to moles ATP by using the conversion factor: 31 kJ/mol ATP

SOLUTION

1. ΔG°

$$\Delta G^\circ = \Delta G_f^\circ\, C_6H_{12}O_6(aq) - 2\Delta G_f^\circ\, C_3H_6O_3(aq)$$
$$= -919 \text{ kJ} - 2(-559 \text{ kJ}) = +199 \text{ kJ}$$

2. mol ATP

$$199 \text{ kJ} \times \frac{1 \text{ mol ATP}}{31 \text{ kJ}} = 6.4 \text{ mol ATP}$$

CHEMISTRY **BEYOND** THE CLASSROOM

Rubber Elasticity: An Entropic Phenomenon

Leslie Sperling, Lehigh University

Molecular Structure of Rubbery Materials

Along with such materials as plastics, adhesives, fibers, and coatings, rubber is polymeric in nature. Such materials consist of long chains, with molecular masses generally of the order of 50,000 to 500,000 g/mol. Common rubbery materials—often called elastomers—include automotive tires and rubber bands.

For a polymer to exhibit rubber elasticity, it must have two properties:

1. It must be *crosslinked* or *vulcanized*. Crosslinking is the chemical joining together of polymer chains, usually by sulfur bonds at random positions, to make a three-dimensional network (see Figure A).
2. It must be above its glass transition temperature, which means that the polymer chains have sufficient thermal energy to move freely. Many rubbery materials have glass transition temperatures around 200 K, below which they are glassy, like plastics.

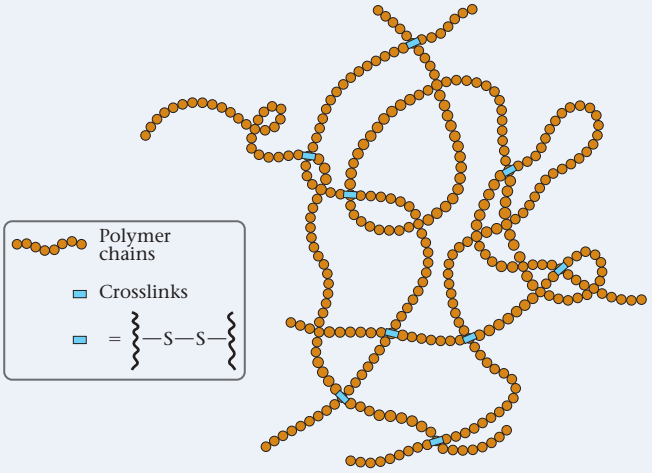


Figure A Schematic of polymer chains randomly placed in space, with crosslinks also placed randomly, but frequently averaging every 5,000–10,000 g/mol along the chains.

Common rubbery materials consist of butadiene and styrene statistical copolymers, written poly(butadiene-*stat*-styrene). The butadiene polymer has the repeating structure ($—CH_2—CH=CH—CH_2^-$) while styrene has the repeating structure

$$—CH_2—\underset{\displaystyle C_6H_5}{\overset{\displaystyle |}{CH}}—$$

How Does Entropy Apply to Elastomeric Materials?

Entropy is a measure of disorder in materials. Relaxed polymer chains with a random conformation (shape in space), like cooked spaghetti or a box of fishing worms, have a high degree of entropy, which is favored by Mother Nature. If the chains are stretched out (stressed), the number of conformations the chains can have in space is limited, and the entropy is reduced (see Figure B). The ratio of final length to initial length is denoted α.

For materials such as rubber bands, the quantity α may be as large as five. At that point, the chains are substantially fully extended. Further stretching may break the rubber band, actually severing the polymer chains at the break point (a chemical reaction!).

There is an interesting demonstration experiment that you can do with a rubber band, preferably a large and/or thick one. Touch the unstretched rubber band to your lips. Then, stretch the rubber band rapidly and immediately, retouch it to your lips. The rubber band will be warmer. This motion creates a thermodynamic cycle in which the system goes through a series of different states and then returns to its original state. The cycle acts as a heat engine.

The major applications of rubbery materials today include automotive tires, rubber bands, tubing of various kinds, electric wire insulation, elastomeric urethane fibers for undergarments, and silicone rubber. Such types of polymers are important materials in our twenty-first-century world.

References

1. A. J. Etzel, S. J. Goldstein, H. J. Panabaker, D. G. Fradkin, and L. H. Sperling, *J. Chem. Ed.*, **63**, 731 (1986).
2. L. H. Sperling, *Introduction to Physical Polymer Science*, 4th Ed., Wiley, New York, 2006.

Figure B Pulling down on the elastomer. The chains become oriented in the elongational direction, lowering the entropy of the system.

Key Concepts

1. Deduce the sign of ΔS for a process from randomness considerations.
   (Example 16.1; Problems 7–14)
2. Calculate $\Delta S°$ for a reaction, using Table 16.1.
   (Example 16.2; Problems 17–22)
3. Calculate $\Delta G°$ at any temperature, knowing $\Delta H°$ and $\Delta S°$.
   (Examples 16.3, 16.5; Problems 23–26)
4. Calculate $\Delta G°$ at 25°C from free energies of formation.
   (Examples 16.4, 16.7–16.9; Problems 27–32)

5. Calculate the temperature at which $\Delta G^\circ = 0$. **(Example 16.6; Problems 39–44, 49–54)**
6. Calculate ΔG from ΔG°, knowing all pressures and/or concentrations. **(Example 16.7; Problems 55–60)**
7. Relate ΔG° to K. **(Example 16.8; Problems 61–70)**
8. Calculate ΔG° for coupled reactions. **(Example 16.9; Problems 71–76)**

