

CHAPTER TWENTY

Thermodynamics: Entropy, Free Energy, and the Direction of Chemical Reactions

20.1 THE SECOND LAW OF THERMODYNAMICS: PREDICTING SPONTANEOUS CHANGE

A **spontaneous change** of a system is one that occurs by itself under specified conditions, without an ongoing input of energy from outside the system.

- The freezing of water, for example, is spontaneous at 1 atm and -5°C .
- A spontaneous process such as burning or falling may need a little "push" to get started—a spark to ignite gasoline, a shove to knock a book off your desk—but once the process begins, it keeps going without the need for any external input of energy.

In contrast, for a **nonspontaneous change** to occur, the surroundings must supply the system with a continuous input of energy.

- A book falls spontaneously, but it rises only if something else, such as a human hand (or a hurricane-force wind), supplies energy in the form of work.

A chemical reaction proceeding toward equilibrium is an example of a spontaneous change. But why is there a drive to attain equilibrium? And what determines the value of the equilibrium constant? Can we tell the direction of a spontaneous change in cases that are not as obvious as burning gasoline or falling books?

limitations of the First Law of Thermodynamics

- The first law of thermodynamics (the law of conservation of energy); the internal energy (E) of a system, the sum of the kinetic and potential energy of all its particles, changes when heat (q) and/or work (w) are added or removed:

$$\Delta E = q + w$$

- The system and surroundings together constitute the universe (univ):

$$E_{\text{univ}} = E_{\text{sys}} + E_{\text{surr}}$$

- Heat and/or work gained by the system is lost by the surroundings, and vice versa:

$$(q + w)_{\text{sys}} = - (q + w)_{\text{surr}}$$

- It follows from these ideas that the total energy of the universe is constant:

$$\Delta E_{\text{sys}} = - \Delta E_{\text{surr}}$$

therefore

$$\Delta E_{\text{sys}} + \Delta E_{\text{surr}} = 0 = \Delta E_{\text{univ}}$$

NOTE: Any modern statement of conservation of energy must take into account mass-energy equivalence and the processes in stars, which convert enormous amounts of matter into energy. These can be included by stating that the total mass-energy of the universe is constant.

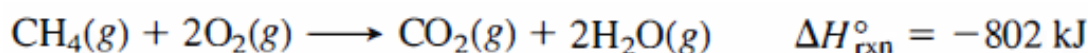
Is the first law sufficient to explain **why** a natural process takes place as it does?

When gasoline burns in your car's engine, the first law states that the potential energy difference between the chemical bonds in the fuel mixture and those in the exhaust gases is converted to the kinetic energy of the moving car and its parts plus the heat released to the environment.

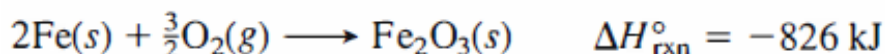
However, the first law does not help us make sense of the **direction of the change**. Why doesn't the heat released in the car engine convert exhaust fumes back into gasoline and oxygen?

The Sign of ΔH Cannot Predict Spontaneous Change

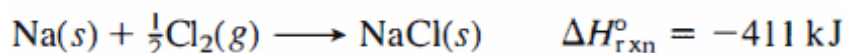
- Many **spontaneous processes** are **exothermic**.
 - All combustion reactions, such as methane burning, are spontaneous and exothermic:



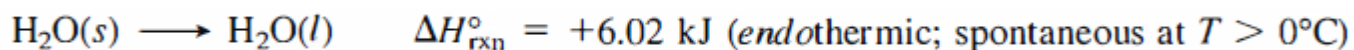
- Iron metal oxidizes spontaneously and exothermically:



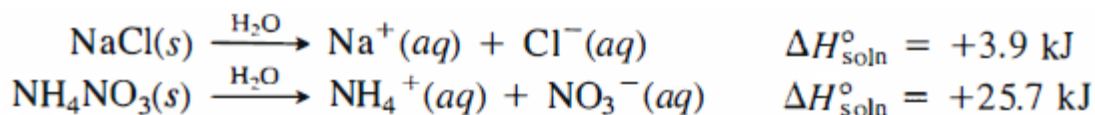
- Ionic compounds, such as NaCl, form spontaneously and exothermically from their elements:



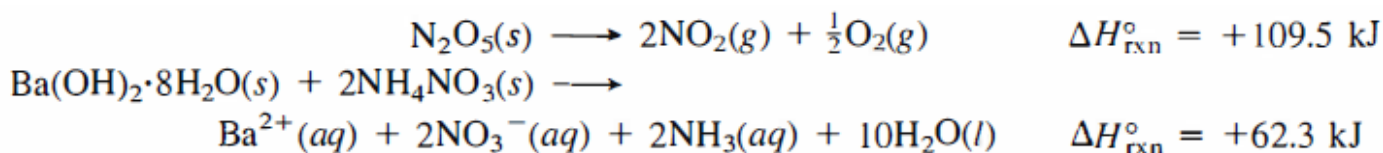
- However, in many other cases, an **endothermic** process is **spontaneous**:
 - All melting and vaporizing are endothermic changes that are spontaneous under proper conditions.



- Most water-soluble salts have a positive $\Delta H_{\text{soln}}^{\circ}$ yet dissolve spontaneously:



➤ Some endothermic chemical changes are also spontaneous:



Freedom of Particle Motion and Dispersal of Particle Energy

What features common to the previous endothermic processes can help us see why they occur spontaneously?

A change in the **freedom of motion of particles** in a system and in the **dispersal of their energy** of motion is **the key factor determining the direction of a spontaneous process**.

less freedom of particle motion \longrightarrow more freedom of particle motion
localized energy of motion \longrightarrow dispersed energy of motion

Phase change: solid \longrightarrow liquid \longrightarrow gas
Dissolving of salt: crystalline solid + liquid \longrightarrow ions in solution
Chemical change: crystalline solids \longrightarrow gases + ions in solution

In each spontaneous process, the particles have more freedom of motion and, therefore, their energy of motion has more levels over which to be dispersed.

Entropy and the Number of Microstates

How freedom of motion and dispersal of energy relate to spontaneous change?

- Molecules have quantized states. The complete quantum state of the molecule at any instant is given by a combination of its particular **electronic**, **translational**, **rotational**, and **vibrational** states.

- Each quantized state of the system is called a **microstate**, and every microstate has the same total energy at a given set of conditions.
- With each microstate equally possible for the system, the laws of probability say that, over time, all microstates are equally occupied.
- In 1877, the Austrian mathematician and physicist Ludwig Boltzmann defined the entropy (S) of a system in terms of the number of microstates, W:

$$S = k \ln W$$

where k, the Boltzmann constant, is the universal gas constant (R) divided by Avogadro's number (N_A), or R/N_A , and equals 1.38×10^{-23} J/K. Because W is just a number it has no units, S has units of J/K.

From this relationship, we conclude that

- A system with fewer microstates (smaller W) among which to spread its energy has lower entropy (lower S).
- A system with more microstates (larger W) among which to spread its energy has higher entropy (higher S).

Thus, for our earlier examples,

lower entropy (fewer microstates) \longrightarrow higher entropy (more microstates)

Phase change: solid \longrightarrow liquid \longrightarrow gas

Dissolving of salt: crystalline solid + liquid \longrightarrow ions in solution

Chemical change: crystalline solids \longrightarrow gases + ions in solution

Changes in Entropy

- If the number of microstates increases during a physical or chemical change, there are more ways for the energy of the system to be dispersed among them. Thus, the entropy increases:

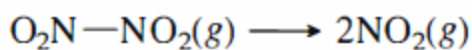
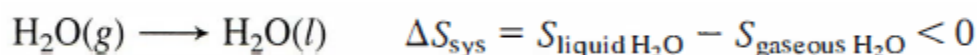
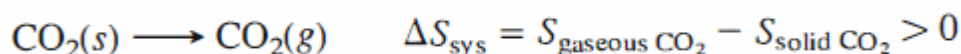
$$S_{\text{more microstates}} > S_{\text{fewer microstates}}$$

If the number of microstates decreases, the entropy decreases.

