16

Entropy, Free Energy, and Chemical Reactions

Maximum disorder was our equilibrium.

T. E. Lawrence, *Seven Pillars of Wisdom* (1926)

The previous chapter answered a fundamental question: "If a chemical reaction takes place by itself, will it give off or absorb heat?" This is a useful question for builders of heat engines and designers of reaction vessels. But an even more fundamental question is the following: "If left to itself, will a given reaction take place at all without outside interference?" This question of **spontaneity** is the subject of this chapter.

16-1 SPONTANEITY, REVERSIBILITY, AND EQUILIBRIUM

If we place equivalent amounts of hydrogen and oxygen gases in a container and apply a flame or a platinum catalyst, there will be a violent explosion. The H_2 and O_2 will disappear, and water vapor will form in their place. Similarly, a mixture of H_2 and Cl_2, if triggered by light, will explode and produce HCl gas. In contrast, a mixture of H_2 and N_2 gases will react much less violently, and the final product will be a mixture of H_2, N_2, and NH_3 gases.

The water and HCl reactions are good illustrations of highly spontaneous processes. As we saw in Chapter 4, a **spontaneous process** is one

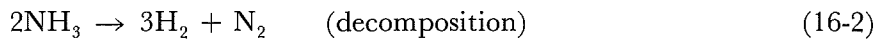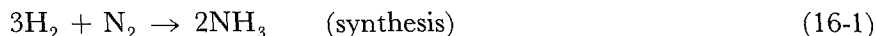that has enough impetus to proceed on its own without further input from the rest of the universe.* We shall learn later in this chapter how that impetus is measured. For the moment we can say that the reaction to produce HCl from H_2 and Cl_2,

$$H_2 + Cl_2 \rightarrow 2HCl$$
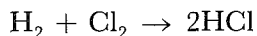
has a far greater tendency to occur than the reverse process, dissociation of HCl,

$$2HCl \rightarrow H_2 + Cl_2$$
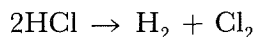
The reaction synthesizing ammonia from H_2 and N_2 also has a somewhat greater initial tendency to occur than the decomposition reaction. Reaction 16-1 has more of a drive than reaction 16-2:

$$3H_2 + N_2 \rightarrow 2NH_3 \qquad \text{(synthesis)} \qquad (16\text{-}1)$$

$$2NH_3 \rightarrow 3H_2 + N_2 \qquad \text{(decomposition)} \qquad (16\text{-}2)$$

But as more NH_3 accumulates, and as less N_2 and H_2 are left, synthesis becomes slower and decomposition accelerates. Ammonia decomposes more rapidly as more of it is present to decompose. At some concentration of H_2, N_2, and NH_3, the two reactions proceed at the same rate. Ammonia is produced exactly as fast as it is broken down. Although synthesis and decomposition still occur at the molecular level, we see no net change in the composition of the gas mixture. The gas gives the appearance of having ceased to change. This condition of balance between two opposing reactions is called **chemical equilibrium**.

A reaction that is at equilibrium is a **reversible reaction**. To understand what this means, let's examine our equilibrium mixture of H_2, N_2, and NH_3. An increase in pressure favors reaction 16-1 over 16-2 because 16-1 leads to a smaller number of moles (or molecules) of gas and relieves the stress on the system caused by the pressure increase. Similarly, a decrease in pressure favors the decomposition of ammonia to produce more moles of gas. Both of these are applications of Le Chatelier's principle: When a system at equilibrium is subjected to a stress of any kind, the system shifts toward a new equilibrium condition in such a way as to relieve that stress. The synthesis of ammonia from its elements is an exothermic process; the ΔH^0_{298} of reaction 16-1 is -92.38 kJ per mole of reaction, as written, or -46.19 kJ mole^{-1} of ammonia. If the temperature of the container is increased, reaction 16-1 will be hindered, and reaction 16-2 will be favored

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*In a strict sense, spontaneity has nothing to do with time. A thermodynamically spontaneous reaction is one that will occur on its own, even if it requires virtually forever to do so. The role of a catalyst is to bring about in a short time that which would occur anyway, but only over a longer time interval. Thermodynamics answers the question, "Will it occur, eventually?" To answer the question, "How soon will it occur?" we must turn to kinetics (Chapter 22).

because it absorbs heat and partially counteracts the temperature increase. If more ammonia is added to the container from an outside source, reaction 16-1 will be hindered again and 16-2 will be favored because it relieves the stress of the added ammonia. Le Chatelier's principle is useful in predicting qualitatively what an equilibrium system will do when acted upon by an outside influence.

If the N_2–H_2–NH_3 system is truly at equilibrium, the changes in pressure, temperature, or concentration of one component required to alter the relative rates of the two reactions are infinitesimally small. Just as the lightest weight can tip a balance in mechanical equilibrium, so the smallest change can affect a system in chemical equilibrium. This is why the term *reversible* is applied to such situations. A fingertip touch cannot halt a falling boulder, and an infinitesimal change in pressure, temperature, concentration, or any other variable cannot halt the explosion of H_2 and Cl_2 or the less spectacular reaction of N_2 and H_2 before equilibrium is reached. Such chemical systems are not at equilibrium; their processes are irreversible.

In summary, an equilibrium process is reversible, and a nonequilibrium or spontaneous process is irreversible. We shall want to know how to calculate the equilibrium conditions for a system of chemical substances, for two main reasons: because it is often useful to know the relative amounts of reactants and products at equilibrium, and because the distance of a given chemical situation from equilibrium is a measure of how strong the drive is in a direction toward equilibrium.

16-2   HEAT, ENERGY, AND MOLECULAR MOTION

When an object is heated, its molecular motion increases. Heat is not a fluid that can be forced away from the atoms by friction. Instead, it is an expression of the state of motion of the molecules and atoms, which are made to move more rapidly by the mechanical forces of friction. These conclusions were suggested by experiments that demonstrated the mechanical equivalence of work and heat, and were made palatable by the kinetic theory of gases and its extension to the molecular theory of liquids and solids.

In previous chapters we talked about two types of energy that an object could have: kinetic energy and potential energy. Kinetic energy is possessed by a moving body and is represented by $E_k = \frac{1}{2}mv^2$. Potential energy is possessed by a body because of where that body is. If a mass can perform work by moving from point A to point B in space, we say that the body has a greater gravitational potential energy at A than at B. If we want, we can talk about a gravitational potential field in which the body moves, but we are only rephrasing the observation, not explaining it. The idea of a gravitational field *comes from* the observation that work can be done when the body moves from one place to another. Similarly, if a positive or negative

charge can be made to do work as it moves from point A to point B, we say that the charge has a greater electrostatic potential energy at A than it has at B. Again, we can describe (not explain) the observation by talking about an electrostatic field.

Now we have a third kind of energy to deal with: the energy possessed by a body because its atoms and molecules are in a state of motion, even though the body might be stationary. This molecular motion is heat, and it is measured by the temperature of the object. The temperature scale is based on the expansion behavior of an ideal gas, as we noted in Chapter 3. Heat is measured in the same units as work and energy. The amount of heat required for a mole of a substance to experience a temperature increase of 1 K is called the **heat capacity** of the substance and is measured in $J K^{-1}$ mole^{-1} (joules per kelvin per mole).

If this third kind of energy did not exist, the first law of thermodynamics would be

$$\Delta E = E_2 - E_1 = -w$$

and would read as follows: The change in the internal energy of a system balances any work that the system does on its surroundings. Or, since $-w$ represents work done on the system by its surroundings, the equation also would state that the increase in internal energy of the system equals the work done on it from the outside. This work could be used to accelerate objects in the system and give them greater kinetic energy, or it could be used to lift them and give them greater potential energy.

The full statement of the first law,

$$\Delta E = E_2 - E_1 = q - w$$

is as follows: The change in the internal energy of a system is the sum of the work done on it by the environment and the increase in random motion given its molecules by the environment. This increase in molecular motion is described as a flow of heat.

It is always possible to change work into heat. Friction is often used as an example because it is so simple. A block, moving as a unit with a large velocity, but with its molecules in relatively slow random motion, comes to a stop on a surface because of friction. After it stops, it has no velocity of motion as a unit. However, its molecules, and the molecules of the surface on which it had been sliding, are moving with greater individual speed than before. If the object is partly a gas, this motion may be straight-line motion throughout the container. If it is a solid, the motion will be vibration of atoms and molecules around average positions in the crystal. In either case, large-scale motion has been converted to microscopic motion.

This process is not completely reversible. The example of a skidding automobile in Section 3-6 is an illustration of this fact. Generally, we cannot take random molecular motion and convert it to coordinated motion of the entire object with 100% efficiency. The expression of our inability to do this is the **second law of thermodynamics**. Two slightly different versions of the

second law were proposed in the middle of the nineteenth century. One version, by William Thomson, says this: *One cannot convert a quantity of heat completely into work without wasting some of this heat at a lower temperature.* The other version, by Rudolf Clausius, says this: *One cannot transfer heat from a cold object to a hot object without using work to make the transfer.* Both statements are *summaries of experience,* and are "statements of impotence." They are statements about the *limitations* on what we can do in the real world. Either can be shown to follow if the other is assumed first.

16-3 ENTROPY AND DISORDER

Either form of the second law of thermodynamics leads, with the help of some calculus that we shall not reproduce here, to a new state function, S. This new state function is called the **entropy** of the system. We shall not use the most general expression for entropy, but one special case is useful. If an amount of heat, q, is added to a system *in a reversible manner* at a temperature T, then the entropy of the system increases by

$$\Delta S = \frac{q}{T} \tag{16-3}$$

If the heat is added *irreversibly,* the entropy increases by more than q/T:

$$\Delta S > \frac{q_{\text{irr}}}{T} \tag{16-4}$$

The quantity q/T is a lower limit to the entropy increase that is applicable only when the heat transfer is reversible, that is, when the object being heated is in thermal equilibrium with the object donating the heat. Heat flows from one body to another because they are *not* in equilibrium, and it would take an infinite time for reversible heat flow to take place. Truly reversible processes are idealizations for real, irreversible processes. What we should say is that in any real (irreversible) process, the entropy increase will be greater than q/T; but the more slowly and carefully we carry out the heat transfer, the less ΔS will exceed q/T.

The entropy as derived from the second law has no obvious molecular interpretation. But Ludwig Boltzmann (1844–1906), an Austrian physicist, showed in 1877 that entropy has a fundamental molecular significance: It is a measure of the **disorder** of a system. Boltzmann proposed that entropy, S, is related to the number of different microscopic ways of obtaining a specified macroscopically definable and observable situation. If the number of equivalent ways of constructing a situation is W, then the entropy is proportional to the logarithm of W:

$$S = k \ln W \tag{16-5}$$

The proportionality constant, k, is the gas constant per molecule, or

$$k = \frac{R}{N} \tag{16-6}$$

where R is the familiar ideal gas constant and N is Avogadro's number. Appropriately enough, we now call k **Boltzmann's constant**.