Key Equations

Entropy change	$\Delta S^\circ = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}}$
Gibbs-Helmholtz equation	$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
Free energy change	$\Delta G^\circ = \sum \Delta G_f^\circ \text{ products} - \sum \Delta G_f^\circ \text{ reactants}$
	$\Delta G = \Delta G^\circ + RT \ln Q$
	$\Delta G^\circ = -RT \ln K$

Key Terms

entropy
free energy
spontaneous processes
standard entropy change
standard free energy change
standard free energy of formation

Summary Problem

Consider formic acid, HCOOH. It is given off by many insects when they sting their victims. Its name comes from *formica*, the Latin name for ant. Extensively used by the textile industry, it can be obtained by the exposure of methyl alcohol (an alcohol present in gasohol) to air.

$$CH_3OH(aq) + O_2(g) \longrightarrow HCOOH(aq) + H_2O(l)$$

The following data may be useful:

$CH_3OH(aq)$: $\Delta H_f^\circ = -246$ kJ/mol; $S^\circ = 133.1$ J/mol · K
$HCOOH(aq)$: $\Delta H_f^\circ = -425$ kJ/mol; $S^\circ = 163$ J/mol · K

(a) Calculate ΔH° and ΔS° for the process.

(b) Is the reaction spontaneous at 25°C? At 100°C?

(c) The heat of vaporization for formic acid is 23.1 kJ/mol. Its normal boiling point is 101°C. Calculate ΔS° for the reaction

$$HCOOH(l) \longrightarrow HCOOH(g)$$

(d) What is the standard molar entropy for $HCOOH(g)$ taking S° for $HCOOH(l)$ to be 129 J/mol · K?

(e) Calculate ΔG at 25°C for the formation of formic acid from methyl alcohol (equation given earlier) when [HCOOH] = 0.250 M, $P_{O_2} = 0.75$ atm, and $[CH_3OH] = 0.0100$ M.

(f) Calculate ΔG° for the ionization of formic acid at 25°C. ($K_a = 1.9 \times 10^{-4}$)

Answers

(a) $\Delta H^\circ = -465$ kJ; $\Delta S^\circ = -105$ J/K
(b) $\Delta G^\circ = -434$ kJ; yes; yes
(c) 61.8 J/K
(d) 191 J/mol · K
(e) −425 kJ
(f) 21.2 kJ

Questions and Problems

Even-numbered questions and Challenge Problems have answers in Appendix 5 and fully worked solutions in the *Student Solutions Manual*.

16-1 Spontaneous Processes

1. Which of the following processes are spontaneous?
   (a) building a sand castle
   (b) outlining your chemistry notes
   (c) wind scattering leaves in a pile
2. Which of the following processes are spontaneous?
   (a) ice cream melting at 75°F
   (b) sorting a list of names alphabetically
   (c) gathering leaves in a pile

3. Which of the following processes are spontaneous?
(a) a ball rolling down a hill
(b) a drop of ink dispersing in water
(c) melting wax at 10°C

4. Which of the following processes are spontaneous?
(a) cleaning up your desk
(b) building a house of cards
(c) sugar dissolving in hot water

5. On the basis of your experience, predict which reactions are spontaneous:
(a) $PbO_2(s) \longrightarrow Pb(s) + O_2(g)$
(b) $N_2(l) \longrightarrow N_2(g)$ at 25°C
(c) $C_6H_{12}O_6(s) \longrightarrow C_6H_{12}O_6(l)$ at 25°C
(d) $Ca^{2+}(aq) + CO_3{}^{2-}(aq) \longrightarrow CaCO_3(s)$

6. On the basis of your experience, predict which of the following reactions are spontaneous.
(a) $CO_2(s) \longrightarrow CO_2(g)$ at 25°C
(b) $NaCl(s) \longrightarrow NaCl(l)$ at 25°C
(c) $2NaCl(s) \longrightarrow 2Na(s) + Cl_2(g)$
(d) $CO_2(g) \longrightarrow C(s) + O_2(g)$

16-2 Entropy, *S*

7. In each of the following pairs, choose the substance with a lower entropy.
(a) $H_2O(l)$ at 10°C, $H_2O(l)$ at 30°C
(b) C (graphite), C (diamond)
(c) $Cl_2(l)$, $Cl_2(g)$, both at room temperature

8. In each of the following pairs, choose the substance with a lower entropy.
(a) One mole of $O_2(g)$ with 758 mm Hg pressure, one mole of $O_2(g)$ with 493 mm Hg pressure, both at room temperature
(b) glucose (*s*), glucose (*aq*)
(c) $Hg(l)$, $Hg(g)$, both at room temperature

9. Predict the sign of ΔS for the following:
(a) a lake freezing
(b) ice cream thawing
(c) a candle burning
(d) weeding a garden

10. Predict the sign of ΔS for the following:
(a) precipitating solid AgCl from a solution containing Ag^+ and Cl^- ions
(b) dissolving sugar in hot coffee
(c) glass turning into sand

11. Predict the sign of $\Delta S°$ for each of the following reactions.
(a) $2Na(s) + Cl_2(g) \longrightarrow 2NaCl(s)$
(b) $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$
(c) $C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$
(d) $NH_4NO_3(s) + H_2O(l) \longrightarrow 2NH_3(g) + O_2(g)$

12. Predict the sign of $\Delta S°$ for each of the following reactions:
(a) $CCl_4(l) + 5O_2(g) \longrightarrow CO_2(g) + 4ClO_2(g)$
(b) $8H_2O(l) + S_8(s) \longrightarrow 8H_2S(g) + 4O_2(g)$
(c) $Br_2(l) \longrightarrow Br_2(s)$
(d) $2NH_3(g) \longrightarrow N_2(g) + 3H_2(g)$