- Like internal energy (E) and enthalpy (H), entropy is a thermodynamic state function, which means it depends only on the present state of the system, not on the path it took to arrive at that state. Therefore, the change in entropy of the system (ΔS_{sys}) depends only on the difference between its final and initial values:

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

Examples;



$$\Delta S_{\text{sys}} = \Delta S_{\text{rxn}} = S_{\text{final}} - S_{\text{initial}} = S_{\text{products}} - S_{\text{reactants}} = 2S_{\text{NO}_2} - S_{\text{N}_2\text{O}_4} > 0$$

Quantitative Meaning of the Entropy Change

Two approaches for quantifying an entropy change look different but give the same result.

- The first is a statistical approach based on the number of microstates possible for the particles in a system.
- The second is based on the heat absorbed (or released) by a system.

We'll explore both in a simple case of 1 mol of an ideal gas, say neon, expanding from 10 L to 20 L at 298 K:



Figure 20.1 A shows a container consisting of two identical flasks connected by a stopcock, with 1 mol of neon in the left flask and an evacuated right flask. We know

from experience that when we open the stopcock, the gas will expand to fill both flasks with 0.5 mol each-but why?

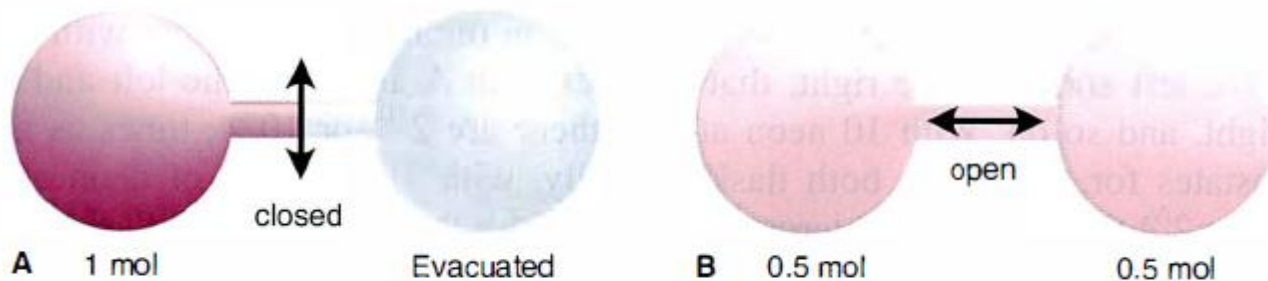


Figure 20.1 Spontaneous expansion of a gas The container consists of two identical flasks connected by a stopcock. A, With the stopcock closed, 1 mol of neon gas occupies one flask, and the other is evacuated. B, Open the stopcock, and the gas expands spontaneously until each flask contains 0.5 mol.

First Approach

Let's start with one neon atom and think through what happens as we add more atoms and open the stopcock (Figure 20.2).

- Opening the stopcock increases the volume, which increases the number of possible particle locations and, thus, translational energy levels. As a result, the system has 2^1 , or 2, times as many microstates possible when the atom moves through both flasks (final state, W_{final}) as when it is confined to one flask (initial state, W_{initial}).
- With 2 atoms, A and B, moving through both flasks, there are 2^2 , or 4, times as many microstates as when they are confined initially to one flask.
- Add another atom and there are 2^3 , or 8, times as many microstates when the stopcock is open-some number with all three in the left, that number with A and B in the left and C in the right, that number with A and C in the left and B in the right, and so on.
- With 10 neon atoms, there are 2^{10} , or 1024, times as many microstates for the gas in both flasks.

- Finally, with 1 mol (N_A) of neon atoms, there are 2^{N_A} times as many microstates possible for the atoms in both flasks (W_{final}) as in one flask (W_{initial})
In other words, for 1 mol, we have

$$W_{\text{final}}/W_{\text{initial}} = 2^{N_A}$$

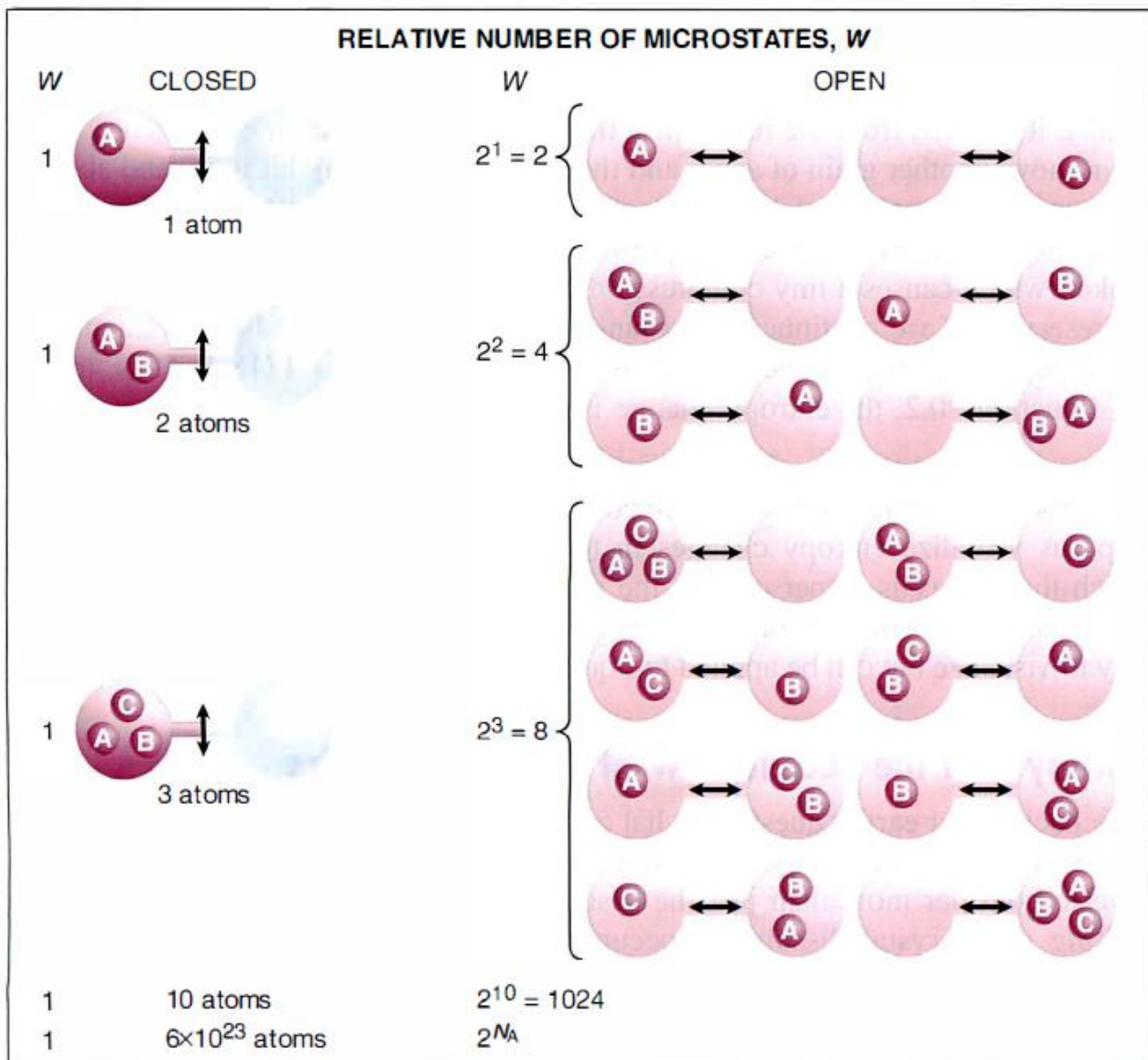


Figure 20.2 Expansion of a gas and the increase in number of microstates. When a gas confined to one flask is allowed to spread through two flasks, the energy of the particles is dispersed over more microstates, and so the entropy is higher. Each combination of particles in the available volume represents a different microstate. The increase in the number of possible microstates that occurs when the volume increases is given by 2^n , where n is the number of particles.