The important physical quantity in the equation is the number of ways of obtaining a given state, W. There is only one way of putting together a perfect crystal, provided of course that the molecules are indistinguishable from one another and are motionless, packed against their neighbors (which means at absolute zero temperature). For a perfect crystal with motionless molecules at 0 K, $W = 1$ and $S = k \ln 1 = 0$. In contrast, there are many equivalent ways of building a liter of a certain gas at a given temperature and pressure. The individual positions of molecules in a gas do not have to be specified, nor do their individual speeds. A gas will match the given specifications if the total number of its molecules of each kind and its total energy per mole are correct; all gases that satisfy these conditions will appear alike to an outside observer. It follows that for a gas, W is large, so $\ln W$ is a positive number, and $S = k \ln W$ is greater than zero. Of course, even a perfect crystal will have some entropy if it is warmed above 0 K, since the individual molecules will begin to vibrate about their equilibrium positions in the crystal lattice, and there will be several ways of constructing a vibrating-molecule crystal, all of which will look the same to the external observer. The entropy of a crystal of rock salt at room temperature, however, will be far less than that of a comparable quantity of gas.

Boltzmann made the crucial connection between thermodynamic *entropy* and *disorder*. Any situation that is so definite that it can be put together only in one or a small number of ways is recognized by our minds as orderly. Any situation that could be reproduced in thousands or in millions of different but entirely equivalent ways is disorderly. Boltzmann's law tells us that the most perfect, orderly object conceivable in the universe would be a perfect crystal at absolute zero. Anything else—a crystal at any temperature above 0 K, a liquid, a gas, or a mixture of substances—is more disordered and hence has a positive entropy. The higher the entropy, S, the greater the disorder.

When we combine Boltzmann's ideas about entropy with thermodynamics, we arrive at one of the most important principles of science: *In any real, spontaneous processes, including chemical reactions, the disorder of the universe always increases.* In any isolated system, in which the total energy cannot change, a spontaneous reaction is one in which entropy (and disorder) increases. No process that produces order, or lowers the entropy, can occur without outside help. If we supply enough energy, we can make a reaction occur even though entropy decreases in the process. But if we do not provide enough energy, a reaction leading to increased order will not take place.

Life in a Nine-Point Universe

What do we mean when we say that entropy, S, can be calculated from the expression $S = k \ln W$, in which W is the number of equivalent ways the molecules can be arranged to give the same observable result? Why should a gas inevitably have a higher entropy than a crystal of the same substance? It is hard to answer such questions in our own universe without getting bogged down in mathematics. But it is much easier in an imaginary universe with only four atoms in it, and only nine places where the atoms can be.

Imagine that the nine places in our mini-universe are arranged in the 3×3 grid shown in Figure 16-1a. All four atoms placed in a close-packed square will constitute a crystal in our imaginary space, and any other arrangement of the four atoms will be called a gas. Examples of crystals and gases are given in Figure 16-1b. If we examine every possible arrangement of four atoms in a nine-point universe, how many of these arrangements will lead to crystals and how many to gases?

First of all, how many total arrangements are there for both gases *and* crystals? The first atom can go to any one of nine places in the universe. The second atom has only eight places left open, the third has seven places, and the final atom has only six unoccupied places. The total number of ways of placing four atoms in the nine locations appears to be $9 \times 8 \times 7 \times 6 = 3024$ ways.

This is not quite correct, because we have overcounted. The answer of 3024 would be correct if the atoms had names or labels, and if arrangements of the type shown in Figure 16-1c really were different. But atoms have no labels. If by some miraculous process we could photograph the atoms at a chosen instant and study them we could tell the difference between the four arrangements in Figure 16-1b because the atoms occupy different places. However, we could see absolutely no difference among the arrangements in Figure 16-1c, because one atom is just like every other atom of the same type. The most that we could say is that atoms were present at positions 3, 4, 7, and 8 of our mini-universe (Figure 16-1d).

How can we correct for this overcounting? How do we "remove the labels" from the atoms? As a correction factor, how many different label shufflings can be made for each arrangement of four atoms? Label a could be given to any one of the four atoms, label b to any of the remaining three, label c to two, and label d then has to go to the last atom. There are $4 \times 3 \times 2 \times 1 = 24$ meaningless permutations of labels for every really different arrangement of atoms. We have overcounted by a multiplicative factor of 24. Hence the 3024 ways of arranging atoms must be divided by 24 to remove the labels on the atoms. The number of different ways of arranging four *indistinguishable* atoms among nine locations is

$$W = \frac{9 \times 8 \times 7 \times 6}{4 \times 3 \times 2 \times 1} = \frac{3024}{24} = 126$$
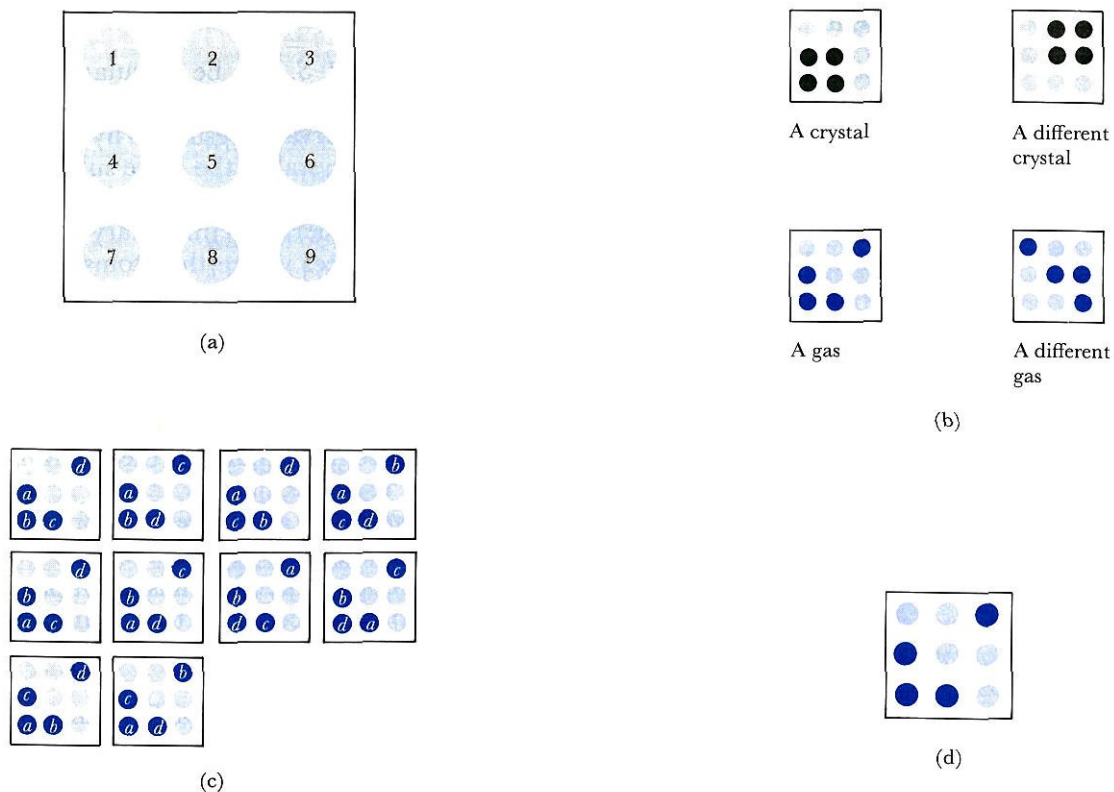
Figure 16-1

A mini-universe with only nine "locations" or places where an object can be, and only four objects to fill them. (a) The "universe." (b) Different arrangements of atoms leading to different gases and crystals. (c) If atoms had labels, all these patterns and others like them would represent different arrangements of atoms. (d) But since atoms do not have names or labels, and all look alike, all the pictures in (c) correspond to a single atomic arrangement: four atoms at positions 3, 4, 7, and 8. From Dickerson and Geis, *Chemistry, Matter, and the Universe.*

If you are skeptical about the logic of the derivation just given, you may check all 126 arrangements in Figure 16-2. Of the 126 possible arrangements, only four are crystals (shown in black), and the other 122 are gases. Even in such a tiny and restricted universe, a gas is far more likely to result from a random arrangement of atoms than is a crystal. This is true because the specifications for a crystal are so much more restrictive:

Crystal: Four adjacent atoms in a square

Gas: Four atoms in any arrangement *except* those that lead to a crystal

For crystals, $W_c = 4$, and for gases, $W_g = 122$, so a gas is more than 30 times as likely to occur randomly as is a crystal.
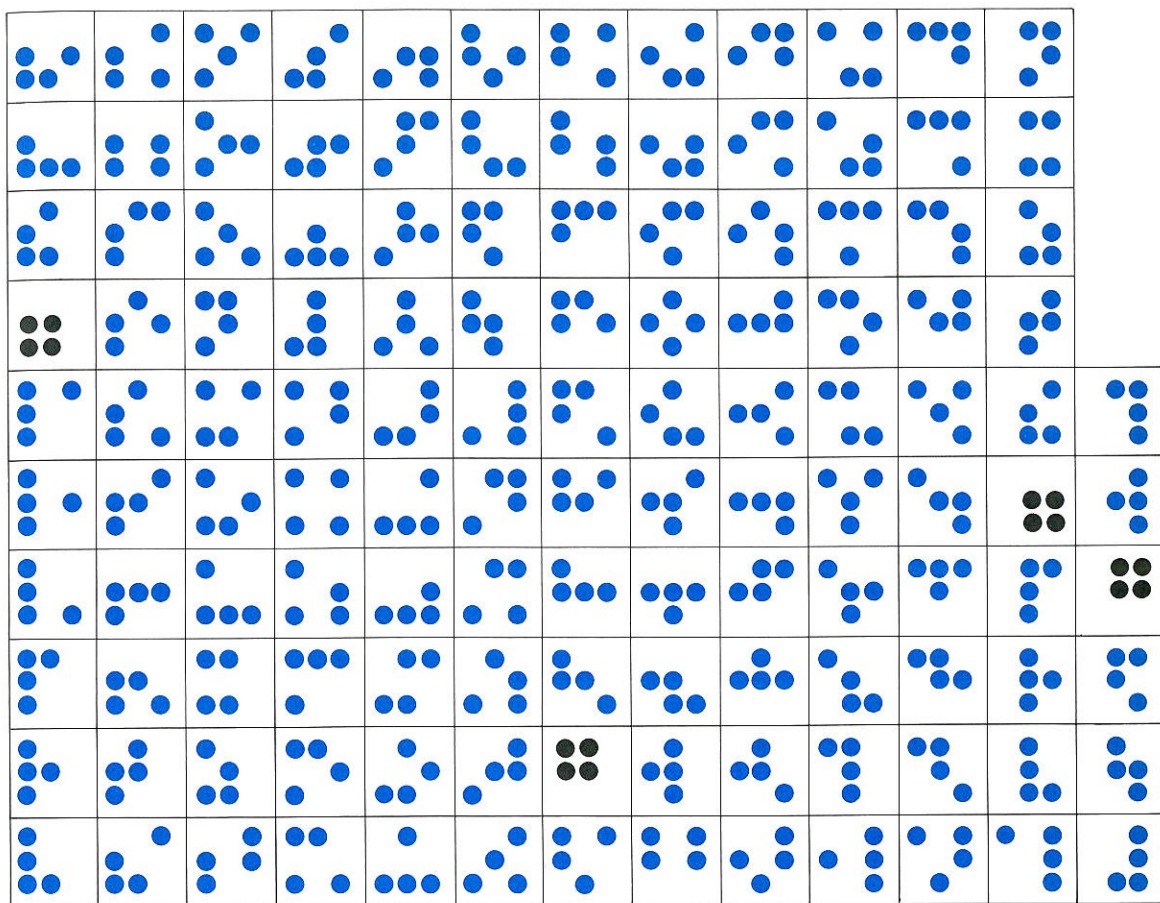
Figure 16-2 Out of the 126 possible arrangements of four atoms in our nine-point universe, only the four shown in black are "crystals." The others, shown with dark-colored dots, are "gases." From Dickerson and Geis, *Chemistry, Matter, and the Universe.*

If we were to repeat the experiment with four atoms in a 4×4 "universe," we would find that

$$W = \frac{16 \times 15 \times 14 \times 13}{4 \times 3 \times 2 \times 1} = 1820$$

different arrangements would be possible, of which only 9 would be crystalline and 1811 would be gases (Figure 16-3). In that universe, a gas is more than 200 times as probable as a crystal.