13. Predict the sign of $\Delta S°$ for each of the following reactions.
(a) $O_3(g) \longrightarrow O_2(g) + O(g)$
(b) $PCl_3(g) + Cl_2(g) \longrightarrow PCl_5(g)$
(c) $CuSO_4(s) + 5H_2O(l) \longrightarrow CuSO_4 \cdot 5H_2O(s)$

14. Predict the sign of $\Delta S°$ for each of the following reactions.
(a) $H_2(g) + Ni^{2+}(aq) \longrightarrow 2H^+(aq) + Ni(s)$
(b) $Cu(s) + 2H^+(aq) \longrightarrow H_2(g) + Cu^{2+}(aq)$
(c) $N_2O_4(g) \longrightarrow 2NO_2(g)$

15. Predict the order of the following reactions in terms of increasing ΔS:
(a) $2H_2O_2(l) \longrightarrow 2H_2O(l) + O_2(g)$
(b) $Si(s) + O_2(g) \longrightarrow SiO_2(s)$
(c) $Br_2(g) + 3I_2(g) \longrightarrow 2BrI_3(l)$
(d) $NH_3(g) + HBr(g) \longrightarrow NH_4Br(s)$

16. Predict the order of the following reactions in terms of increasing ΔS:
(a) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$
(b) $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$
(c) $C(g) + O_2(g) \longrightarrow CO_2(s)$
(d) $I_2(g) + Cl_2(g) \longrightarrow 2ICl(g)$

17. Use Table 16.1 to calculate $\Delta S°$ for each of the following reactions.
(a) $CO(g) + 2H_2(g) \longrightarrow CH_3OH(l)$
(b) $N_2(g) + O_2(g) \longrightarrow 2NO(g)$
(c) $BaCO_3(s) \longrightarrow BaO(s) + CO_2(g)$
(d) $2NaCl(s) + F_2(g) \longrightarrow 2NaF(s) + Cl_2(g)$

18. Use Table 16.1 to calculate $\Delta S°$ for each of the following reactions:
(a) $4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$
(b) $2H_2O_2(l) + N_2H_4(l) \longrightarrow N_2(g) + 4H_2O(g)$
(c) $C(s) + O_2(g) \longrightarrow CO_2(g)$
(d) $CH_4(g) + 3Cl_2(g) \longrightarrow CHCl_3(l) + 3HCl(g)$

19. Use Table 16.1 to calculate $\Delta S°$ for each of the following reactions.
(a) $2Cl^-(aq) + I_2(s) \longrightarrow Cl_2(g) + 2I^-(aq)$
(b) $SO_4{}^{2-}(aq) + 4H^+(aq) + Cd(s) \longrightarrow Cd^{2+}(aq) + SO_2(g) + 2H_2O(l)$
(c) $2Br^-(aq) + 2H_2O(l) \longrightarrow Br_2(l) + H_2(g) + 2OH^-(aq)$

20. Use Table 16.1 to calculate $\Delta S°$ for each of the following reactions.
(a) $5NO(g) + 3MnO_4{}^-(aq) + 4H^+(aq) \longrightarrow 5NO_3{}^-(aq) + 3Mn^{2+}(aq) + 2H_2O(l)$
(b) $6Fe^{2+}(aq) + CrO_4{}^{2-}(aq) + 8H^+(aq) \longrightarrow Cr(s) + 6Fe^{3+}(aq) + 4H_2O(l)$
(c) $C_2H_2(g) + \frac{5}{2}O_2(g) \longrightarrow 2CO_2(g) + H_2O(g)$

21. Use Table 16.1 to calculate $\Delta S°$ for each of the following reactions:
(a) $2Cr(s) + 3CO_2(g) \longrightarrow Cr_2O_3(s) + 3CO(g)$
(b) $4C(s) + O_2(g) + 6H_2(g) \longrightarrow 2C_2H_5OH(l)$
(c) $N_2O_4(g) + 4H_2(g) \longrightarrow N_2(g) + 4H_2O(g)$
(d) $2CuO(s) \longrightarrow 2Cu(s) + O_2(g)$

22. Use Table 16.1 to calculate $\Delta S°$ for each of the following reactions.
(a) $2HNO_3(l) + 3H_2S(g) \longrightarrow 4H_2O(l) + 2NO(g) + 3S(s)$
(b) $PCl_5(g) + 4H_2O(l) \longrightarrow 5Cl^-(aq) + H_2PO_4{}^-(aq) + 6H^+(aq)$
(c) $MnO_4{}^-(aq) + 3Fe^{2+}(aq) + 4H^+(aq) \longrightarrow 3Fe^{3+}(aq) + MnO_2(s) + 2H_2O(l)$

16-4 Standard Free Energy Change, $\Delta G°$

23. Calculate $\Delta G°$ at 82°C for reactions in which
(a) $\Delta H° = 293$ kJ; $\Delta S° = -695$ J/K
(b) $\Delta H° = -1137$ kJ; $\Delta S° = 0.496$ kJ/K
(c) $\Delta H° = -86.6$ kJ; $\Delta S° = -382$ J/K

24. Calculate $\Delta G°$ at 72°C for reactions in which
(a) $\Delta H° = -136$ kJ; $\Delta S° = +457$ J/K
(b) $\Delta H° = 41.5$ kJ; $\Delta S° = -0.288$ kJ/K
(c) $\Delta H° = -795$ kJ; $\Delta S° = -861$ J/K

25. Calculate $\Delta G°$ at 355 K for each of the reactions in Question 17. State whether the reactions are spontaneous.

26. Calculate $\Delta G°$ at 415 K for each of the reactions in Question 18. State whether the reactions are spontaneous.