Now let's find ΔS_{sys} through the Boltzmann equation, $S = k \ln W$. From Appendix A, we know that $\ln A - \ln B = \ln A/B$. Thus,

$$\Delta S_{\text{sys}} = S_{\text{final}} - S_{\text{initial}} = k \ln W_{\text{final}} - k \ln W_{\text{initial}} = k \ln (W_{\text{final}}/W_{\text{initial}})$$

$$\begin{aligned} \Delta S_{\text{sys}} &= R/N_A \ln 2^{N_A} = (R/N_A)N_A \ln 2 = R \ln 2 = (8.314 \text{ J/mol}\cdot\text{K})(0.693) \\ &= 5.76 \text{ J/mol}\cdot\text{K} \end{aligned}$$

or, for 1 mol, $\Delta S_{\text{SYS}} = 5.76 \text{ J/K}$

Second Approach

In the second approach, the entropy change is defined by

$$\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T}$$

where T is the temperature at which the heat change occurs and q is the heat absorbed.

The subscript "rev" refers to a **reversible process**, one that occurs *slowly enough* for equilibrium to be maintained continuously, so that the direction of the change can be reversed by an *infinitesimal* reversal of conditions.

A truly reversible expansion of an ideal gas can only be imagined, but we can approximate it by placing the 10-L neon sample in a piston-cylinder assembly surrounded by a heat reservoir maintained at 298 K, with a beaker of sand on the piston exerting the pressure.

- We remove one grain of sand (an "infinitesimal" change in pressure), and the gas expands a tiny amount, raising the piston and doing work on the surroundings, $-w$. If the neon behaves ideally, it absorbs from the reservoir a tiny increment of heat q , equivalent to $-w$.
- We remove another grain of sand, and the gas expands a tiny bit more and absorbs another tiny increment of heat. This expansion is very close to being reversible because we can reverse it at any point by putting a grain of sand

back into the beaker, which causes a tiny compression of the gas and a tiny release of heat into the reservoir.

- If we continue this expansion process to 20 L and apply calculus to add together all the tiny increments of heat, we find q_{rev} is 1718 J. Thus, applying the equation above, the entropy change is

$$\Delta S_{\text{sys}} = q_{\text{rev}}/T = 1718 \text{ J}/298 \text{ K} = 5.76 \text{ J/K}$$

This is the same result we obtained by the statistical approach.

Entropy and the Second Law of Thermodynamics

Now back to our earlier question: what criterion determines the direction of a spontaneous change?

- Second Law: all real processes occur **spontaneously** in the direction that **increases the entropy** of the universe (**system plus surroundings**)

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

- Entropy of the system may decrease or increase, entropy of the surroundings may also decrease or increase, but the entropy of the universe (system plus surroundings) must always increase in a spontaneous process.

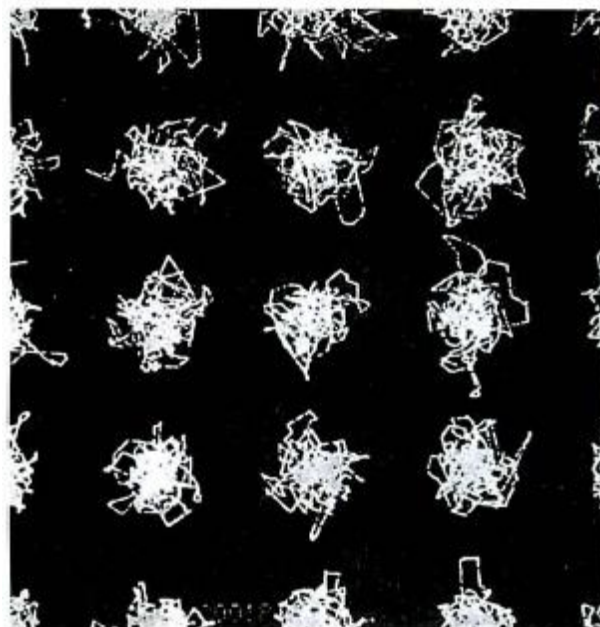
Standard Molar Entropies and the Third Law

- Both entropy and enthalpy are state functions, but the nature of their values differs in a fundamental way.
- We cannot determine absolute enthalpies because we have no baseline value for the enthalpy of a substance. Therefore, we measure only enthalpy changes.
- In contrast, *we can determine the **absolute** entropy of a substance.* To do so

requires application of the **third law of thermodynamics**, which states that a perfect crystal has zero entropy at a temperature of absolute zero; $S_{\text{sys}} = 0$ at 0 K.

- At absolute zero, all particles in the crystal have the minimum energy, and there is only one way it can be dispersed: $W = 1$, so $S = k \ln 1 = 0$. When we warm the crystal, its total energy increases, so the particles' energy can be dispersed over more microstates (Figure 20.3). Thus, $W > 1$, $\ln W > 0$, and $S > 0$.

Figure 20.3 Random motion in a crystal. This computer simulation shows the paths of the particle centers in a crystalline solid. At any temperature greater than 0 K, each particle moves about its lattice position. The higher the temperature, the more vigorous the movement. Adding thermal energy increases the total energy, and the particle energies can be distributed over more microstates; thus, the entropy increases.



- The entropy of a substance at a given temperature is therefore an absolute value that is equal to the entropy increase obtained when the substance is heated from 0 K to that temperature.
- The standard molar entropy (S°) has unit of $\text{J/mol} \cdot \text{K}$. The S° values at 298 K for many elements, compounds, and ions appear, with other thermodynamic variables, in **Appendix B**.

Predicting Relative S° Values of a System

Based on an understanding of systems at the molecular level and the effects of heat absorbed, we can often predict how the entropy of a substance is affected by temperature, physical state, dissolution, and atomic or molecular complexity.

1. Temperature changes. For a given substance, S° increases as the temperature rises. Consider these typical values for copper metal:

T (K):	273	295	298
S° :	31.0	32.9	33.2

The temperature increases as heat is absorbed ($q > 0$), which represents an increase in the average kinetic energy of the particles.

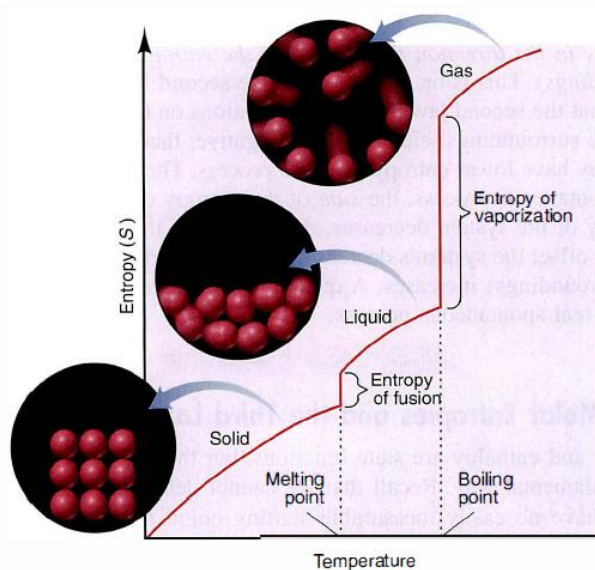
2. Physical states and phase changes. S° increases for a substance as it changes from a solid to a liquid to a gas:

	Na	H ₂ O	C(graphite)
$S^\circ(s \text{ or } l)$:	51.4(s)	69.9(l)	5.7(s)
$S^\circ(g)$:	153.6	188.7	158.0

Figure 20.4 shows the entropy of a typical substance as it is heated. Note the **gradual increase** within a phase as the temperature rises and the **large, sudden increase** at the phase change. Note that $\Delta S^\circ_{\text{vap}} \gg \Delta S^\circ_{\text{fus}}$.

Figure 20.4

The increase in entropy from solid to liquid to gas. A plot of entropy vs. temperature shows the gradual increase in entropy within a phase and the abrupt increase with a phase change. The molecular-scale views depict the increase in freedom of motion of the particles as the solid melts and, even more so, as the liquid vaporizes.