When we jump to the real world, with many times Avogadro's number of atoms and many, many places for atoms to be, W becomes astronomical. It is then easier to use a logarithmic representation to keep down powers

Figure 16-3

With four atoms in a 16-point universe, there are 9 random arrangements leading to crystals, and 1811 yielding gases. From Dickerson and Geis, *Chemistry, Matter, and the Universe.*
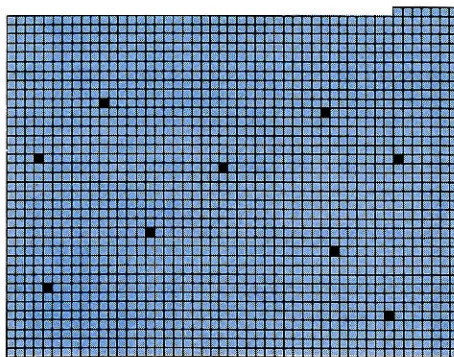
of 10, reducing 10 and 10,000,000 and 100,000,000,000,000 (or 10^1, 10^7, and 10^{14}) to a more manageable 1, 7, and 14. The entropy, S, is simply the number of ways of obtaining a given state of matter, expressed logarithmically instead of linearly:

$$S = k \ln W = 2.303 \, k \log_{10} W \tag{16-7}$$

16-4   ENTROPY AND CHEMICAL INTUITION

Boltzmann gave us a very precise interpretation of entropy in terms of order and disorder at the molecular level. In Appendix 3, along with standard heats of formation, there are tabulated standard entropies of substances, S^0_{298}. These values were *not* obtained from Boltzmann's $S = k \ln W$ expression. They are the results of thermal measurements of heat capacities of solids, liquids, and gases; of heats of fusion and heats of vaporization, from room temperature down to within extrapolation distance of absolute zero. (One learns in advanced courses how to calculate values for S from such purely thermal data.) These tabulated values of S^0_{298} are sometimes called **third-law entropies** because the logic of their calculation from thermal data is incomplete without the assumption of the **third law of thermodynamics**: *The entropy of a perfect crystal at absolute zero is zero.* The third law is obvious, of course, if you accept Boltzmann's statistical interpretation of S.

The beauty of third-law entropies is that, although they were not derived from Boltzmann's statistical interpretation, they agree with it completely. Let's look at matter through Boltzmann's eyes, and interpret these measured third-law entropies in terms of order and disorder. We can see several clear-cut trends, and they all become obvious if we replace the word *entropy* with *disorder*.

1. The entropy (or disorder) increases whenever a liquid or a solid is converted to a gas. Examples from Appendix 3 are

Substance:	$Na(s)$	$Br_2(l)$	$I_2(s)$	$H_2O(l)$	$CH_3OH(l)$
S^0 (solid or liquid):	51.0	152.3	117.0	69.9	127.0
S^0 (gas):	153.6	245.4	260.6	188.7	236.0

The units of entropy here and elsewhere are $J\ K^{-1}\ mole^{-1}$, or entropy units (e.u.) $mole^{-1}$, an entropy unit being defined as a joule per kelvin. In each case, the third-law entropy of the condensed phase is around 100 e.u. $mole^{-1}$ less than that of the same substance as a gas, because gases are inherently more disordered.

2. Entropy increases when a solid or a liquid is dissolved in water or other solvent:

Substance:	$CH_3OH(l)$	$HCOOH(l)$	$NaCl(s)$
S^0 (solid or liquid):	127.0	129	72.4
S^0 (after solution in H_2O):	132.3	164	115.4

The entropy of methanol, CH_3OH, rises only slightly, for a mole of methanol molecules interspersed among water molecules is only slightly more disordered than a mole of pure liquid methanol. Formic acid, $HCOOH$, undergoes a larger entropy increase when it is dissolved, because the molecules partially dissociate into protons and formate ions, $HCOO^-$, producing two entities where only one was present before. The crystal lattice of sodium chloride breaks up completely into hydrated Na^+ and Cl^- ions, leading to an increase in disorder even though some water molecules are tied up by hydrating the ions. Notice that the entropy figure for NaCl was obtained from Appendix 3 by adding the entropies of the two ions:

$$60.2\ (Na^+) + 55.2\ (Cl^-) = 115.4\ e.u.\ mole^{-1}$$

3. Entropy falls when a gas is dissolved in water or other solvent:

Substance:	$CH_3OH(g)$	$HCOOH(g)$	$HCl(g)$
S^0 (gas):	236	251	186.7
S^0 (after solution in H_2O):	132.3	164	55.2

Dissolving a gas in water is somewhat like condensing it to a liquid, in terms of closeness of neighbor molecule contacts. As before, the entropy of a dissolved ionic compound is found by adding the entropies of its hydrated ions.

4. Entropy rises with increasing mass, other things being equal:

Substance:	F_2	Cl_2	Br_2	I_2		O	O_2	O_3
S^0 (gas):	203	223	245	261		161	205	238

This is an important principle, but one that requires quantum mechanics for an explanation. Simple quantum theory tells us that as the mass and size of an atom or molecule increase, the spacings between its energy levels decrease. A large, massive object with a certain total energy hence has more quantum states available to it, so W is larger and $S = k \ln W$ is greater. This is illustrated in Figure 16-4 with four molecules having a total of six units of energy, for light molecules with widely spaced energy levels (Figure 16-4a) and for heavier molecules with closely spaced energy levels (Figure 16-4b).

5. Entropy is lower in covalently bonded solids, with strong, directional bonds, than in solids with partial metallic character:

C (diamond):	2.44	C (graphite):	5.69
Sn (gray, diamond):	44.8	Sn (white, metallic):	51.5

Both diamond and gray tin have a tetrahedrally bonded, three-dimensional covalently bonded structure. Both graphite in its packed two-dimensional sheets and white tin with its metallic packing of atoms are less orderly than the two diamond structures, so their entropy is greater.

6. In general, entropy rises with increasing softness and with weakness of bonds between atoms:

Figure 16-4

Entropy increases with mass. A heavier molecule has more closely spaced energy levels, and there are more ways of obtaining a mole of such molecules having a given total energy. In this example, four molecules together have six units of energy, and we can represent the energy of each molecule by locating it on a diagram of possible molecular energy levels. (a) Light molecule with widely spaced energy levels; $W = 2$. (b) Heavier molecule with more closely spaced energy levels; $W = 8$. From Dickerson and Geis, *Chemistry, Matter, and the Universe.*

(a)

(b)
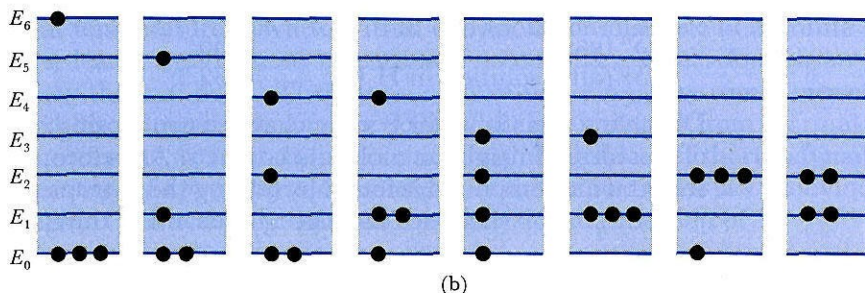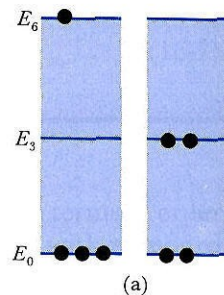
Substance:	C(di)	Be(s)	SiO$_2$(s)	Pb(s)	Hg(l)	Hg(g)
S^0:	2.44	9.54	41.8	64.9	77.4	174.9
State:	diamond	hard metal	quartz	soft metal	liquid	gas

7. Entropy increases with chemical complexity. This principle holds for ionic salt crystals with increasing numbers of ions per mole:

Substance:	NaCl	MgCl$_2$	AlCl$_3$
$S^0(s)$:	72.4	89.5	167

It also holds for crystals such as CuSO$_4 \cdot n$H$_2$O with increasing numbers of water molecules of hydration:

n:	0	1	3	5
S^0:	113	150	225	305

and for organic compounds with larger carbon frameworks:

Substance:	CH$_4$	C$_2$H$_6$	C$_3$H$_8$	C$_4$H$_{10}$
$S^0(g)$:	186	230	270	310

The molar entropies for pure elements in different physical states are plotted in Figure 16-5. All metallic solids have entropies below 80 e.u. mole^{-1}, monatomic gases lie between 130 and 180 e.u. mole^{-1}, and diatomic and polyatomic gases have higher entropies yet. Third-law entropies, although they come purely from thermal measurements, tell us something about molecular structure if we know how to interpret them. Although entropy originated as a rather abstract concept involving heat, it has a clear molecular interpretation. Entropy is a direct and quantitative measure of disorder.

16-5 FREE ENERGY AND SPONTANEITY IN CHEMICAL REACTIONS

What determines whether or not a chemical reaction is spontaneous? What measurable or calculable properties for the system of H$_2$, Cl$_2$, and HCl indicate that the reaction of H$_2$ and Cl$_2$ is explosively spontaneous under conditions for which the decomposition of HCl to H$_2$ and Cl$_2$ is scarcely detectable at all? Marcellin Berthelot and Julius Thomsen,* French and

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*This Berthelot is not the Berthollet you already have encountered, nor is this Thomsen any of the Thomsons or Thompsons of past reference. For clarity, here is a brief glossary of these gentlemen:

Claude Berthollet (1748–1822). French chemist, opponent of definite proportions for compounds.

Marcellin Berthelot (1827–1907). French thermodynamicist.