27. From the values for $\Delta G_f°$ given in Appendix 1, calculate $\Delta G°$ at 25°C for each of the reactions in Question 19.

28. Follow the directions of Problem 27 for each of the reactions in Question 20.

29. Use standard entropies and heats of formation to calculate $\Delta G_f°$ at 25°C for
(a) cadmium(II) chloride (s).
(b) methyl alcohol, $CH_3OH(l)$.
(c) copper(I) sulfide (s).

30. Follow the directions of Question 29 for the following compounds:
(a) solid ammonium nitrate
(b) liquid methyl alcohol
(c) solid copper(II) sulfide

31. It has been proposed that wood alcohol, CH_3OH, a relatively inexpensive fuel to produce, be decomposed to produce methane. Methane is a natural gas commonly used for heating homes. Is the decomposition of wood alcohol to methane and oxygen thermodynamically feasible at 25°C and 1 atm?

32. A student warned his friends not to swim in a river close to an electric plant. He claimed that the ozone produced by the plant turned the river water to hydrogen peroxide, which would bleach hair. The reaction is

$$O_3(g) + H_2O(l) \longrightarrow H_2O_2(aq) + O_2(g)$$

Assuming that the river water is at 25°C and all species are at standard concentrations, show by calculation whether his claim is plausible. Take $\Delta G_f°$ $O_3(g)$ at 25°C to be +163.2 kJ/mol and $\Delta G_f°$ $H_2O_2(aq) = -134$ kJ/mol.

33. Sodium carbonate, also called "washing soda," can be made by heating sodium hydrogen carbonate:

$$2NaHCO_3(s) \longrightarrow Na_2CO_3(s) + CO_2(g) + H_2O(l)$$
$$\Delta H° = +135.6 \text{ kJ}; \Delta G° = +34.6 \text{ kJ at } 25°C$$

(a) Calculate $\Delta S°$ for this reaction. Is the sign reasonable?
(b) Calculate $\Delta G°$ at 0 K; at 1000 K.

34. The reaction between magnesium metal and water (l) produces solid magnesium hydroxide and hydrogen gas. Calculate $\Delta G°$ for the formation of one mole of $Mg(OH)_2$ at 27°C and at 39°C.

35. In the laboratory, $POCl_3$ (phosphorus oxychloride) is used in the manufacture of phosphate esters, which are used in flame retardants and pesticides. It can be prepared by the following reaction at 25°C:

$$2PCl_3(g) + O_2(g) \longrightarrow 2POCl_3(g)$$
$$\Delta H° = -572 \text{ kJ}; \Delta G° = -518.7 \text{ kJ}$$

(a) Calculate $\Delta S°$. Is the sign reasonable?
(b) Calculate $S°$ for $POCl_3$.
(c) Calculate $\Delta H_f°$ for $POCl_3$.

36. Oxygen can be made in the laboratory by reacting sodium peroxide and water.

$$2Na_2O_2(s) + 2H_2O(l) \longrightarrow 4NaOH(s) + O_2(g)$$
$$\Delta H° = -109.0 \text{ kJ}; \Delta G° = -148.4 \text{ kJ at } 25°C$$

(a) Calculate $\Delta S°$. Is the sign reasonable?
(b) Calculate $S°$ for $Na_2O_2(s)$.
(c) Calculate $\Delta H_f°$ for $Na_2O_2(s)$.

37. Phosgene, $COCl_2$, can be formed by the reaction of chloroform, $CHCl_3(l)$, with oxygen:

$$2CHCl_3(l) + O_2(g) \longrightarrow 2COCl_2(g) + 2HCl(g)$$
$$\Delta H° = -353.2 \text{ kJ}; \Delta G° = -452.4 \text{ kJ at } 25°C$$

(a) Calculate $\Delta S°$ for the reaction. Is the sign reasonable?
(b) Calculate $S°$ for phosgene.
(c) Calculate $\Delta H_f°$ for phosgene.

38. When permanganate ions in aqueous solution react with cobalt metal in strong acid, the equation for the reaction that takes place is

$$2MnO_4^-(aq) + 16H^+(aq) + 5Co(s) \longrightarrow 2Mn^{2+}(aq) + 5Co^{2+}(aq) + 8H_2O(l)$$
$$\Delta H° = -2024.6 \text{ kJ}; \Delta G° \text{ at } 25°C = -1750.9 \text{ kJ}$$

(a) Calculate $\Delta S°$ for the reaction at 25°C.
(b) Calculate $S°$ for Co^{2+}, given $S°$ for Co is 30.04 J/mol·K.

16-5 Effect of Temperature, Pressure, and Concentration on Reaction Spontaneity

Temperature Dependence of Spontaneity

39. Discuss the effect of temperature change on the spontaneity of the following reactions at 1 atm:
(a) $Al_2O_3(s) + 2Fe(s) \longrightarrow 2Al(s) + Fe_2O_3(s)$
$\Delta H° = 851.4$ kJ; $\Delta S° = 38.5$ J/K
(b) $N_2H_4(l) \longrightarrow N_2 + 2H_2(g)$
$\Delta H° = -50.6$ kJ; $\Delta S° = 0.3315$ kJ/K
(c) $SO_3(g) \longrightarrow SO_2(g) + \frac{1}{2}O_2(g)$
$\Delta H° = 98.9$ kJ; $\Delta S° = 0.0939$ kJ/K

40. Discuss the effect of temperature on the spontaneity of reactions with the following values for $\Delta H°$ and $\Delta S°$.
(a) $\Delta H° = 128$ kJ; $\Delta S° = 89.5$ J/K
(b) $\Delta H° = -20.4$ kJ; $\Delta S° = -156.3$ J/K
(c) $\Delta H° = -127$ kJ; $\Delta S° = 43.2$ J/K

41. At what temperature does $\Delta G°$ become zero for each of the reactions in Problem 39? Explain the significance of your answers.