3. Dissolving a solid or liquid. The entropy of a dissolved solid or liquid is usually greater than the entropy of the pure solute, but the nature of solute and solvent and the dissolving process affect the overall entropy change (Figure 20.5):

	NaCl	AlCl ₃	CH ₃ OH
$S^\circ(s \text{ or } l)$:	72.1(s)	167(s)	127(l)
$S^\circ(aq)$:	115.1	-148	132

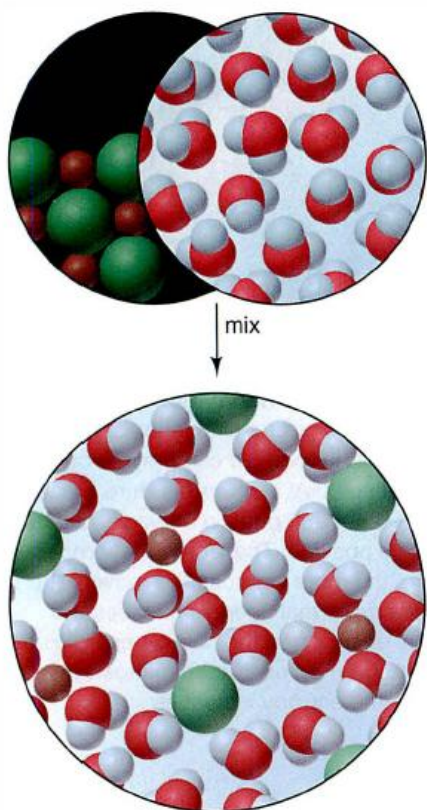


Figure 20.5

The entropy change accompanying the dissolution of a salt.

When a crystalline salt and pure liquid water form a solution, the entropy change has two contributions: a positive contribution as the crystal separates into ions and the pure liquid disperses them, and a negative contribution as water molecules become organized around each ion. The relative magnitudes of these contributions determine the overall entropy change. The entropy of a salt solution is usually greater than that of the solid and water.

- When an ionic solid dissolves in water, the entropy of the ions themselves is greater in the solution than in the crystal. However, some of the water molecules become organized around the ions, their motions restricted (see Figure 13.2), which makes a negative contribution to the overall entropy change. This negative contribution can dominate and lead to negative S° values for the ions in solution.

For example, the $\text{Al}^{3+}_{(aq)}$ ion has such a negative S° value (- 313 J/mol· K).

- An S° value for a hydrated ion can be negative because it is relative to the S° value for the hydrated proton, $H^+_{(aq)}$, which is assigned a value of 0. In other words, $Al^{3+}_{(aq)}$ has a lower entropy than $H^+_{(aq)}$.
- For molecular solutes, the increase in entropy upon dissolving is typically much smaller than for ionic solutes. For a solid such as glucose, there is no separation into ions, and for a liquid such as ethanol, the breakdown of a crystal structure is absent as well.
- Furthermore, in pure ethanol and in pure water, the molecules form many H bonds, so there is relatively little change in their freedom of motion when they are mixed (Figure 20.6). The small increase in the entropy of dissolved ethanol arises from the random mixing of the molecules.

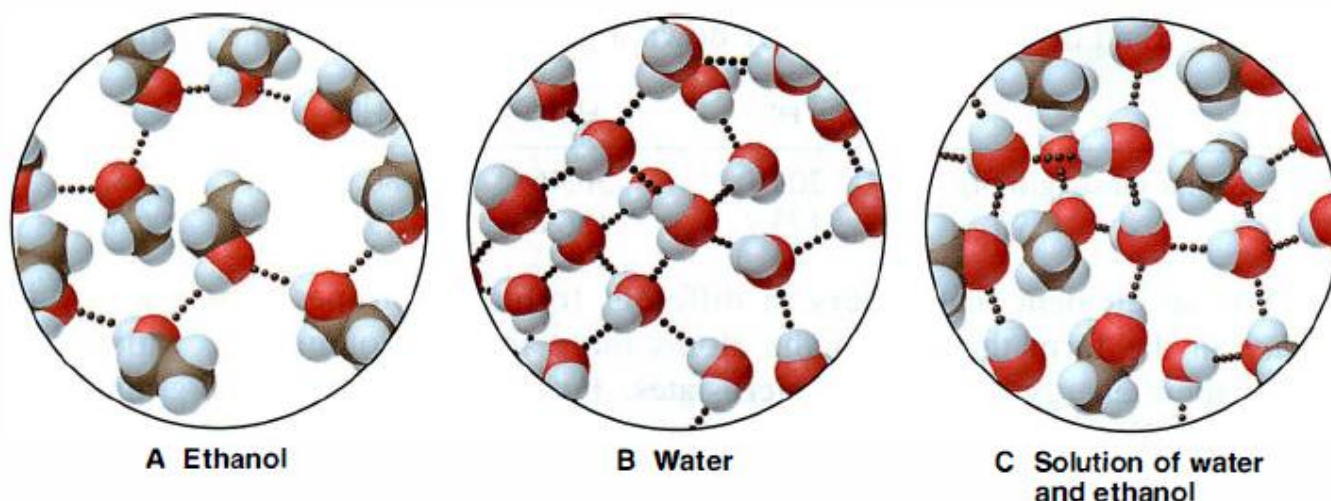


Figure 20.6 The small increase in entropy when ethanol dissolves in water. Pure ethanol (A) and pure water (B) have many intermolecular H bonds. C, In a solution of these two substances, the molecules form H bonds to one another, so their freedom of motion does not change significantly. Thus, the entropy increase is relatively small and is due solely to random mixing.

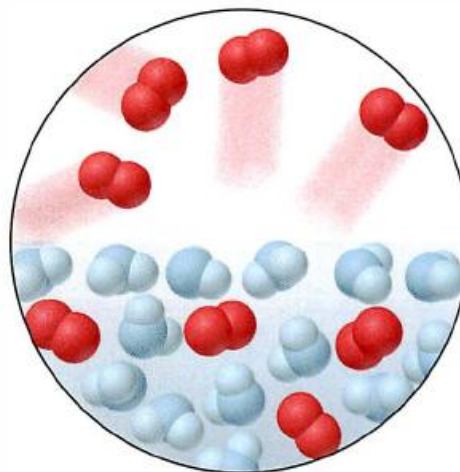
4. Dissolving a gas. The particles in a gas always lose freedom when they dissolve in a liquid or solid. Therefore, the entropy of a solution of a gas in a liquid or a solid is always less than the entropy of the gas.

For instance, when gaseous O_2 [$S^\circ(g) = 205.0 \text{ J/mol}\cdot\text{K}$] dissolves in water, its entropy decreases dramatically [$S^\circ(aq) = 110.9 \text{ J/mol}\cdot\text{K}$] (Figure 20.7). When a gas

dissolves in another gas, however, the entropy increases from the mixing of the molecules.

Figure 20.7

The large decrease in entropy of a gas when it dissolves in a liquid. The chaotic movement and high entropy of molecules of O₂ are reduced greatly when the gas dissolves in water.



5. Atomic size or molecular complexity. For elements within a periodic group, energy levels (microstates) become closer together for heavier atoms.

➤ Entropy increases down the group:

	Li	Na	K	Rb	Cs
Atomic radius (pm):	152	186	227	248	265
Molar mass (g/mol):	6.941	22.99	39.10	85.47	132.9
$S^\circ(s)$:	29.1	51.4	64.7	69.5	85.2

The same trend of increasing entropy down a group holds for similar compounds:

	HF	HCl	HBr	HI
Molar mass (g/mol):	20.01	36.46	80.91	127.9
$S^\circ(g)$:	173.7	186.8	198.6	206.3

➤ For an element that occurs in different forms (**allotropes**), the entropy is higher in the form that allows the atoms more freedom of motion, which disperses their energy over more microstates.

For example, the S° of graphite is 5.69 J/mol·K, whereas the S° of diamond is 2.44 J/mol·K. In diamond, covalent bonds extend in three dimensions, allowing the atoms little movement; in graphite, covalent bonds extend only within a two-

dimensional sheet, and motion of the sheets relative to each other is relatively easy.