Benjamin Thompson (1753–1814). American adventurer and spy, Bavarian munitions maker, founder of Royal Institution, London.
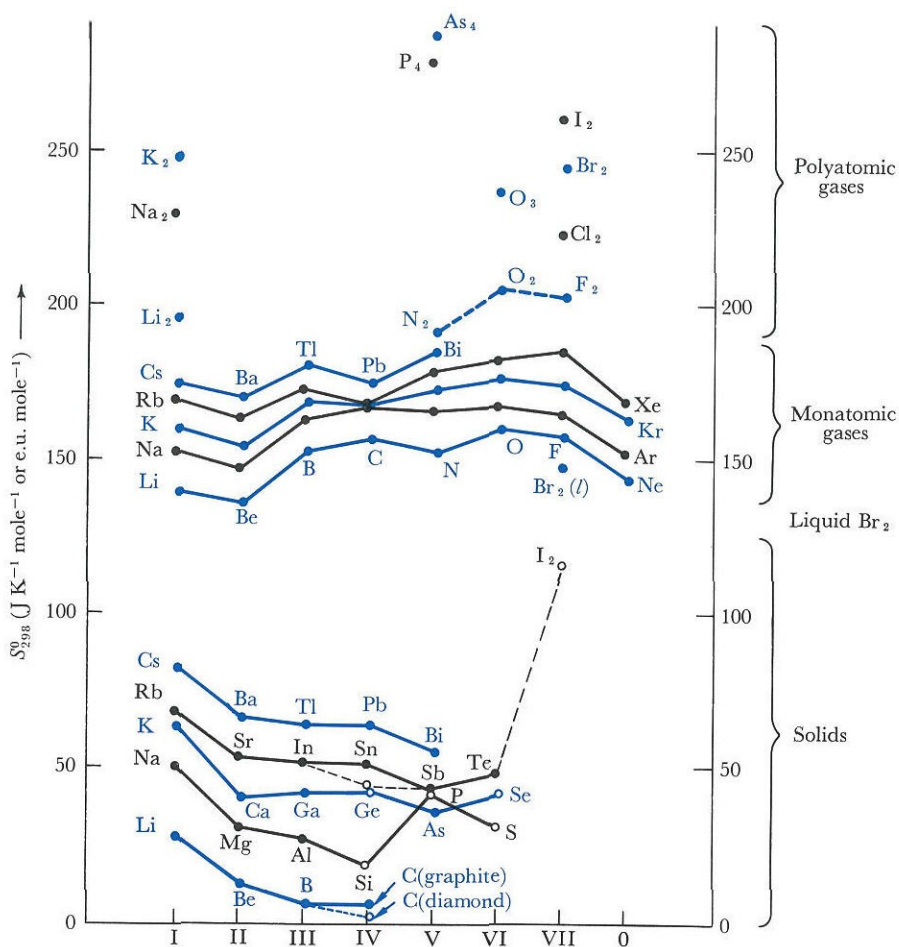
Figure 16-5   Third-law entropies in joules per kelvin per mole or entropy units per mole for various elements as solids, liquids, and monatomic and polyatomic gases. Polyatomic gases have higher entropies than monatomic gases because the mass of the molecular unit is greater. All monatomic gases have approximately the same entropy per mole, with a gradual increase in entropy with mass. Solids with stronger bonds have lower entropies. Filled circles in solids indicate metallic structures; open circles, nonmetallic structures. The two structures for carbon are graphite (filled) and diamond (open). The two structures for tin are metallic white tin (filled) and gray tin with the diamond structure (open). The entropy of the molecular solid of I_2 molecules is similar to those of crystals of other polyatomic small molecules such as ICN (129), glycine (109), oxalic acid (120), and urea (105).

Figure 16-6

If the principle of Berthelot and Thomsen were correct and all spontaneous reactions liberated heat, then enthalpy, *H*, would be a chemical potential function that is minimized at equilibrium. This is not so; we can find spontaneous processes that absorb heat. The most obvious is the evaporation of a liquid.
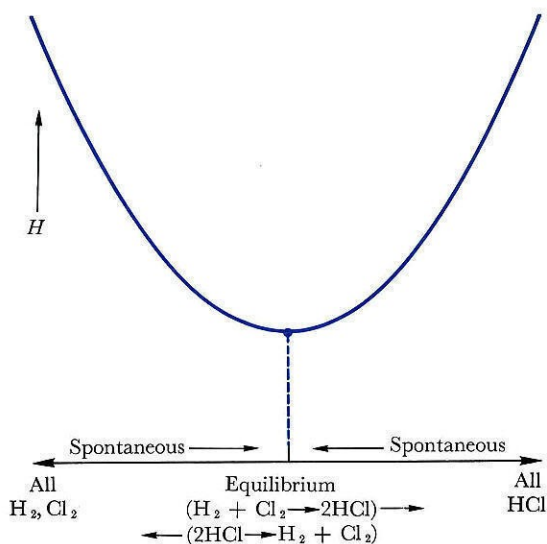
Danish thermodynamicists, proposed the wrong answer, in 1878, in the form of their *principle of Berthelot and Thomsen:* Every chemical change accomplished without the intervention of an external energy tends toward the production of the body or the system of bodies that sets free the most heat. In other words, all spontaneous reactions are exothermic.

If the principle of Berthelot and Thomsen were correct, and if the enthalpy of a system of reacting chemicals *decreased* during any spontaneous process, equilibrium would occur at the minimum of enthalpy since any spontaneous process is moving toward equilibrium. The plot of enthalpy, *H*, against the extent of reaction on the horizontal axis would look something like Figure 16-6.

Unfortunately for the principle, we can easily find exceptions: reactions that are spontaneous but absorb heat. One of these is the vaporization of water or any other substance at a partial pressure less than its vapor pressure. When a pan of water evaporates, heat is absorbed:

$$H_2O(l) \rightarrow H_2O(g) \qquad \Delta H_{298}^0 = +44.0 \text{ kJ mole}^{-1}$$

If the principle of Berthelot and Thomsen were true, all gases would con-

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William Thomson (1824–1907). British thermodynamicist, later Lord Kelvin.

Julius Thomsen (1826–1909). Danish thermodynamicist.

J. J. Thomson (1856–1940). British physicist, discoverer of electron, Nobel Prize in 1906.

G. P. Thomson (1892–1976). British physicist, Nobel Prize in 1937 for electron diffraction. Son of J. J. Thomson.

dense spontaneously to liquids, and all liquids would solidify to solids since by doing so they would give off enthalpy.

Like the vaporization of water, the solution of ammonium chloride crystals in water is both spontaneous and endothermic:

$$NH_4Cl(s) + H_2O \rightarrow NH_4(aq)^+ + Cl(aq)^- \qquad \Delta H_{298}^0 = +15.1 \text{ kJ}$$
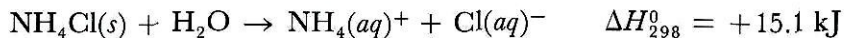
Adding water to solid NH_4Cl makes a beaker cold enough to freeze pure water on the outside of the beaker. Yet we do not see dilute solutions of ammonium chloride separate spontaneously into crystals and pure water simply because heat would be released in the process.

As a last example, dinitrogen pentoxide is an unstable solid that reacts, sometimes explosively, to produce NO_2 and O_2:

$$N_2O_5(s) \rightarrow 2NO_2(g) + \tfrac{1}{2}O_2(g) \qquad \Delta H_{298}^0 = +109.5 \text{ kJ}$$
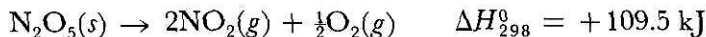
However, a large quantity of heat is absorbed in this decomposition.

There are many other examples of spontaneous processes that absorb heat. We cannot find the point of equilibrium by minimizing H. Enthalpy is not a measure of the tendency of a reaction to proceed spontaneously.

The three preceding reactions occur despite their requirement of heat because their products are much more disordered than their reactants. Water vapor is more disordered and has a higher entropy than liquid water. Hydrated NH_4^+ and Cl^- ions have a higher entropy than crystalline NH_4Cl. Gaseous NO_2 and O_2 are more disordered and have a higher entropy than solid N_2O_5. A chemical system seeks not only the state of lowest energy or enthalpy, but also the state of greatest disorder, probability, or entropy. A new state function can be defined, the **free energy**, G:

$$G \equiv H - TS \tag{16-8}$$

We can show very simply that for reactions at constant pressure and temperature *any reaction is spontaneous whose free energy decreases.* If we look at the total free energy, G, of a collection of compounds in a beaker at constant temperature, the change in total free energy brought about by chemical reaction is related to the changes in enthalpy and entropy by

$$\Delta G = \Delta H - T \Delta S \tag{16-9}$$

But $H = E + PV$, and at constant pressure

$$\Delta H = \Delta E + P \Delta V$$

and by the first law of thermodynamics

$$\Delta E = q - w$$

Let us assume that no electrical or other work is done, aside from PV work as the reactants and products expand and contract. Then $w = P \Delta V$. And if we substitute into the preceding equations in reverse order,

$$\Delta E = q - P \Delta V$$
$$\Delta H = q - P \Delta V + P \Delta V = q$$

This last equation states that the enthalpy change equals the heat of reaction at constant pressure, which we already have encountered. Substituting q for ΔH into equation 16-9 yields

$$\Delta G = q - T\,\Delta S \qquad\qquad (16\text{-}10)$$

For a reversible reaction, we mentioned previously (equation 16-3) that $\Delta S = q/T$. Therefore, $q = T\,\Delta S$, and

$$\Delta G = 0 \qquad\qquad (16\text{-}11)$$

for a reversible reaction carried out at constant pressure and temperature. What happens in an irreversible reaction? Does the free energy increase, decrease, or do both, depending on the circumstances?

We can answer this question by using equation 16-4. In any real, irreversible reaction, the entropy change is *greater* than q/T. Thus $\Delta S > q/T$, or $T\,\Delta S > q$. Therefore, by equation 16-10, $\Delta G < 0$ for such a reaction.

Both results can be summarized as follows: *In any spontaneous reaction at constant pressure and temperature, the free energy, G, always decreases. When the reaction system reaches equilibrium, G is at a minimum, and ΔG equals zero.* This behavior of G is represented in Figure 16-7.

It is difficult to overestimate the importance of these results to chemists. Free energy is now seen to be the touchstone by which we can determine in advance whether a given reaction will proceed spontaneously, remain at equilibrium, or occur spontaneously in the reverse direction.
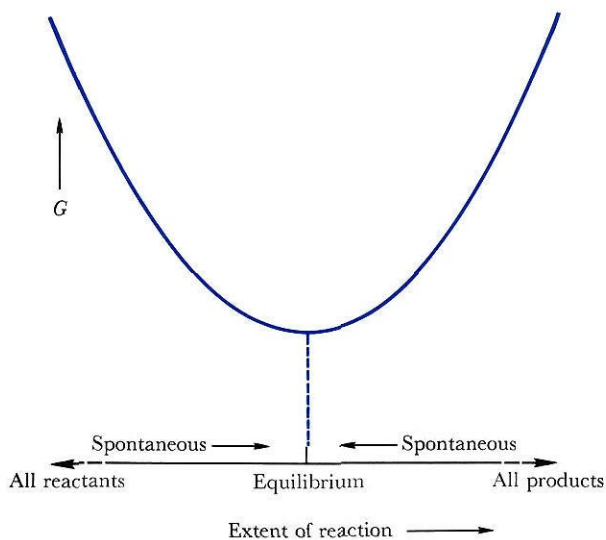

Figure 16-7   The true chemical potential function under conditions of constant pressure and temperature is the free energy, *G*. In all spontaneous reactions, the free energy decreases, and at equilibrium the free energy change of the reaction in either direction is zero.