42. Over what temperature range are the reactions in Problem 40 spontaneous?

43. For the reaction

$$2Cl^-(aq) + Br_2(l) \longrightarrow Cl_2(g) + 2Br^-(aq)$$

calculate the temperature at which $\Delta G° = 0$.

44. For the reaction

$$SnO_2(s) + 2CO(g) \longrightarrow 2CO_2(g) + Sn(s)$$

calculate the temperature at which $\Delta G° = 0$.

45. For the decomposition of Ag_2O:

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

(**a**) Obtain an expression for $\Delta G°$ as a function of temperature. Prepare a table of $\Delta G°$ values at 100 K intervals between 100 K and 500 K.
(**b**) Calculate the temperature at which $\Delta G° = 0$.

46. Consider the following hypothetical equation

$$A(s) + B(s) \longrightarrow C(s) + D(s)$$

where $\Delta H° = 492$ kJ and $\Delta S° = 327$ J/K.
(**a**) Obtain an expression for $\Delta G°$ as a function of temperature. Prepare a table of $\Delta G°$ values at 100 K intervals between 100 K and 500 K.
(**b**) Find the temperature at which $\Delta G°$ becomes zero.

47. Two possible ways of producing iron from iron ore are
(**a**) $Fe_2O_3(s) + \frac{3}{2}C(s) \longrightarrow 2Fe(s) + \frac{3}{2}CO_2(g)$
(**b**) $Fe_2O_3(s) + 3H_2(g) \longrightarrow 2Fe(s) + 3H_2O(g)$
Which of these reactions proceeds spontaneously at the lower temperature?

48. Manganese is a metal used in making stainless steel alloys. It can be obtained from pyrolusite, an ore containing MnO_2. If the production process calls for as low a temperature as possible, the ore could be
(**a**) decomposed on heating, producing Mn and O_2.
(**b**) heated with hydrogen gas, producing Mn and steam.
(**c**) heated with coke (C(*s*)), producing Mn and CO_2.

49. Red phosphorus is formed by heating white phosphorus. Calculate the temperature at which the two forms are at equilibrium, given

white P: $\Delta H_f° = 0.00$ kJ/mol; $S° = 41.09$ J/mol·K
red P: $\Delta H_f° = -17.6$ kJ/mol; $S° = 22.80$ J/mol·K

50. Organ pipes in unheated churches develop "tin disease," in which white tin is converted to gray tin. Given

white Sn: $\Delta H_f° = 0.00$ kJ/mol; $S° = 51.55$ J/mol·K
gray Sn: $\Delta H_f° = -2.09$ kJ/mol; $S° = 44.14$ J/mol·K

calculate the equilibrium temperature for the transition.

51. Sulfur has about 20 different allotropes. The most common are rhombic sulfur (the stable form at 25°C and 1 atm) and monoclinic sulfur. They differ in their crystal structures. Given

S(*s*, monoclinic): $\Delta H_f° = 0.30$ kJ/mol, $S° = 0.0326$ kJ/mol·K

at what temperature are the two forms in equilibrium?

52. Pencil "lead" is almost pure graphite. Graphite is the stable elemental form of carbon at 25°C and 1 atm. Diamond is an allotrope of graphite. Given

diamond: $\Delta H_f° = 1.9$ kJ/mol; $S° = 2.4$ J/mol·K

at what temperature are the two forms in equilibrium at 1 atm?

$$C \text{ (graphite)} \rightleftharpoons C \text{ (diamond)}$$

53. Given the following data for sodium

Na(*s*): $S° = 51.2$ J/mol·K
Na(*g*): $S° = 153.6$ J/mol·K $\quad \Delta H_f° = 108.7$ kJ/mol

estimate the temperature at which sodium sublimes at 1 atm.

$$Na(s) \rightleftharpoons Na(g)$$

54. Given the following data for bromine:

$Br_2(l)$; $S° = 152.2$ J/mol·K
$Br_2(g)$; $S° = 245.4$ J/mol·K $\quad \Delta H_f° = 30.91$ kJ/mol

Estimate the normal boiling point of bromine.

Effect of Concentration/Pressure on Spontaneity

55. Show by calculation, using Appendix 1, whether dissolving lead(II) chloride

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$

is spontaneous at 25°C
(**a**) when $[Pb^{2+}] = 1.0\ M$; $[Cl^-] = 2.0\ M$.
(**b**) when $[Pb^{2+}] = 1.0 \times 10^{-5}\ M$; $[Cl^-] = 2.0 \times 10^{-5}\ M$.

56. Show by calculation whether the reaction

$$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq) \qquad \Delta G° = 18.0 \text{ kJ}$$

is spontaneous at 25°C when
(**a**) $[H^+] = [F^-] = 0.78\ M$ and $[HF] = 0.24\ M$
(**b**) $[H^+] = [F^-] = 0.0030\ M$ and $[HF] = 1.85\ M$

57. For the reaction

$$2H_2O(l) + 2Cl^-(aq) \longrightarrow H_2(g) + Cl_2(g) + 2OH^-(aq)$$

(**a**) calculate $\Delta G°$ at 25°C.
(**b**) calculate ΔG at 25°C when $P_{H_2} = P_{Cl_2} = 0.250$ atm, $[Cl^-] = 0.335\ M$, and the pH of the solution is 11.98.

58. For the reaction

$$2H_2O(l) + 2Br^-(aq) \longrightarrow H_2(g) + Br_2(l) + 2OH^-(aq)$$

(**a**) Calculate $\Delta G°$ at 25°C.
(**b**) Calculate ΔG at 25°C when $P_{H_2} = 0.878$ atm, $[Br^-] = 0.423\ M$, and the pH of the solution is 9.72.