- For compounds, entropy increases with chemical complexity, that is, with the number of atoms in a formula unit or molecule of the compound. This trend holds for both ionic and covalent substances, as long as they are in the same phase:

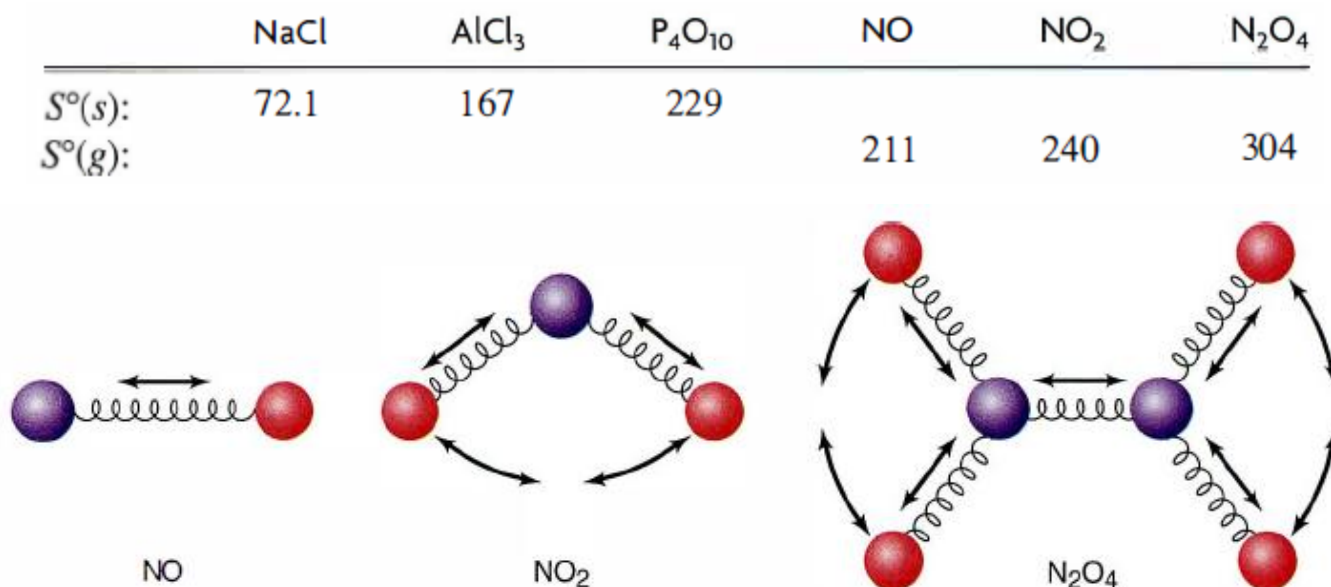


Figure 20.8 Entropy and vibrational motion. A diatomic molecule, such as NO, can vibrate in only one way. NO₂ can vibrate in more ways, and N₂O₄ in even more. Thus, as the number of atoms increases, a molecule can disperse its vibrational energy over more microstates, and so has higher entropy.

- For larger molecules, we also consider how one part of a molecule moves relative to other parts. A long hydrocarbon chain can rotate and vibrate in more ways than a short one, so entropy increases with chain length. A ring compound, such as cyclopentane (C₅H₁₀), has lower entropy than the corresponding chain compound, pentene (C₅H₁₀), because the ring structure restricts freedom of motion:

	CH ₄ (g)	C ₂ H ₆ (g)	C ₃ H ₈ (g)	C ₄ H ₁₀ (g)	C ₅ H ₁₀ (g)	C ₅ H ₁₀ (cyclo, g)	C ₂ H ₅ OH(l)
S° :	186	230	270	310	348	293	161

When gases are compared with liquids, the effect of physical state usually dominates that of molecular complexity. Gaseous methane has a greater entropy than liquid ethanol even though ethanol molecules are more complex.

SAMPLE PROBLEM 20.1 Predicting Relative Entropy Values

Problem Choose the member with the higher entropy in each of the following pairs, and justify your choice [assume constant temperature, except in part (e)]:

- (a) 1 mol of $\text{SO}_2(g)$ or 1 mol of $\text{SO}_3(g)$ (b) 1 mol of $\text{CO}_2(s)$ or 1 mol of $\text{CO}_2(g)$
(c) 3 mol of $\text{O}_2(g)$ or 2 mol of $\text{O}_3(g)$ (d) 1 mol of $\text{KBr}(s)$ or 1 mol of $\text{KBr}(aq)$
(e) Seawater at 2°C or at 23°C (f) 1 mol of $\text{CF}_4(g)$ or 1 mol of $\text{CCl}_4(g)$

Plan In general, we know that particles with more freedom of motion or more dispersed energy have higher entropy and that raising the temperature increases entropy. We apply the general categories described in the text to choose the member with the higher entropy.

Solution (a) 1 mol of $\text{SO}_3(g)$. For equal numbers of moles of substances with the same types of atoms in the same physical state, the more atoms in the molecule, the more types of motion available, and thus the higher the entropy.

(b) 1 mol of $\text{CO}_2(g)$. For a given substance, entropy increases in the sequence $s < l < g$.

(c) 3 mol of $\text{O}_2(g)$. The two samples contain the same number of oxygen atoms but different numbers of molecules. Despite the greater complexity of O_3 , the greater number of molecules dominates in this case because there are many more microstates possible for three moles of particles than for two moles.

(d) 1 mol of $\text{KBr}(aq)$. The two samples have the same number of ions, but their motion is more limited and their energy less dispersed in the solid than in the solution.

(e) Seawater at 23°C . Entropy increases with rising temperature.

(f) 1 mol of $\text{CCl}_4(g)$. For similar compounds, entropy increases with molar mass.

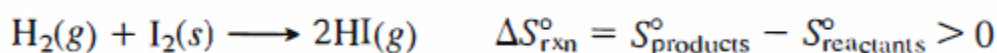
FOLLOW-UP PROBLEM 20.1 For 1 mol of substance at a given temperature, select the member in each pair with the higher entropy, and give the reason for your choice:

- (a) $\text{PCl}_3(g)$ or $\text{PCl}_5(g)$ (b) $\text{CaF}_2(s)$ or $\text{BaCl}_2(s)$ (c) $\text{Br}_2(g)$ or $\text{Br}_2(l)$

20.2 CALCULATING THE CHANGE IN ENTROPY OF A REACTION

Entropy Changes in the System: Standard Entropy of Reaction ($\Delta S^\circ_{\text{rxn}}$)

- In a chemical reaction involving gases, if the number of moles of gas increases, $\Delta S^\circ_{\text{rxn}}$ is usually positive; if the number decreases, $\Delta S^\circ_{\text{rxn}}$ is usually negative.



- We can combine S° values to find the standard entropy of reaction, $\Delta S^\circ_{\text{rxn}}$:

$$\Delta S^\circ_{\text{rxn}} = \sum m S^\circ_{\text{products}} - \sum n S^\circ_{\text{reactants}}$$

where m and n are the amounts (mol) of the individual species, given by their coefficients in the balanced equation.

For the formation of ammonia, we have

$$\Delta S^\circ_{\text{rxn}} = [(2 \text{ mol NH}_3)(S^\circ \text{ of NH}_3)] - [(1 \text{ mol N}_2)(S^\circ \text{ of N}_2) + (3 \text{ mol H}_2)(S^\circ \text{ of H}_2)]$$

$$\Delta S^\circ_{\text{rxn}} = [(2 \text{ mol})(193 \text{ J/mol}\cdot\text{K})] - [(1 \text{ mol})(191.5 \text{ J/mol}\cdot\text{K}) + (3 \text{ mol})(130.6 \text{ J/mol}\cdot\text{K})]$$

$$\Delta S^\circ_{\text{rxn}} = -197 \text{ J/K}$$

SAMPLE PROBLEM 20.2 Calculating the Standard Entropy of Reaction, $\Delta S^\circ_{\text{rxn}}$

Problem Calculate $\Delta S^\circ_{\text{rxn}}$ for the combustion of 1 mol of propane at 25°C:



Plan To determine $\Delta S^\circ_{\text{rxn}}$, we apply Equation 20.4. We predict the sign of $\Delta S^\circ_{\text{rxn}}$ from the change in the number of moles of gas: 6 mol of gas yields 3 mol of gas, so the entropy will probably decrease ($\Delta S^\circ_{\text{rxn}} < 0$).