One last item of thermodynamic ingenuity needs to be mentioned. Since G, like the functions H, T, and S of which it is composed, is a state function, it does not matter if the pressure and temperature change during a reaction, so long as they are brought back to the starting pressure and temperature at the conclusion of the reaction. The preceding comments about G and equilibrium, although derived for unchanging pressure and unchanging temperature, apply equally well to a high-temperature explosion, provided that the reaction vessel and its contents are returned to 298 K and 1 atm at the conclusion of the reaction.*

Free Energy Changes When External Work Is Done

In a reversible process in which no external work is involved, as we have just seen, the free energy of a reacting system does not change: $\Delta G = 0$. What happens if, during the reversible process, the system does electrical, magnetic, or gravitational work on its surroundings? We shall need the answer to this question in Chapter 19, where we treat electrochemical cells.

If PV work is not the only kind of work involved, then

$$w = P\,\Delta V + w_{\text{ext}} \qquad (16\text{-}12)$$

in which w_{ext} represents all other kinds of work. Hence,

$$\Delta E = q - P\,\Delta V - w_{\text{ext}}$$

and the enthalpy and free energy changes are derived as in the preceding pages:

$$\Delta H = q - w_{\text{ext}}$$
$$\Delta G = q - T\,\Delta S - w_{\text{ext}} = -w_{\text{ext}}$$

This final result is the object of our derivation:

$$\Delta G = -w_{\text{ext}} \qquad (16\text{-}13)$$

When a chemical system does work on its surroundings in a reversible manner, the decrease in free energy of the system exactly balances the work done *other than* pressure–volume work. In an electrochemical cell, the work done by the cell is a measure of the decrease of free energy within the cell. Conversely, if a potential is applied across the terminals of an electrolysis cell of the type discussed in Section 1-7, the electrical work done on the cell (measured by methods that we shall examine in Chapter 19) is identical to the increase in free energy of the chemicals in the cell. When water is dissociated electrolytically by passing a current through it, the electrical work required is stored as the increase in free energy of hydrogen

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*In this chapter we deal with reactions at 298 K only. Free energies are sensitive to temperature changes; we will see examples in the next chapter.

and oxygen gas from the free energy of liquid water:

$$H_2O(l) \rightarrow H_2(g) + \tfrac{1}{2}O_2(g) \qquad \Delta G^0 = +237.2 \text{ kJ}$$
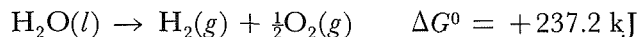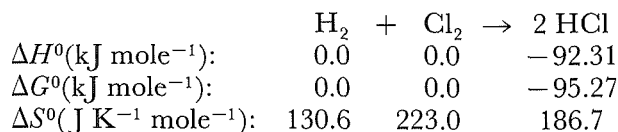
This free energy can be recovered as heat when hydrogen and oxygen gases are burned. Alternatively, if the proper apparatus is used, the free energy can be converted to work again. (A fuel cell such as the one for generating electricity in lunar space capsules uses this $H_2 + \tfrac{1}{2}O_2$ reaction. If the gases are simply burned, part of the free energy is converted to heat and, by the second law, is not recoverable as work. The trick in efficient utilization of energy is to avoid turning it into heat at any step in the process. This is the secret of the efficiency of metabolic processes [Chapter 21].)

Calculations with Standard Free Energies

Standard free energies of formation of compounds from elements in their standard states are tabulated in Appendix 3. The standard state for a gas, pure liquid, or pure solid is the same as with enthalpies: gas at 1 atm partial pressure, pure liquid, pure solid—usually at 298 K. The standard state for a solute in solution is a concentration of 1 mole per liter of solution, or a $1M$ solution. The standard state of a solution component for tabulating enthalpy was not this $1M$ solution, but was a solution so dilute that adding more solvent had no additional heat effect. However, since enthalpy does not change very much with concentration (unlike free energy, as we shall see in Section 16-6) we can also use the tabulated enthalpy values as if they were for $1M$ solutions.

Let's return to our chemical examples and interpret them in terms of free energy. The explosive reaction of H_2 with Cl_2 has the following molar free energies, enthalpies, and entropies of reaction:

	H_2	$+$	Cl_2	$\rightarrow$	$2\,HCl$
ΔH^0(kJ mole^{-1}):	0.0		0.0		-92.31
ΔG^0(kJ mole^{-1}):	0.0		0.0		-95.27
ΔS^0(J K^{-1} mole^{-1}):	130.6		223.0		186.7

The reaction liberates 92.31 kJ of heat *per mole* of HCl produced, and the free energy decreases by more than this amount: 95.27 kJ mole^{-1} HCl. Where does this extra impetus for reaction come from?

For the reaction as written, which produces 2 moles of HCl, $\Delta H^0 = -184.6$ kJ and $\Delta G^0 = -190.5$ kJ. The entropy of the reaction is $\Delta S^0 = 2 \times (186.7) - 130.6 - 223.0 = +19.8$ e.u. Thus, $T\,\Delta S^0$ is 298 K $\times$ 19.8 e.u. = 5900 J or 5.90 kJ. Equation 16-9 is verified:

$$\begin{aligned} \Delta G = &\ \Delta H - T\,\Delta S \\ -190.5 = &\ -184.6 - 5.9 \\ -190.5 = &\ -190.5 \end{aligned}$$

Two moles of HCl are slightly more disordered and have a slightly higher entropy than 1 mole each of H_2 and Cl_2 gases. Most of the drive behind

the reaction, as expressed by the free energy, comes from the liberation of heat, but 3% of it originates because the products have a higher entropy than the reactants.

A standard free energy of -191 kJ indicates a tremendous impetus toward reaction—the impetus that often accompanies an explosion. Now let's look at a gentler reaction, that of making ammonia from hydrogen and nitrogen.

Example 1

What are the changes in standard free energy, enthalpy, and entropy for the reaction $3H_2 + N_2 \rightarrow 2NH_3$? Do the heat and the disorder factors promote or oppose this reaction in the direction written?

Solution

From the data in Appendix 3,

$$\Delta G^0 = 2(-16.64) - 3(0.0) - (0.0) = -33.28 \text{ kJ}$$
$$\Delta H^0 = 2(-46.19) - 3(0.0) - (0.0) = -92.38 \text{ kJ}$$
$$\Delta S^0 = 2(192.5) - 3(130.59) - (191.49) = -198.26 \text{ e.u.}$$

and at 298 K, $T \Delta S^0 = -59.08$ kJ.

Checking equation 16-9, we find that

$$\Delta G = \Delta H - T \Delta S$$
$$-33.28 = -92.38 + 59.08$$

The reaction is favored by the liberation of 92.38 kJ of heat, but opposed by 59.08 kJ because the products are so much more ordered and have 198.3 e.u. lower entropy than the reactants. Another way of considering the reaction is to say that, of the 92.38 kJ of heat liberated, 59.08 kJ were required to pay for the creation of an ordered system, and only 33.28 kJ remain to drive the reaction.

The drive toward the synthesis of ammonia is much smaller than the drive toward the synthesis of HCl, primarily because of the entropy factor. Is it ever possible for the entropy term to overwhelm the heat term and send the reaction in the direction opposite to that indicated by enthalpy alone? Yes, it is, and these are precisely the instances in which the principle of Berthelot and Thomsen fails.

Example 2

Calculate the free energy, enthalpy, and entropy changes for the vaporization of liquid water. Check equation 16-9 with your results. Which term is responsible for the evaporation's taking place?

This is a trick question. The *standard* values are $\Delta G^0 = +8.60$ kJ, $\Delta H^0 = +44.01$ kJ, $\Delta S^0 = 118.8$ e.u., $T\Delta S^0 = +35.41$ kJ. It still looks as if water should not evaporate. But all that this means is that if water vapor at a partial pressure of 1 atm is present at 298 K, it will condense spontaneously. If the partial pressure of the water is only a few millimeters, it will evaporate spontaneously instead. The dependence of ΔG on concentration is the topic of the next section.

Example 3

Calculate the free energy, enthalpy, and entropy changes for the reaction $NH_4Cl(s) \rightarrow NH_4(aq)^+ + Cl(aq)^-$. (The solvent, water, is assumed to be present in equal concentrations before and after reaction, and is omitted.) Do the heat and entropy terms promote or oppose the solution of ammonium chloride?

Solution

$\Delta G^0 = -6.77$ kJ, $\Delta H^0 = +15.14$ kJ, $\Delta S^0 = +73.4$ e.u.; $T\Delta S^0 = +21.9$ kJ. The enthalpy change opposes the reaction by 15.14 kJ, but the entropy change favors it by 21.9 kJ. The net drive in free energy is 6.77 kJ.

Example 4

Calculate the free energy, enthalpy, and entropy changes for the decomposition of N_2O_5,

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

Solution

$$\Delta G^0 = 2(+51.84) + \tfrac{1}{2}(0.0) - (134) = {}^- 30.3 \text{ kJ}$$
$$\Delta H^0 = 2(+33.85) + \tfrac{1}{2}(0.0) - (41.8) = +109.5 \text{ kJ}$$
$$\Delta S^0 = 2(+240.5) + \tfrac{1}{2}(205.0) - (113) = +470 \text{ e.u.}$$

$$T\Delta S^0 = \frac{298 \times (470 \text{ J K}^{-1})}{1000 \text{ J kJ}^{-1}} = +140 \text{ kJ}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$
$$-30.3 = +109.5 - 140$$
$$-30.3 \simeq -30.5$$

The disadvantage of having to absorb about 110 kJ of heat on decomposition is more than compensated by the greater entropy of the gaseous products, and the reaction proceeds with a standard driving force of about 30 kJ of free energy.

In summary, the drive of a reaction, carried out at constant pressure and temperature, is measured by its free energy change. If the free energy change is negative, the reaction is spontaneous; if the free energy change is positive, the reaction is spontaneous in the reverse direction; if the free energy change is zero, reactants and products are at equilibrium. The free energy change has two components: $\Delta G = \Delta H - T\Delta S$. A large decrease in enthalpy, meaning the emission of heat, favors a reaction. But there is a second factor as well. A large increase in entropy when reactants form products also favors reaction. The entropy term at normal temperatures is generally small, so ΔG and ΔH have the same sign. In such cases, spontaneous reactions *are* exothermic. Yet there are other instances in which the entropy and enthalpy terms work against one another, and even in which the entropy term dominates. This is especially true in reactions in which solids or liquids change to gases or solutions as products.