59. Consider the reaction

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

(**a**) Calculate $\Delta G°$ at 25°C.
(**b**) If the partial pressures of SO_2 and SO_3 are kept at 0.400 atm, what partial pressure should O_2 have so that the reaction just becomes nonspontaneous (i.e., $\Delta G = +1.0$ kJ)?

60. Consider the reaction

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

(**a**) Calculate $\Delta G°$ at 25°C.
(**b**) What should the concentration of Ag^+ and Cl^- be so that $\Delta G = -1.0$ kJ (just spontaneous)? Take $[Ag^+] = [Cl^-]$.
(**c**) The K_{sp} for AgCl is 1.8×10^{-10}. Is the answer to (b) reasonable?

16-6 The Free Energy Change and the Equilibrium Constant

61. Consider the reaction

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

Use the appropriate tables to calculate
(**a**) $\Delta G°$ at 552°C (**b**) K at 552°C

62. Consider the reaction

$$NH_4^+(aq) \rightleftharpoons H^+(aq) + NH_3(aq)$$

Use ΔG_f° for $NH_3(aq)$ at 25°C = −26.7 kJ/mol and the appropriate tables to calculate

(a) ΔG° at 25°C (b) K_a at 25°C

63. Consider the following reaction at 25°C:

$$Cl_2(g) \rightleftharpoons 2Cl(g) \qquad K = 1.0 \times 10^{-37}$$

(a) Calculate ΔG° for the reaction at 25°C.
(b) Calculate ΔG_f° for Cl(g) at 25°C.

64. Consider the reaction

$$N_2O(g) + NO_2(g) \longrightarrow 3NO(g) \qquad K = 4.4 \times 10^{-19}$$

(a) Calculate ΔG° for the reaction at 25°C.
(b) Calculate ΔG_f° for N_2O at 25°C.

65. For the reaction

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

$K = 2.2 \times 10^{11}$ at 473 K and 4.6×10^8 at 533 K. Calculate ΔG° at both temperatures.

66. Consider the decomposition of N_2O_4 at 100°C.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad K = 11$$

(a) What is ΔG° at that temperature?
(b) What is K at 25°C? (ΔG_f° for N_2O_4 = 97.9 kJ/mol)

67. Use the values for ΔG_f° in Appendix 1 to calculate K_{sp} for barium sulfate at 25°C. Compare with the value given in Chapter 15.

68. Given that ΔH_f° for HF(aq) is −320.1 kJ/mol and S° for HF(aq) is 88.7 J/mol·K, find K_a for HF at 25°C.

69. At 25°C, a 0.327 M solution of a weak acid HX has a pH of 5.12. What is ΔG° for the dissociation of the weak acid?

70. A 0.250 M solution of a weak base R_2NH has a pH of 10.60 at 25°C. What is ΔG° for the dissociation of the weak base in water at 25°C?

$$R_2NH(aq) + H_2O \longrightarrow R_2NH_2^+(aq) + OH^-(aq)$$

16-7 Additivity of Free Energy Changes; Coupled Reactions

71. Given the following standard free energies at 25°C,

$$SO_2(g) + 3CO(g) \longrightarrow COS(g) + 2CO_2(g) \qquad \Delta G^\circ = -246.5 \text{ kJ}$$
$$CO(g) + H_2O(g) \longrightarrow CO_2(g) + H_2(g) \qquad \Delta G^\circ = -28.5 \text{ kJ}$$

find ΔG° at 25°C for the following reaction.

$$SO_2(g) + CO(g) + 2H_2(g) \longrightarrow COS(g) + 2H_2O(g)$$

72. Given the following standard free energies at 25°C for the following reactions:

$$N_2O_5(g) \longrightarrow 2NO(g) + \tfrac{3}{2}O_2(g) \qquad \Delta G^\circ = -59.2 \text{ kJ}$$
$$NO(g) + \tfrac{1}{2}O_2(g) \longrightarrow NO_2(g) \qquad \Delta G^\circ = -35.6 \text{ kJ}$$

Calculate ΔG° at 25°C for the following reaction:

$$2NO_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow N_2O_5(g)$$

73. Natural gas, which is mostly methane, CH_4, is a resource that the United States has in abundance. In principle, ethane can be obtained from methane by the reaction

$$2CH_4(g) \longrightarrow C_2H_6(g) + H_2(g)$$

(a) Calculate ΔG° at 25°C for the reaction. Comment on the feasibility of this reaction at 25°C.
(b) Couple the reaction above with the formation of steam from the elements:

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(g) \qquad \Delta G^\circ = -228.6 \text{ kJ}$$

What is the equation for the overall reaction? Comment on the feasibility of the overall reaction.

74. Theoretically, one can obtain zinc from an ore containing zinc sulfide, ZnS, by the reaction

$$ZnS(s) \longrightarrow Zn(s) + S(s)$$

(a) Show by calculation that this reaction is not feasible at 25°C.
(b) Show that by coupling the above reaction with the reaction

$$S(s) + O_2(g) \longrightarrow SO_2(g)$$

the overall reaction, in which Zn is obtained by roasting in oxygen, is feasible at 25°C.

75. When glucose, $C_6H_{12}O_{11}$, is metabolized to CO_2 and H_2O in living systems, the first step is the conversion of glucose to glucose-6-phosphate.

$$\text{glucose} + H_3PO_4 \longrightarrow \text{glucose-6-phosphate} + H_2O \qquad \Delta G^\circ = 13.4 \text{ kJ}$$

This nonspontaneous reaction can be made to proceed by coupling it with the hydrolysis of ATP.

$$ATP + H_2O \longrightarrow ADP + H_3PO_4 \qquad \Delta G^\circ = -31.0 \text{ kJ}$$

(a) Write an equation for the coupled reaction and calculate ΔG°.
(b) Estimate the number of moles of ATP required to convert glucose to glucose-6-phosphate.