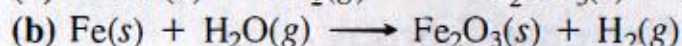
Solution Calculating $\Delta S^\circ_{\text{rxn}}$. Using Appendix B values,

$$\begin{aligned} \Delta S^\circ_{\text{rxn}} &= [(3 \text{ mol CO}_2)(S^\circ \text{ of CO}_2) + (4 \text{ mol H}_2\text{O})(S^\circ \text{ of H}_2\text{O})] \\ &\quad - [(1 \text{ mol C}_3\text{H}_8)(S^\circ \text{ of C}_3\text{H}_8) + (5 \text{ mol O}_2)(S^\circ \text{ of O}_2)] \\ &= [(3 \text{ mol})(213.7 \text{ J/mol}\cdot\text{K}) + (4 \text{ mol})(69.9 \text{ J/mol}\cdot\text{K})] \\ &\quad - [(1 \text{ mol})(269.9 \text{ J/mol}\cdot\text{K}) + (5 \text{ mol})(205.0 \text{ J/mol}\cdot\text{K})] \\ &= -374 \text{ J/K} \end{aligned}$$

Check $\Delta S^\circ < 0$, so our prediction is correct. Rounding gives $[3(200) + 4(70)] - [270 + 5(200)] = 880 - 1270 = -390$, close to the calculated value.

Comment Remember that when there is no change in the amount (mol) of gas, you *cannot* confidently predict the sign of $\Delta S^\circ_{\text{rxn}}$.

FOLLOW-UP PROBLEM 20.2 Balance the following equations, predict the sign of $\Delta S^\circ_{\text{rxn}}$ if possible, and calculate its value at 25°C:



Entropy Changes in the Surroundings: The Other Part of the Total

- The second law dictates that decreases in the entropy of the system can occur only if increases in the entropy of the surroundings outweigh them.
- The essential role of the surroundings is to either add heat to the system or remove heat from it. In essence, the surroundings function as an enormous heat source or heat sink, one so large that its temperature remains constant, even though its entropy changes through the loss or gain of heat.
- The surroundings participate in the two possible types of enthalpy changes as follows:

For an exothermic change: $q_{\text{sys}} < 0$, $q_{\text{surr}} > 0$, and $\Delta S_{\text{surr}} > 0$

For an endothermic change: $q_{\text{sys}} > 0$, $q_{\text{surr}} < 0$, and $\Delta S_{\text{surr}} < 0$

- The temperature of the surroundings at which the heat is transferred also affects ΔS_{surr} .

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

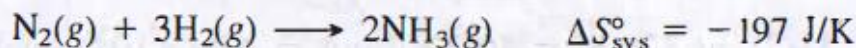
Recall that for a process at constant pressure, the heat (q_p) is ΔH , so

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

This means that we can calculate ΔS_{surr} by measuring ΔH_{sys} and the temperature T at which the change takes place.

SAMPLE PROBLEM 20.3 Determining Reaction Spontaneity

Problem At 298 K, the formation of ammonia has a negative $\Delta S_{\text{sys}}^{\circ}$:



Calculate ΔS_{univ} , and state whether the reaction occurs spontaneously at this temperature.

Plan For the reaction to occur spontaneously, $\Delta S_{\text{univ}} > 0$, and so ΔS_{surr} must be greater than $+197 \text{ J/K}$. To find ΔS_{surr} , we need $\Delta H_{\text{sys}}^{\circ}$, which is the same as $\Delta H_{\text{rxn}}^{\circ}$. We use ΔH_f° values from Appendix B to find $\Delta H_{\text{rxn}}^{\circ}$. Then, we use $\Delta H_{\text{rxn}}^{\circ}$ and the given T (298 K) to find ΔS_{surr} . To find ΔS_{univ} , we add the calculated ΔS_{surr} to the given $\Delta S_{\text{sys}}^{\circ}$ (-197 J/K).

Solution Calculating $\Delta H_{\text{sys}}^{\circ}$:

$$\begin{aligned} \Delta H_{\text{sys}}^{\circ} &= \Delta H_{\text{rxn}}^{\circ} \\ &= [(2 \text{ mol NH}_3)(-45.9 \text{ kJ/mol})] - [(3 \text{ mol H}_2)(0 \text{ kJ/mol}) + (1 \text{ mol N}_2)(0 \text{ kJ/mol})] \\ &= -91.8 \text{ kJ} \end{aligned}$$

Calculating ΔS_{surr} :

$$\Delta S_{\text{surr}} = -\frac{\Delta H_{\text{sys}}^{\circ}}{T} = -\frac{-91.8 \text{ kJ} \times \frac{1000 \text{ J}}{1 \text{ kJ}}}{298 \text{ K}} = 308 \text{ J/K}$$

Determining ΔS_{univ} :

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}}^{\circ} + \Delta S_{\text{surr}} = -197 \text{ J/K} + 308 \text{ J/K} = 111 \text{ J/K}$$

$\Delta S_{\text{univ}} > 0$, so the reaction occurs spontaneously at 298 K (see figure in margin).

Check Rounding to check the math, we have

$$\begin{aligned} \Delta H_{\text{rxn}}^{\circ} &\approx 2(-45 \text{ kJ}) = -90 \text{ kJ} \\ \Delta S_{\text{surr}} &\approx -(-90,000 \text{ J})/300 \text{ K} = 300 \text{ J/K} \\ \Delta S_{\text{univ}} &\approx -200 \text{ J/K} + 300 \text{ J/K} = 100 \text{ J/K} \end{aligned}$$

Given the negative $\Delta H_{\text{rxn}}^{\circ}$, Le Châtelier's principle predicts that low temperature should favor NH_3 formation, and so the answer is reasonable.

Comments 1. Note that ΔH° has units of kJ, whereas ΔS has units of J/K. Don't forget to convert kJ to J, or you'll introduce a large error.

2. This example highlights the distinction between thermodynamic and kinetic considerations. Even though NH_3 forms spontaneously, it does so slowly; in the industrial production of ammonia by the Haber process (Section 17.6), a catalyst is used to form NH_3 at a practical rate.

FOLLOW-UP PROBLEM 20.3 Does the oxidation of $\text{FeO}(\text{s})$ to $\text{Fe}_2\text{O}_3(\text{s})$ occur spontaneously at 298 K?

The Entropy Change and the Equilibrium State

- For a process spontaneously approaching equilibrium, $\Delta S_{\text{univ}} > 0$.
- When the process reaches equilibrium, $\Delta S_{\text{univ}} = 0$.

$$\text{At equilibrium: } \Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0 \quad \text{or} \quad \Delta S_{\text{sys}} = -\Delta S_{\text{surr}}$$

For example, let's calculate ΔS_{univ} for a phase change. For the vaporization-condensation of 1 mol of water at 100°C (373 K),



$$\begin{aligned} \Delta S_{\text{sys}}^{\circ} &= \sum m S_{\text{products}}^{\circ} - \sum n S_{\text{reactants}}^{\circ} = S^{\circ} \text{ of H}_2\text{O}(g; 373 \text{ K}) - S^{\circ} \text{ of H}_2\text{O}(l; 373 \text{ K}) \\ &= 195.9 \text{ J/K} - 86.8 \text{ J/K} = 109.1 \text{ J/K} \end{aligned}$$

$$\Delta S_{\text{surr}} = -\frac{\Delta H_{\text{sys}}^{\circ}}{T}$$

$$\Delta S_{\text{surr}} = -\frac{\Delta H_{\text{vap}}^{\circ}}{T} = -\frac{40.7 \times 10^3 \text{ J}}{373 \text{ K}} = -109 \text{ J/K}$$

$$\Delta S_{\text{univ}} = 109 \text{ J/K} + (-109 \text{ J/K}) = 0$$

For the reverse change (condensation), ΔS_{univ} also equals zero, but ΔS_{sys} and ΔS_{surr} have signs opposite those for vaporization. A similar treatment of a chemical change shows the same result: the entropy change of the forward reaction is equal in magnitude but opposite in sign to the entropy change of the reverse reaction.

Spontaneous Exothermic and Endothermic Reactions: A Summary

We can now see why exothermic and endothermic spontaneous reactions occur. No matter what its enthalpy change, a reaction occurs because the total entropy of the reacting system and its surroundings increases. The two possibilities are 1. For an exothermic reaction $\Delta H_{\text{sys}} < 0$, and $\Delta S_{\text{surr}} > 0$.

- ✓ If the reacting system yields products whose entropy is greater than that of the reactants ($\Delta S_{\text{sys}} > 0$), the total entropy change ($\Delta S_{\text{sys}} + \Delta S_{\text{surr}}$) will be positive

(Figure 20.9A).