Thus far, we have used only standard concentrations, meaning 1 atm partial pressure for gases, pure liquids, and pure solids for condensed phases, and $1M$ solutions for solutes. How does free energy change with changes in concentration?

16-6   FREE ENERGY AND CONCENTRATION

To this point, we have managed to avoid calculus. We shall need it briefly to derive the equation for the dependence of free energy on concentration, but shall not use it thereafter. Recall the basic definition of free energy,

$$G = H - TS = E + PV - TS$$

Instead of looking at small but finite changes (ΔG, ΔE, ΔS) at constant temperature, as in equation 16-9, let's examine infinitesimally small changes (dG, dE, and dS) under the most general experimental conditions. Then the equation for the basic definition of free energy becomes

$$dG = dE + P\,dV + V\,dP - T\,dS - S\,dT$$

The first law of thermodynamics, expressed in the form of infinitesimally small changes, is

$$dE = dq - dw \tag{16-14}$$

and the free energy expression is

$$dG = dq - dw + P\,dV + V\,dP - T\,dS - S\,dT$$

We can simplify this expression considerably. If the reaction takes place at constant temperature, then $S\,dT = 0$ since dT, the change in temperature, is zero. If the reaction is reversible, $dq = T\,dS$, and if only PV or expansion work is permitted, $dw = P\,dV$. All terms on the right except one cancel, and

$$dG = V\,dP \tag{16-15}$$

For 1 mole of an ideal gas, $V = RT/P$, and

$$dG = RT\frac{dP}{P} = RT\,d\ln P \tag{16-16}$$

Our last use of calculus is the integration (summing all the infinitesimal changes) of this equation:

$$G_2 = G_1 + RT\ln\frac{p_2}{p_1} \tag{16-17}$$

This equation means that if we know the molar free energy of an ideal gas at partial pressure p_1 to be G_1, the molar free energy at some other partial pressure p_2 is G_2. Although we derived this for a reversible change of conditions from p_1 to p_2, once we have it we can use it for irreversible changes as well, since by the state function properties of G it is irrelevant how we go from state 1 to state 2.

Now let us make state 1 our chosen standard state of 1 atm partial pressure and make state 2 any state at all. The more general form of equation 16-17 then is

$$G = G^0 + RT\ln\left(\frac{p}{p^0}\right) \tag{16-18}$$

in which $p^0 = 1$ atm. For the free energy of the compound in the standard state, G^0, we can use instead the free energy of formation from Appendix 3, ΔG^0 at 298 K. This is legitimate because, in any chemical reaction, matter is neither created nor destroyed, and both reactants and products must be made from the *same type and quantity of elements* in their standard states. When we adapt equation 16-18 to ΔG for whole reactions, the contributions of the elements will cancel in reactants and products.

We can now calculate how the free energy of ammonia depends on its partial pressure in a mixture of gases (or more precisely, the free energy of formation of ammonia from its elements in their standard states). Because the standard free energy of formation of ammonia at 298 K is -16.64 kJ mole^{-1},

$$G_{\mathrm{NH_3}} = -16.64 + RT\ln\left(\frac{p_{\mathrm{NH_3}}}{1\text{ atm}}\right)$$

$$G_{\mathrm{NH_3}} = -16.64 + 2.303\,RT\log_{10}\left(\frac{p_{\mathrm{NH_3}}}{1\text{ atm}}\right)$$

Since $R = 8.314$ J deg^{-1} mole^{-1} and $T = 298$ K, $2.303\,RT = 5706$ J mole^{-1} or 5.706 kJ mole^{-1} (this is a handy number to remember). Thus

$$G_{\mathrm{NH_3}} = -16.64 + 5.706\log_{10}\left(\frac{p_{\mathrm{NH_3}}}{1\text{ atm}}\right)$$

The molar free energy of ammonia is plotted against partial pressure in Figure 16-8. (This is actually the molar free energy of formation of ammonia at a specified pressure, from H_2 and N_2 in their standard states.) Note that the plot is a straight line because pressure was plotted on a logarithmic scale. The ratio of partial pressure to partial pressure in the standard state is usually abbreviated as the **activity**, a:

$$a = \frac{p}{p^0}$$

Since the standard state is 1 atm, the activity is numerically equal to the partial pressure of the gas, but activity has no units. This makes activity easier to use; we do not find ourselves wondering how, in the expression "ln p," we can take the logarithm of a number with units attached to it, and then having to remember that the proper form of the logarithm is "ln $(p/1$ atm)."

In summary, for ammonia we can write the general expression for the relationship between free energy and pressure as

$$G_{NH_3} = G^0_{NH_3} + RT \ln a_{NH_3}$$

We can do the same for all the reactants and products, j, in a chemical process:

$$G_j = G^0_j + RT \ln a_j = G^0_j + 2.303\ RT \log_{10} a_j \tag{16-19}$$

Figure 16-8

The free energy of a gas depends on its partial pressure according to the expression $G = G^0 + RT \ln (p/p^0)$. This plot is of the free energy of ammonia, as given by $G_{NH_3} = -16.64 + 5.706 \log_{10} (p_{NH_3}/1$ atm). Pressure, p, is plotted on a logarithmic scale.
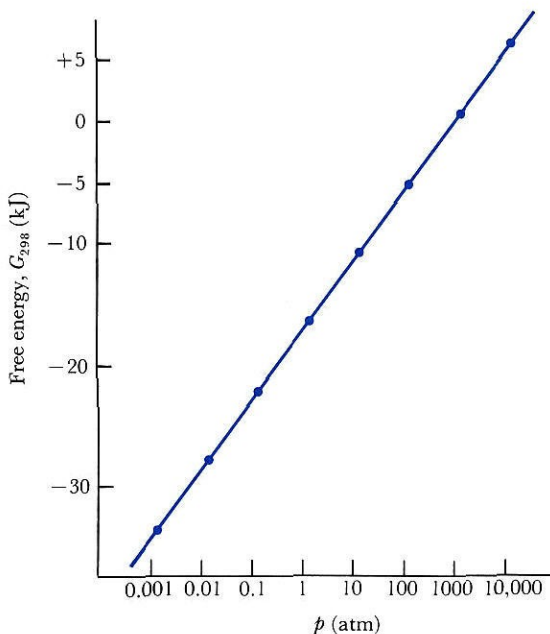
Let's apply this to the synthesis of ammonia and see what we can learn. In writing the equation as

$$N_2 + 3H_2 \rightleftarrows 2NH_3$$
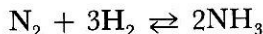
we have changed from the single arrow to a double arrow because we now are considering both the forward and the reverse reactions. For each of the reactants and products, we can write

$$
\begin{aligned}
G_{N_2} &= G^0_{N_2} + RT \ln a_{N_2} \\
G_{H_2} &= G^0_{H_2} + RT \ln a_{H_2} \\
G_{NH_3} &= G^0_{NH_3} + RT \ln a_{NH_3}
\end{aligned}
$$

The total free energy of the chemical reaction is

$$
\begin{aligned}
\Delta G &= 2G_{NH_3} - G_{N_2} - 3G_{H_2} \\
\Delta G &= 2G^0_{NH_3} - G^0_{N_2} - 3G^0_{H_2} + 2RT \ln a_{NH_3} - RT \ln a_{N_2} - 3RT \ln a_{H_2}
\end{aligned}
$$

The first three terms on the right are the *standard* free energy of reaction that we have already used, and are combined as ΔG^0. Then if we take the coefficients in front of the RT terms inside the logarithms as exponents, we can write

$$\Delta G = \Delta G^0 + RT \ln a^2_{NH_3} - RT \ln a_{N_2} - RT \ln a^3_{H_2}$$

Finally,

$$\Delta G = \Delta G^0 + RT \ln \left(\frac{a^2_{NH_3}}{a_{N_2} a^3_{H_2}} \right) \qquad (16\text{-}20)$$

Take a close look at the ratio in parentheses. It is the ratio of activities of products to reactants, and in fact is simply the reaction quotient, Q of Chapter 4, with concentrations expressed in terms of activities rather than moles per liter:

$$Q \equiv \left(\frac{a^2_{NH_3}}{a_{N_2} a^3_{H_2}} \right) \qquad (16\text{-}21)$$

This is a more general treatment than we saw previously, and will lead to a more general concept of equilibrium. This reaction quotient, Q, can be calculated for any given set of experimental conditions from the partial pressures of reactants and products.

The true free energy change in the ammonia reaction is the combination of the standard free energy change (for which $Q = 1$ and $\ln Q = 0$) and the reaction quotient term describing the actual experimental conditions. With numbers inserted, equation 16-20 becomes

$$\Delta G = -33.30 + 5.706 \log_{10} Q \qquad \text{(units of kJ)} \qquad (16\text{-}22)$$

Note that since $\Delta G^0 = 2G^0_{NH_3} - G^0_{N_2} - 3G^0_{H_2} = 2\,\Delta G^0_{NH_3}$, the free energy value in equation 16-22 is twice the value in Appendix 3 for the free energy of formation of 1 mole of NH_3 gas.

Table 16-1 lists the results of applying equation 16-22 to 11 different sets of starting conditions for ammonia synthesis. These are not successive points in the same reaction from the same starting conditions; they are each separate conditions. If the concentrations of reactants and products were as shown in each experiment, what would be the free energy change in the ammonia synthesis reaction? These are the ΔG values at the right of the table. We shall defer until Chapter 17 the question of how to follow a given reaction from start to finish.

In experiment A, nitrogen and hydrogen gases are at 1 atm partial pressure, and there is no ammonia present. Hence, the drive for the production of ammonia is infinitely strong. But as soon as the ammonia concentration is even 10^{-3} atm, the free energy change has increased from $-\infty$ to -67.51 kJ, and the drive to produce more ammonia has slackened (experiment B). If we were to set up experiment C, with N_2 and H_2 at 1 atm partial pressure and NH_3 at 0.1 atm, we would find that the free energy is -44.69 kJ. The more products and the less reactants there are, the smaller is the drive to produce more products. At uniform concentrations of 1 atm, the standard free energy results (experiment D). In experiment E, the excess of ammonia makes the drive smaller than in the standard state. In experiments F, G, and H, the drive toward products is stopped entirely. This is the

Table 16-1

Free Energy of Synthesis of Ammonia at 298 K

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
$$\Delta G = -33.30 + 5.706 \log_{10} Q$$
$$Q = \frac{a_{NH_3}^2}{a_{N_2} a_{H_2}^3}$$

Experiment	a_{N_2}	a_{H_2}	a_{NH_3}	Q	$5.706 \log_{10} Q$ (kJ)	ΔG (kJ)
A	1	1	0	0	$-\infty$	$-\infty$
B	1	1	0.001	10^{-6}	-34.24	-67.51
C	1	1	0.1	10^{-2}	-11.64	-44.69
D	1	1	1	1	0	-33.30
E	1	1	100	10^4	$+22.83$	-10.44
F	1	1	825	6.8×10^5	$+33.30$	0
G	1.47	0.01	1	6.8×10^5	$+33.30$	0
H	0.01	0.1	2.61	6.8×10^5	$+33.30$	0
I	0.01	0.1	26.1	6.8×10^7	$+44.77$	$+11.50$
J	0.01	0.01	100	10^{12}	$+68.48$	$+35.21$
K	0	1	1	∞	$+\infty$	$+\infty$

equilibrium state. At equilibrium

$$\Delta G = 0 \qquad \text{and} \qquad \Delta G^0 = -RT \ln Q$$

As we saw in Chapter 4, the reaction quotient at equilibrium is the **equilibrium constant**, K_{eq}. We can calculate the value of this equilibrium constant from the standard free energy of the reaction:

$$K_{eq} = \frac{a_{NH_3}^2}{a_{N_2}a_{H_2}^3} = e^{-(\Delta G^0/RT)} = 10^{-[(-33.30)/2.303\, RT]} = 6.8 \times 10^5$$

If the reaction quotient is smaller than the equilibrium constant, products will be formed spontaneously. Whenever conditions are such that the reaction quotient is greater than the equilibrium constant, K_{eq}, the reaction will be spontaneous in the reverse direction (experiments, I, J, and K in Table 16-1). When the reaction quotient equals the equilibrium constant, $Q = K_{eq}$, the forward and reverse reactions proceed at the same rate, and the reacting system of chemicals is at equilibrium.