76. Consider the following reactions at 25°C:

$$C_6H_{12}O_6(aq) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O \qquad \Delta G^\circ = -2870 \text{ kJ}$$
$$ADP(aq) + HPO_4^{2-}(aq) + 2H^+(aq) \longrightarrow ATP(aq) + H_2O \qquad \Delta G^\circ = 31 \text{ kJ}$$

Write an equation for a coupled reaction between glucose, $C_6H_{12}O_6$, and ADP in which $\Delta G^\circ = -390$ kJ.

Unclassified

77. At 1200 K, an equilibrium mixture of CO and CO_2 gases contains 98.31 mol percent CO and some solid carbon. The total pressure of the mixture is 1.00 atm. For the system

$$CO_2(g) + C(s) \rightleftharpoons 2CO(g)$$

calculate

(a) P_{CO} and P_{CO_2} (b) K (c) ΔG° at 1200 K

78. A protein is said to be denatured when it loses some of its unique characteristics because its structure is changed. The enthalpy change for the denaturation of a certain protein is 142 kJ/mol, while its entropy change is 278 J/K. What is the minimum temperature at which the protein would denature spontaneously?

79. A student is asked to prepare a 0.030 M aqueous solution of $PbCl_2$.

(a) Is this possible at 25°C? (*Hint:* Is dissolving 0.030 mol of $PbCl_2$ at 25°C possible?)
(b) If the student used water at 100°C, would this be possible?

80. Some bacteria use light energy to convert carbon dioxide and water to glucose and oxygen:

$$6CO_2(g) + 6H_2O(l) \longrightarrow C_6H_{12}O_6(aq) + 6O_2(g)$$
$$\Delta G^\circ = 2870 \text{ kJ at } 25^\circ C$$

Other bacteria, those that do not have light available to them, couple the reaction

$$H_2S(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) + S(s)$$

to the glucose synthesis above. Coupling the two reactions, the overall reaction is

$$24H_2S(g) + 6CO_2(g) + 6O_2(g) \longrightarrow C_6H_{12}O_6(aq) + 18H_2O(l) + 24S(s)$$

Show that the reaction is spontaneous at 25°C.

81. Calculate the first and second ionization constants (K_{a1} and K_{a2}) for the ionization of the diprotic acid H_2SO_4 given the following information:

$H_2SO_4(aq)$: $\Delta H_f^\circ = -902.9$ kJ $\quad S^\circ = 17.14$ J/K

82. Carbon monoxide poisoning results when carbon monoxide replaces oxygen bound to hemoglobin. The oxygenated form of hemoglobin, $Hb \cdot O_2$ carries O_2 to the lungs.

$$Hb \cdot O_2(aq) + CO(g) \rightleftharpoons Hb \cdot CO(aq) + O_2(g)$$

At 98.6°F (37°C), ΔG° for the reaction is about −14 kJ. What is the ratio of $[Hb \cdot O_2]$ to $[Hb \cdot CO]$ when the pressure of CO is the same as that of O_2?

83. The formation constant for the following reaction at 25°C

$$Zn^{2+}(aq) + 4NH_3(aq) \rightleftharpoons Zn(NH_3)_4{}^{2+}(aq)$$

is 3.6×10^8.

(a) What is ΔG° at this temperature?

(b) If standard state concentrations of the reactants and products are combined, in which direction will the reaction proceed?

(c) What is ΔG when $[Zn(NH_3)_4{}^{2+}] = 0.010\ M$, $[Zn^{2+}] = 0.0010\ M$ and $[NH_3] = 3.5 \times 10^{-4}$?

Conceptual Problems

84. Determine whether each of the following statements is true or false.

(a) An exothermic reaction is spontaneous.

(b) When ΔG° is positive, the reaction cannot occur under any conditions.

(c) ΔS° is positive for a reaction in which there is an increase in the number of moles.

(d) If ΔH° and ΔS° are both negative, ΔG° will be negative.

85. Which of the following quantities can be taken to be independent of temperature? independent of pressure?

(a) ΔH for a reaction **(b)** ΔS for a reaction

(c) ΔG for a reaction **(d)** S for a substance

86. Fill in the blanks:

(a) ΔH° and ΔG° become equal at _____ K.

(b) ΔG° and ΔG are equal when Q = _____.

(c) S° for steam is _____ than S° for water.

87. Fill in the blanks:

(a) At equilibrium, ΔG is _____.

(b) For $C_6H_6(l) \rightleftharpoons C_6H_6(g)$, ΔH° is _____. (+, −, 0).

(c) When a pure solid melts, the temperature at which liquid and solid are in equilibrium and $\Delta G^\circ = 0$ is called _____.

88. In your own words, explain why

(a) ΔS° is negative for a reaction in which the number of moles of gas decreases.

(b) we take ΔS° to be independent of T, even though entropy increases with T.

(c) a solid has lower entropy than its corresponding liquid.

89. Consider the following reaction with its thermodynamic data:

$2A(g) + B_2(g) \longrightarrow 2AB(g)$ $\Delta H^\circ < 0$; $\Delta S^\circ < 0$; ΔG° at 60°C = +10 kJ

Which statements about the reaction are true?

(a) When $\Delta G = 1$, the reaction is at equilibrium.

(b) When $Q = 1$, $\Delta G = \Delta G^\circ$.