- ✓ If, on the other hand, the entropy of the system decreases as the reaction occurs ($\Delta S_{\text{sys}} < 0$), the entropy of the surroundings must increase even more ($\Delta S_{\text{surr}} \gg 0$) to make the total ΔS positive (Figure 20.9B).

2. For an endothermic reaction $\Delta H_{\text{sys}} > 0$, and $\Delta S_{\text{surr}} < 0$. Therefore, the only way an endothermic reaction can occur spontaneously is if ΔS_{sys} is positive and large enough ($\Delta S_{\text{sys}} \gg 0$) to outweigh the negative ΔS_{surr} (Figure 20.9C).

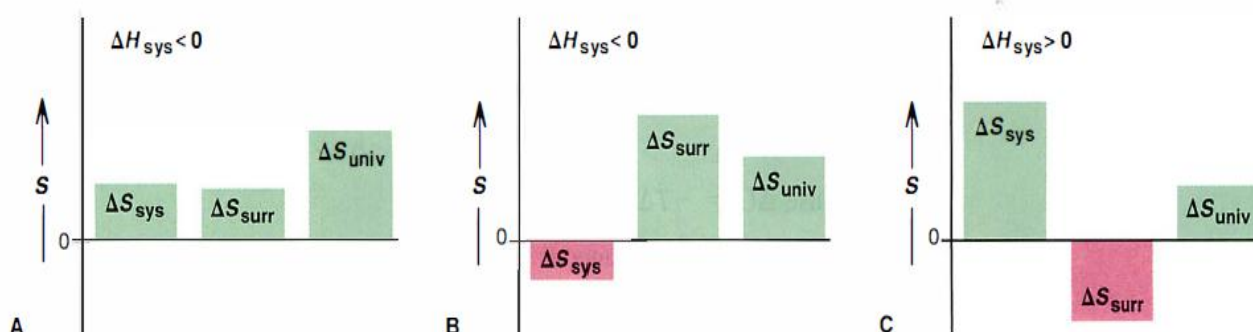


Figure 20.9 Components of ΔS_{univ} for spontaneous reactions. For a reaction to occur spontaneously, ΔS_{univ} must be positive. **A**, An exothermic reaction in which ΔS_{sys} increases; the size of ΔS_{surr} is not

important. **B**, An exothermic reaction in which ΔS_{sys} decreases; ΔS_{surr} must be larger than ΔS_{sys} . **C**, An endothermic reaction in which ΔS_{sys} increases; ΔS_{surr} must be smaller than ΔS_{sys} .

20.3 ENTROPY, FREE ENERGY, AND WORK

By making two separate measurements, ΔS_{sys} and ΔS_{surr} we can predict whether a reaction will be spontaneous at a particular temperature. It would be useful, however, to have one **criterion for spontaneity** that we can find by examining the system only. **The Gibbs free energy**, or simply free energy (**G**), is a function that combines the system's enthalpy and entropy:

$$G = H - TS$$

This function provides the criterion for spontaneity we've been seeking.

Free Energy Change and Reaction Spontaneity

The entropy change of the universe is the sum of the entropy changes of the system and the surroundings:

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

At constant pressure,

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

So:

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

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

From $G = H - TS$, the Gibbs equation shows us the change in the free energy of the system at constant temperature and pressure:

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

Combining this equation with the previous one shows that

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

- $\Delta S_{\text{univ}} > 0$ for a spontaneous process
- $\Delta S_{\text{univ}} < 0$ for a nonspontaneous process
- $\Delta S_{\text{univ}} = 0$ for a process at equilibrium
- $\Delta G < 0$ for a spontaneous process
- $\Delta G > 0$ for a nonspontaneous process
- $\Delta G = 0$ for a process at equilibrium

Calculating Standard Free Energy Changes

The Standard Free Energy Change As we did with the other thermodynamic variables, to compare the free energy changes of different reactions we calculate the standard free energy change (ΔG°), which occurs when all components of the system are in their standard states.

$$\Delta G_{\text{sys}}^\circ = \Delta H_{\text{sys}}^\circ - T\Delta S_{\text{sys}}^\circ$$

SAMPLE PROBLEM 20.4 Calculating $\Delta G_{\text{rxn}}^{\circ}$ from Enthalpy and Entropy Values

Problem Potassium chlorate, a common oxidizing agent in fireworks and matchheads, undergoes a solid-state disproportionation reaction when heated:



Use ΔH_f° and S° values to calculate $\Delta G_{\text{sys}}^{\circ}$ ($\Delta G_{\text{rxn}}^{\circ}$) at 25°C for this reaction.

Plan To solve for ΔG° , we need values from Appendix B. We use ΔH_f° values to calculate $\Delta H_{\text{rxn}}^{\circ}$ ($\Delta H_{\text{sys}}^{\circ}$), use S° values to calculate $\Delta S_{\text{rxn}}^{\circ}$ ($\Delta S_{\text{sys}}^{\circ}$), and then apply Equation 20.7.

Solution Calculating $\Delta H_{\text{sys}}^{\circ}$ from ΔH_f° values (with Equation 6.8):

$$\begin{aligned}\Delta H_{\text{sys}}^{\circ} &= \Delta H_{\text{rxn}}^{\circ} = \sum m\Delta H_f^{\circ}(\text{products}) - \sum n\Delta H_f^{\circ}(\text{reactants}) \\ &= [(3 \text{ mol KClO}_4)(\Delta H_f^{\circ} \text{ of KClO}_4) + (1 \text{ mol KCl})(\Delta H_f^{\circ} \text{ of KCl})] \\ &\quad - [(4 \text{ mol KClO}_3)(\Delta H_f^{\circ} \text{ of KClO}_3)] \\ &= [(3 \text{ mol})(-432.8 \text{ kJ/mol}) + (1 \text{ mol})(-436.7 \text{ kJ/mol})] \\ &\quad - [(4 \text{ mol})(-397.7 \text{ kJ/mol})] \\ &= -144 \text{ kJ}\end{aligned}$$

Calculating $\Delta S_{\text{sys}}^{\circ}$ from S° values (with Equation 20.4):

$$\begin{aligned}\Delta S_{\text{sys}}^{\circ} &= \Delta S_{\text{rxn}}^{\circ} = [(3 \text{ mol KClO}_4)(S^{\circ} \text{ of KClO}_4) + (1 \text{ mol KCl})(S^{\circ} \text{ of KCl})] \\ &\quad - [(4 \text{ mol KClO}_3)(S^{\circ} \text{ of KClO}_3)] \\ &= [(3 \text{ mol})(151.0 \text{ J/mol}\cdot\text{K}) + (1 \text{ mol})(82.6 \text{ J/mol}\cdot\text{K})] \\ &\quad - [(4 \text{ mol})(143.1 \text{ J/mol}\cdot\text{K})] \\ &= -36.8 \text{ J/K}\end{aligned}$$

Calculating $\Delta G_{\text{sys}}^{\circ}$ at 298 K:

$$\Delta G_{\text{sys}}^{\circ} = \Delta H_{\text{sys}}^{\circ} - T\Delta S_{\text{sys}}^{\circ} = -144 \text{ kJ} - \left[(298 \text{ K})(-36.8 \text{ J/K}) \left(\frac{1 \text{ kJ}}{1000 \text{ J}} \right) \right] = -133 \text{ kJ}$$

Check Rounding to check the math:

$$\Delta H^{\circ} \approx [3(-433 \text{ kJ}) + (-440 \text{ kJ})] - [4(-400 \text{ kJ})] = -1740 \text{ kJ} + 1600 \text{ kJ} = -140 \text{ kJ}$$

$$\Delta S^{\circ} \approx [3(150 \text{ J/K}) + 85 \text{ J/K}] - [4(145 \text{ J/K})] = 535 \text{ J/K} - 580 \text{ J/K} = -45 \text{ J/K}$$

$$\Delta G^{\circ} \approx -140 \text{ kJ} - 300 \text{ K}(-0.04 \text{ kJ/K}) = -140 \text{ kJ} + 12 \text{ kJ} = -128 \text{ kJ}$$

All values are close to the calculated ones.

Comments 1. For a spontaneous reaction under *any* conditions, the free energy change, ΔG , is negative. Under standard-state conditions, a spontaneous reaction has a negative *standard* free energy change; that is, $\Delta G^{\circ} < 0$.