General Expressions

So far, we have stated the free energy derivations in terms of the ammonia reaction. Let's generalize to a reaction in which r moles of compound R combine with s moles of S to produce t moles of T and u moles of U:

$$r\,R + s\,S = t\,T + u\,U \tag{16-23}$$

The free energy change for the reaction, ΔG, is

$$\Delta G = t\,G_T + u\,G_U - r\,G_R - s\,G_S \tag{16-24}$$

Each free energy can be expressed in terms of activity:

$$\begin{aligned} G_R &= G_R^0 + RT \ln a_R \\ G_S &= G_S^0 + RT \ln a_S \\ G_T &= G_T^0 + RT \ln a_T \\ G_U &= G_U^0 + RT \ln a_U \end{aligned} \tag{16-25}$$

These can be substituted into equation 16-24,

$$\Delta G = \Delta G^0 + RT \ln Q \tag{16-26}$$

in which

$$\Delta G^0 = t\,G_T^0 + u\,G_U^0 - r\,G_R^0 - s\,G_S^0 \tag{16-27}$$

and

$$Q = \frac{a_T^t a_U^u}{a_R^r a_S^s} \tag{16-28}$$

Equation 16-26 gives the free energy change for the reaction under any conditions. For the special case of equilibrium, $\Delta G = 0$, and

$$Q = K_{eq} \qquad \text{(the equilibrium constant)} \qquad (16\text{-}29)$$

$$-\Delta G^0 = RT \ln K_{eq} \qquad (16\text{-}30)$$

$$K_{eq} = e^{[-\Delta G^0 / RT]} \qquad (16\text{-}31)$$

Notice that the form of the reaction quotient, Q, and the equilibrium constant, K_{eq}, depends only on the overall stoichiometry of the reaction, and not on any particular reaction mechanism. It isn't necessary to know in molecular detail how a reaction takes place to write the equilibrium-constant expression. We first mentioned this labor-saving fact in Chapter 4; now we have given it a thermodynamic proof.

Example 5

Calculate the equilibrium constant at 298 K for the reaction $H_2(g) + Cl_2(g) = 2HCl(g)$, and compare it with the equilibrium constant for the ammonia synthesis.

Solution

We found earlier that the free energy of this reaction is -95.27 kJ mole^{-1} of HCl, or -190.5 kJ for the reaction as written to produce 2 moles of HCl. Thus

$$K_{eq} = e^{[-(-190.5)/RT]} = 10^{+(190.5/5.706)} = 10^{33.4} = 2.5 \times 10^{33}$$

The K_{eq} for the ammonia synthesis is only 6.8×10^5. The HCl reaction is different; equilibrium lies far on the side of much HCl and few reactants. The expression for the amounts of H_2, Cl_2, and HCl at equilibrium is

$$\frac{a^2_{HCl}}{a_{H_2} a_{Cl_2}} = K_{eq} = 2.5 \times 10^{33}$$

If pure HCl gas is enclosed in a container at 1 atm, enough HCl can dissociate spontaneously to yield partial pressures of H_2 and Cl_2 that are approximately 2×10^{-17} atm, hardly a significant amount of either reactant. In Chapter 17 we shall see how to make such statements for reactions that are less completely skewed in one direction than the HCl reaction is.

Summary

In this chapter we have answered an important chemical question that has been deferred since we first began thinking about energy in chemical reac-

tions in Chapter 2: By what criterion can we decide whether a given chemical reaction is spontaneous, and how can we find the conditions of equilibrium? The criterion is free energy, G (at least for reactions run at constant temperature and pressure), and this goal was reached via another new function, entropy, S.

Entropy is a measure of the disorder of a system. It can be calculated, in principle and sometimes in fact, from the number of different microscopic ways of building the same observable situation. Third-law entropies, obtained from purely thermal measurements, agree well with what we would expect for different substances from Boltzmann's statistical explanation of entropy.

The spontaneity of a reaction at constant pressure and temperature is measured by its change in free energy, ΔG, per unit of reaction. For a reaction in which no work other than pressure–volume work is done, if ΔG is negative, the reaction is spontaneous. If ΔG is positive, the reaction is spontaneous in the reverse direction. If ΔG is zero, the reaction is at equilibrium. Expressed another way, the free energy is the chemical potential function that we minimize to find the point of chemical equilibrium.

If electrical work, or some form of work other than pressure–volume work, is involved in a chemical process accomplished in a reversible manner, then the free energy change during the reaction is not zero. Instead, the free energy of the reacting system decreases by an amount equal to the work done on the surroundings: $\Delta G = -w_{\text{ext}}$.

The free energy of a reaction is the net result of two effects, heat and disorder: $\Delta G = \Delta H - T\,\Delta S$. A reaction is favored if it releases heat (ΔH is negative) and if the products are more disordered than the reactants ($-T\,\Delta S$ negative, or ΔS positive). Usually, but not always, ΔH is the dominant term on the right side of the equation.

The free energy of a gas varies with its partial pressure by the relationship $G_2 = G_1 + RT \ln (p_2/p_1)$. The activity of the gas, a, is the ratio of its pressure to that in a standard state of 1 atm pressure. Thus the free energy at any pressure is given by $G = G^0 + RT \ln a$.

The free energy change of a gas reaction varies with the partial pressures of its components according to the expression $\Delta G = \Delta G^0 + RT \ln Q$. The quantity Q is the reaction quotient, first defined in Chapter 4. For the special case of equilibrium, the free energy of reaction is zero, $\Delta G = 0$, and the reaction quotient becomes the equilibrium constant, $Q = K_{\text{eq}}$. Then the *standard* free energy of reaction and the equilibrium constant are related by

$$\Delta G^0 = -RT \ln K_{\text{eq}} \qquad \text{or} \qquad K_{\text{eq}} = e^{-(\Delta G^0/RT)}$$

For any given set of experimental conditions, if the reaction quotient is smaller than the equilibrium constant, the reaction is spontaneous in the forward direction. If Q is greater than K_{eq}, the reverse reaction is spontaneous. At equilibrium, $Q = K_{\text{eq}}$.

1. Interpret the skidding automobile example of Section 3-6 in terms of the first and second laws of thermodynamics. How does the first law enter? How does reversibility or irreversibility enter, and how is it tied to the second law?
2. Explain how heat and kinetic energy represent motion of different orders of size. Which corresponds to motion at the molecular level?
3. Which energy conversion is subject to severe limitations: converting large-scale motion to molecular motion, or converting molecular motion to large-scale motion? In what way does the second law of thermodynamics refer to this dilemma? (Which is easier: mixing a bag of red beans with a bag of white beans, or unmixing them?)
4. How is entropy related to heat and temperature, according to classical thermodynamics? How does the relationship differ, depending on whether the process is carried out reversibly or irreversibly?
5. To what did Boltzmann relate entropy? Why is it convenient for his definition of S to be in logarithmic form?
6. Why is the entropy of a solid less than that of a gas of the same substance?
7. Why, according to Boltzmann, will the entropy of a perfect crystal be zero only at absolute zero temperature?
8. Why should dissolving a solid or liquid in water lead to an increase in entropy, whereas dissolving a gas causes an entropy decrease?
9. Why should entropy increase with mass?
10. Why should the entropy of a cross-linked polymer be less than that of the polymer subunits before they have been polymerized?
11. Does an aqueous solution of calcium ions have a larger entropy before or after hydration by water molecules? Why, then, are the ions hydrated?
12. Which has the higher entropy: a mole of ice or a mole of liquid water? Why, then, does water freeze?
13. Which has the higher enthalpy: a mole of water or a mole of water vapor? Why, then, does water evaporate?
14. What is wrong with the statement, "In all spontaneous processes, the system moves toward a state of lowest energy"? What is the correct statement?
15. What is wrong with the statement, "In all spontaneous processes, the entropy rises"? For what kinds of thermodynamic system is this statement true?
16. How do enthalpy change and entropy change contribute to the total free energy change, at constant temperature?
17. How does your answer to Questions 14–16 lead to the conclusion that spontaneous reactions are those for which the free energy of reaction decreases?

18. How is electrical or other work related to free energy changes in a reaction carried out reversibly at constant pressure and temperature?

19. Appendix 3 tabulates ΔG^0, ΔH^0, and S^0 at 298 K for chemical substances. Show that some of this information is redundant, and could be dispensed with. Why, then, is there duplication of information in these tables? What could you delete from the tables, and how would you calculate it from the data that were left?

20. How does free energy depend on concentrations of reactants and products?

21. What is the thermodynamic activity of a substance? How are the activity and partial pressure of an ideal gas related?

22. What is the relationship between the reaction quotient and the equilibrium constant for a reaction?

23. How can you tell from the numerical value of the reaction quotient whether a given reaction is at equilibrium, spontaneous in the forward direction, or spontaneous in reverse?

Problems

Disorder and entropy

1. In each of the following pairs, which item will have the greater entropy: (a) a packaged deck of cards or the same cards spread out on a table; (b) an assembled automobile or the unassembled parts needed to make the automobile; (c) carbon dioxide, water, nitrogen compounds and minerals, or the tree that grows from them?

2. In each of the following pairs, which state has the higher entropy: (a) a mole of liquid water, or a mole of water vapor at 1 atm pressure and 25°C; (b) a mole of dry ice or a mole of carbon dioxide gas at 1 atm and 195 K; (c) five dimes on a tabletop showing four heads and one tail, or showing three heads and two tails; (d) 100 g of liquid H_2O and 100 g of liquid D_2O (D is the symbol for deuterium) in separate beakers, or the 200 g mixture of the two; (e) a mole of gaseous CO_2, or a mole of CO_2 in the form of carbonated water?