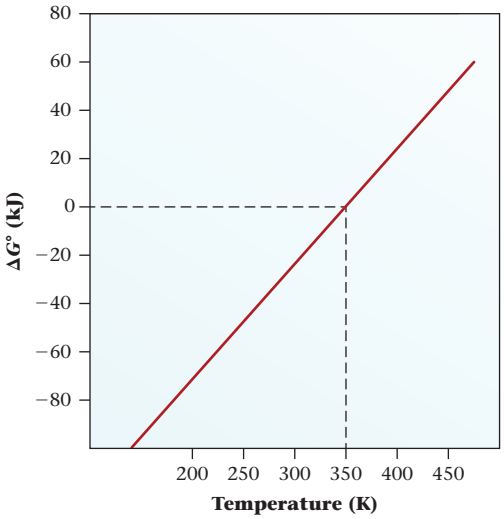
(c) At 75°C, the reaction is definitely nonspontaneous.

(d) At 100°C, the reaction has a positive entropy change.

(e) If A and B_2 are elements in their stable states, S° for A and B_2 at 25°C is 0.

(f) K for the reaction at 60°C is less than 1.

90. Consider the graph below:



(a) Describe the relationship between the spontaneity of the process and temperature.

(b) Is the reaction exothermic?

(c) Is $\Delta S^\circ > 0$?

(d) At what temperature is the reaction at standard conditions likely to be at equilibrium?

(e) Estimate K for the reaction at 97°C.

91. The relationship between ΔG° and T is linear. Draw the graph of a reaction with the properties described below. You need only label the point at which $\Delta G^\circ = 0$.

- The reaction is exothermic.
- $\Delta n_g < 0$ (Δn_g = moles of gas products − moles of gas reactants).
- At 300 K, the system is at equilibrium and $K = 1$.

92. Answer the questions below by writing **LT** (for *is less than*), **GT** (for *is greater than*), **EQ** (for *is equal to*), or **MI** (for *more information required*) in the blanks.

The reaction given below takes place in a cylinder that feels warm to the touch after the reaction is complete.

$$A_2(g) + B_2(g) \longrightarrow 2AB(s)$$

(a) At all temperatures, ΔS° _____ 0.

(b) At all temperatures, ΔH° _____ 0.

(c) At all temperatures, ΔG° _____ 0.

Challenge Problems

93. Consider the following data about ethyl alcohol:

ΔH_{vap} = 42.9 kJ vapor pressure = 392 mm Hg at 63°C

What is $S°$ for $C_2H_5OH(g)$?

94. $\Delta H_f°$ for iodine gas is 62.4 kJ/mol, and $S°$ is 260.7 J/mol·K. Calculate the equilibrium partial pressures of $I_2(g)$, $H_2(g)$, and $HI(g)$ for the system

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

at 500°C if the initial partial pressures are all 0.200 atm.

95. The heat of fusion of ice is 333 J/g. For the process

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

determine

(a) $\Delta H°$ (b) $\Delta G°$ at 0°C (c) $\Delta S°$
(d) $\Delta G°$ at −20°C (e) $\Delta G°$ at 20°C

96. The overall reaction that occurs when sugar is metabolized is

$$C_{12}H_{22}O_{11}(s) + 12O_2(g) \longrightarrow 12CO_2(g) + 11H_2O(l)$$

For this reaction, $\Delta H°$ is −5650 kJ and $\Delta G°$ is −5790 kJ at 25°C.

(a) If 25% of the free energy change is actually converted to useful work, how many kilojoules of work are obtained when one gram of sugar is metabolized at body temperature, 37°C?

(b) How many grams of sugar would a 120-lb woman have to eat to get the energy to climb the Jungfrau in the Alps, which is 4158 m high? ($w = 9.79 \times 10^{-3}\ mh$, where w = work in kilojoules, m is body mass in kilograms, and h is height in meters.)

97. Hydrogen has been suggested as the fuel of the future. One way to store it is to convert it to a compound that can be heated to release the hydrogen. One such compound is calcium hydride, CaH_2. This compound has a heat of formation of −186.2 kJ/mol and a standard entropy of 42.0 J/mol·K. What is the minimum temperature to which calcium hydride would have to be heated to produce hydrogen at one atmosphere pressure?

98. When a copper wire is exposed to air at room temperature, it becomes coated with a black oxide, CuO. If the wire is heated above a certain temperature, the black oxide is converted to a red oxide, Cu_2O. At a still higher temperature, the oxide coating disappears. Explain these observations in terms of the thermodynamics of the reactions

$$2CuO(s) \longrightarrow Cu_2O(s) + \tfrac{1}{2}O_2(g)$$
$$Cu_2O(s) \longrightarrow 2Cu(s) + \tfrac{1}{2}O_2(g)$$

and estimate the temperatures at which the changes occur.

99. K_a for acetic acid ($HC_2H_3O_2$) at 25°C is 1.754×10^{-5}. At 50°C, K_a is 1.633×10^{-5}. Assuming that $\Delta H°$ and $\Delta S°$ are not affected by a change in temperature, calculate $\Delta S°$ for the ionization of acetic acid.

100. Consider the reaction

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

At 500°C, a flask initially has all three gases, each at a partial pressure of 0.200 atm. When equilibrium is established, the partial pressure of HI is determined to be 0.48 atm. What is $\Delta G°$ for the reaction at 500°C?

101. Consider the formation of ammonia from its elements:

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

At what temperature is $K = 1.00$? (*Hint:* Use the thermodynamic tables in Appendix 1.)

102. Consider the formation of $HI(g)$ from $H_2(g)$ and $I_2(g)$.

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

For this reaction, K at 333°C is 98, while K at 527°C is 62.5. Find $S°$ for $I_2(g)$ at 527°C.