Entropy changes

3. Will the entropy change in each of the following processes be positive or negative? Will the disorder in each process increase or decrease?
   a) 1 mole of solid methanol → 1 mole of gaseous methanol
   b) 1 mole of solid methanol → 1 mole of liquid methanol
   c) $\frac{1}{2}$ mole of gaseous O_2 + 2 moles of solid Na → 1 mole of solid Na_2O
   d) 1 mole of solid XeO_4 → 1 mole of gaseous Xe + 2 moles of gaseous O_2
   Rank these four processes in order of increasing ΔS.

4. In 1884, Frederick Trouton discovered that for many liquids the heat of vaporization is directly proportional to the normal boiling point, or that the ratio of heat of vaporization to boiling point is constant:

$$\frac{\Delta H_{vap}}{T_b} = 88 \text{ J K}^{-1} \text{ mole}^{-1}$$

We now would explain Trouton's rule by saying that the molar entropy of vaporization of many liquids is approximately the same, or that the disorder produced by evaporation is comparable for many liquids. But HF is odd in that its molar entropy of vaporization is higher, 105 J K^{-1} mole^{-1}. Why is this so? (*Clue:* The molar entropy of HF gas is not different enough from that of other gases to account for the discrepancy.)

5. Predict the sign of the entropy change in each of the following reactions:

a) $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$
b) $Mg(s) + Cl_2(g) \rightarrow MgCl_2(s)$
c) $Al(s) \rightarrow Al(l)$
d) $I_2(s) \rightarrow I_2(g)$
e) $CH_4(g) + 2O_2(g) \rightarrow$
$$CO_2(g) + 2H_2O(l)$$

In each case give the molecular reason for your answer.

6. Calculate the entropy changes of the following chemical reactions, all at 298 K:

a) $Ba(s) + \frac{1}{2}O_2(g) \rightarrow BaO(s)$
b) $BaCO_3(s) \rightarrow BaO(s) + CO_2(g)$
c) $Br_2(g) \rightarrow 2Br(g)$
d) $H_2(g) + Br_2(l) \rightarrow 2HBr(g)$

Explain the sign of each of the entropy changes by comparing qualitatively the freedom of motion, or molecular disorder, in reactants and products.

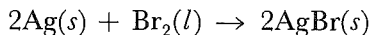7. Explain the entropy increase in the reaction

$$Br_2(l) + Cl_2(g) \rightarrow 2BrCl(g)$$
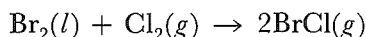
8. Explain the entropy increase in the reaction

$$Br_2(g) + Cl_2(g) \rightarrow 2BrCl(g)$$
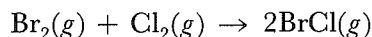
(This is not a repetition of Problem 7.)

Entropy and free energy

9. For the reaction (at 298 K and 1 atm),

$$2Ag(s) + Br_2(l) \rightarrow 2AgBr(s)$$

$\Delta H^0 = -199.2$ kJ mole^{-1} and $\Delta G^0 = -191.6$ kJ mole^{-1}.
a) Calculate the standard entropy change, ΔS^0, for the reaction.
b) What does this value of ΔS^0 tell you about the relative degree of order in reactants and products?

10. The reaction

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$$
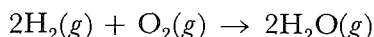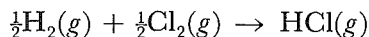
proceeds spontaneously even though there is an increase in order within the system. How can this be?

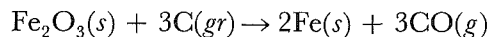11. Calculate the change in entropy, ΔS^0, for the reaction

$$S(s, \text{rhombic}) + O_2(g) \rightarrow SO_2(g)$$
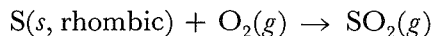
given data in Appendix 3.

12. Using data in Appendix 3, calculate ΔS^0 in two different ways for the reaction

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g) \rightarrow HCl(g)$$

Contributions of *H* and *S* to *G*

13. Calculate the standard free energy change, ΔG^0, for the reaction

$$Fe_2O_3(s) + 3C(gr) \rightarrow 2Fe(s) + 3CO(g)$$

Is this reaction spontaneous at 25°C? Calculate the standard enthalpy change, ΔH^0, and entropy change, ΔS^0, of the reaction at 298 K, and verify that

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

Do the enthalpy change and entropy change work for, or against, spontaneity

in the reaction? Which factor predominates?

14. Calculate ΔG^0, ΔH^0, and ΔS^0 for the reaction (at 298 K),

$$2Ag(s) + Hg_2Cl_2(s) \rightarrow$$
$$2AgCl(s) + 2Hg(l)$$
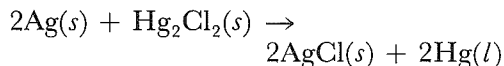
Show that $\Delta G^0 = \Delta H^0 - T\,\Delta S^0$. Is the reaction spontaneous? Do the enthalpy change and entropy change each work for, or against, spontaneity for the reaction? Which factor predominates? Explain the entropy effect on molecular grounds.
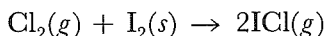
Free energy and K_{eq}

15. What is the standard free energy change for synthesis of ammonia at 298 K? The reaction is

$$3H_2(g) + N_2(g) \rightarrow 2NH_3(g)$$
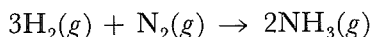
Calculate the equilibrium constant, K_{eq}, and write the expression for K_{eq} in terms of concentrations of reactants and products present at equilibrium.

16. Give the standard free energy change at 25°C for the reaction

$$Cl_2(g) + I_2(s) \rightarrow 2ICl(g)$$

Will the reaction as written be spontaneous under standard conditions? What are the relative contributions of enthalpy and entropy to the spontaneity of the reaction? Which effect predominates? Calculate K_{eq} for this reaction.

Molar entropy

17. Arrange the following substances in order of increasing molar entropy:

$N_2O_4(s)$, $Na(s)$, $NaCl(s)$, $Br_2(l)$, $Br_2(g)$.
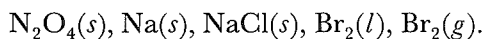
18. Calculate the change in free energy for the reaction that converts diamond to graphite. In view of your answer, why don't diamonds in diamond rings spontaneously turn into lumps of graphite?
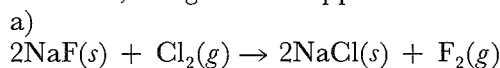
Free energy and spontaneity

19. Consider the reaction
$$CH_4(g) + 2O_2(g) \rightarrow$$
$$CO_2(g) + 2H_2O(l)$$
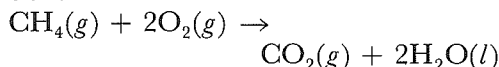
(a) According to the calculated ΔG^0, is this reaction thermodynamically spontaneous? (b) How do you account for the fact that methane and oxygen gases can remain mixed for long periods of time without detectable reaction?

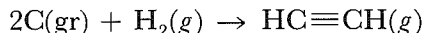20. Calculate ΔG^0 at 25°C for the following reactions, using data in Appendix 3:
a)
$$2NaF(s) + Cl_2(g) \rightarrow 2NaCl(s) + F_2(g)$$
b)
$$PbO_2(s) + 2Zn(s) \rightarrow Pb(s) + 2ZnO(s)$$
In view of your answers, comment on (a) the likelihood of obtaining fluorine gas by treating NaF with chlorine gas, and (b) the use of zinc to reduce PbO_2 to lead.

21. The standard free energy change of the reaction

$$2C(gr) + H_2(g) \rightarrow HC\equiv CH(g)$$

is $+209$ kJ mole^{-1} of acetylene, C_2H_2. (a) Is this a practical route for the synthesis of acetylene at room temperature? What is the equilibrium constant for this reaction? Does it favor reactants, or products? (b) Calculate the free energy change for the reaction

$$2CH_4(g) + \tfrac{3}{2}O_2(g) \rightarrow$$
$$HC\equiv CH(g) + 3H_2O(g)$$
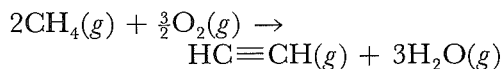
Would this be a better approach for synthesis of acetylene? Why, or why not?

22. Calculate the free energy change associated with the combustion of liquid methanol:

$$CH_3OH(l) + \tfrac{3}{2}O_2(g) \rightarrow$$
$$CO_2(g) + 2H_2O(l)$$
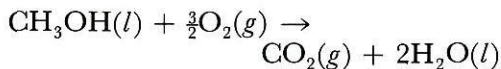
(a) Is this reaction spontaneous under standard conditions? What is the equilibrium constant at 298 K? Does it favor reactants, or products? (b) What effect would an increase in pressure have on the spontaneity of the reaction? (c) What effect would an increase in temperature have on the spontaneity of the reaction?

Change of phase

23. If 333.5 J of heat are required to melt 1 g of ice at $0°C$, what is the molar heat of fusion of ice at this temperature? What is the entropy change when 1 g of ice melts at $0°C$? What is the free energy change for the process?

24. (a) Consider the evaporation of water as a chemical process, and calculate ΔH^0, ΔS^0, and ΔG^0 for the process under standard conditions at $25°C$. (b) Recalling that

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

$$= -RT \ln \frac{a(g)}{a(l)}$$

where $a(g)$ and $a(l)$ are the activities of

H$_2$O gas and liquid, derive an expression for the vapor pressure of water as a function of temperature. (c) Calculate the equilibrium vapor pressure of water at $50°C$ and at $100°C$. (Enthalpy and entropy are essentially constant at these temperatures.)

25. One mole of benzene, C_6H_6, is vaporized at its boiling point under a constant pressure of 1 atm. The heat of vaporization measured in a calorimeter at constant pressure is 30.54 kJ mole^{-1}. The boiling point of benzene at 1 atm is $80°C$. (a) Calculate ΔH^0, ΔG^0, and ΔS^0 for this process. (b) Calculate ΔE^0 for the process, assuming that benzene vapor is an ideal gas. (c) Compare your answers to the standard heat and free energy of vaporization obtained from Appendix 3. Why are the values different? Can you explain the difference using Le Chatelier's principle?

Reversible and irreversible processes

26. A reaction, $A \rightarrow B$, was carried out at $25°C$ in such a way that no useful work was done. In this process, 41.84 kJ mole^{-1} of heat were evolved. In a second experiment, the same overall reaction was carried out in such a way that the maximum amount of useful work was done. In this process, only 1.673 kJ mole^{-1} of heat were evolved. For each of the two reactions, calculate q, w, ΔE^0, ΔH^0, ΔS^0, and ΔG^0.

Suggested Readings

All of the readings for Chapter 15 are useful, plus:

H. A. Bent, *The Second Law: An Introduction to Classical and Statistical Thermodynamics,* Oxford University Press, New York, 1965.

R. E. Dickerson, *Molecular Thermodynamics,* W. A. Benjamin, Menlo Park, Calif., 1969. Somewhat more advanced than Mahan, Nash, or Waser, but with a strong emphasis on the statistical interpretation of entropy.