2. This reaction is spontaneous, but the rate is very low in the solid. When KClO_3 is heated slightly above its melting point, the ions are free to move and the reaction occurs readily.

FOLLOW-UP PROBLEM 20.4 Determine the standard free energy change at 298 K for the reaction $2\text{NO}(g) + \text{O}_2(g) \longrightarrow 2\text{NO}_2(g)$.

The Standard Free Energy of Formation

- Another way to calculate $\Delta G^\circ_{\text{rxn}}$ is with values for the standard free energy of formation (ΔG_f°) of the components.
- ΔG_f° is the free energy change that occurs when 1 mol of compound is made from its elements, with all components in their standard states.

$$\Delta G^\circ_{\text{rxn}} = \sum m \Delta G_f^\circ(\text{products}) - \sum n \Delta G_f^\circ(\text{reactants})$$

- ΔG_f° of an element in its standard state is zero.
- An equation coefficient (m or n above) multiplies ΔG_f° by that number.
- Reversing a reaction changes the sign of ΔG_f° .

SAMPLE PROBLEM 20.5 Calculating $\Delta G^\circ_{\text{rxn}}$ from ΔG_f° Values

Problem Use ΔG_f° values to calculate $\Delta G^\circ_{\text{rxn}}$ for the reaction in Sample Problem 20.4:



Plan We apply Equation 20.8 to calculate $\Delta G^\circ_{\text{rxn}}$.

Solution

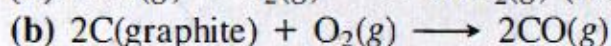
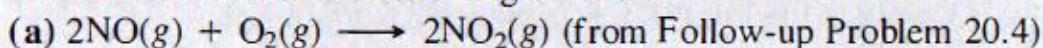
$$\begin{aligned} \Delta G^\circ_{\text{rxn}} &= \sum m \Delta G_f^\circ(\text{products}) - \sum n \Delta G_f^\circ(\text{reactants}) \\ &= [(3 \text{ mol KClO}_4)(\Delta G_f^\circ \text{ of KClO}_4) + (1 \text{ mol KCl})(\Delta G_f^\circ \text{ of KCl})] \\ &\quad - [(4 \text{ mol KClO}_3)(\Delta G_f^\circ \text{ of KClO}_3)] \\ &= [(3 \text{ mol})(-303.2 \text{ kJ/mol}) + (1 \text{ mol})(-409.2 \text{ kJ/mol})] \\ &\quad - [(4 \text{ mol})(-296.3 \text{ kJ/mol})] \\ &= -134 \text{ kJ} \end{aligned}$$

Check Rounding to check the math:

$$\begin{aligned} \Delta G^\circ_{\text{rxn}} &\approx [3(-300 \text{ kJ}) + 1(-400 \text{ kJ})] - 4(-300 \text{ kJ}) \\ &= -1300 \text{ kJ} + 1200 \text{ kJ} = -100 \text{ kJ} \end{aligned}$$

Comment The slight discrepancy between this answer and that obtained in Sample Problem 20.4 is within experimental error. As you can see, when ΔG_f° values are available for a reaction taking place at 25°C, this method is simpler than that in Sample Problem 20.4.

FOLLOW-UP PROBLEM 20.5 Use ΔG_f° values to calculate the free energy change at 25°C for each of the following reactions:



ΔG and the Work a System Can Do

- For a spontaneous process ($\Delta G < 0$) at constant T and P, ΔG is the maximum useful work obtainable from the system ($-w$) as the process takes place:

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

- For a nonspontaneous process ($\Delta G > 0$) at constant T and P, ΔG is the minimum work that must be done to the system to make the process take place.
- The system actually does depends on **how** the free energy is released. Suppose an expanding gas does work by lifting an object. The maximum work could be done only in an infinite number of steps; that is, the maximum work is done by a spontaneous process only if it is carried out **reversibly**.
- In any real process, work is done irreversibly-in a finite number of steps-so we can never obtain the maximum work. The free energy not used for work is lost as heat.

Consider the work done by a battery, a packaged spontaneous redox reaction that releases free energy to the surroundings (flashlight, radio, motor, or other device).

- ✓ If we connect the battery terminals to each other through a short piece of wire, ΔG_{sys} is released all at once but does no work, it just heats the wire and battery and outside air, which increases the freedom of motion of the particles in the universe.
- ✓ If we connect the battery terminals to a motor, ΔG_{sys} is released more slowly, and much of it runs the motor; however, some is still lost as heat.
- ✓ Only if a battery could discharge infinitely slowly could we obtain the maximum work.

The Effect of Temperature on Reaction Spontaneity

The temperature of a reaction influences the magnitude of the $T\Delta S$ term, so, for many reactions, the overall spontaneity depends on the temperature. By scrutinizing the signs of ΔH and ΔS , we can predict the effect of temperature on the sign of ΔG .

Temperature-independent cases. When ΔH and ΔS have opposite signs, the reaction occurs spontaneously either at all temperatures or at none.

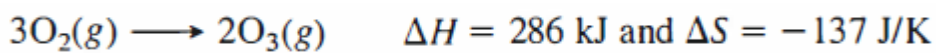
1. Reaction is spontaneous at all temperatures: $\Delta H < 0$, $\Delta S > 0$.

Most combustion reactions are in this category. The decomposition of hydrogen peroxide, a common disinfectant, is also spontaneous at all temperatures:



2. Reaction is nonspontaneous at all temperatures: $\Delta H > 0$, $\Delta S < 0$.

The formation of ozone from oxygen is not spontaneous at any temperature:



Temperature-dependent cases. When ΔH and ΔS have the same sign, the relative magnitudes of the $-T\Delta S$ and ΔH terms determine the sign of ΔG .

3. Reaction is spontaneous at higher temperatures: $\Delta H > 0$ and $\Delta S > 0$. Here, ΔS favors spontaneity ($-T\Delta S < 0$), but ΔH does not. For example,



The oxidation of N_2O occurs spontaneously at $T > 994 \text{ K}$.

4. Reaction is spontaneous at lower temperatures: $\Delta H < 0$ and $\Delta S < 0$. Now, ΔH favors spontaneity, but ΔS does not ($-T\Delta S > 0$). For example,



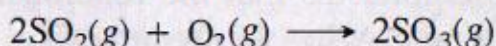
The production of iron(III) oxide occurs spontaneously at any $T < 3005 \text{ K}$.

Table 20.1 Reaction Spontaneity and the Signs of ΔH , ΔS , and ΔG

ΔH	ΔS	$-T\Delta S$	ΔG	Description
–	+	–	–	Spontaneous at all T
+	–	+	+	Nonspontaneous at all T
+	+	–	+ or –	Spontaneous at higher T ; nonspontaneous at lower T
–	–	+	+ or –	Spontaneous at lower T ; nonspontaneous at higher T

SAMPLE PROBLEM 20.6 Determining the Effect of Temperature on ΔG

Problem A key step in the production of sulfuric acid is the oxidation of $\text{SO}_2(g)$ to $\text{SO}_3(g)$:



At 298 K, $\Delta G = -141.6$ kJ; $\Delta H = -198.4$ kJ; and $\Delta S = -187.9$ J/K.

(a) Use the data to decide if this reaction is spontaneous at 25°C , and predict how ΔG will change with increasing T .

(b) Assuming that ΔH and ΔS are constant with T , is the reaction spontaneous at $900.^\circ\text{C}$?

Plan (a) We note the sign of ΔG to see if the reaction is spontaneous and the signs of ΔH and ΔS to see the effect of T . (b) We use Equation 20.6 to calculate ΔG from the given ΔH and ΔS at the higher T (in K).

Solution (a) $\Delta G < 0$, so the reaction is spontaneous at 298 K: SO_2 and O_2 will form SO_3 spontaneously. With $\Delta S < 0$, the term $-T\Delta S > 0$, and this term will become more positive at higher T . Therefore,

ΔG will become less negative, and the reaction less spontaneous, with increasing T .

(b) Calculating ΔG at $900.^\circ\text{C}$ ($T = 273 + 900. = 1173$ K):

$$\Delta G = \Delta H - T\Delta S = -198.4 \text{ kJ} - [(1173 \text{ K})(-187.9 \text{ J/K})(1 \text{ kJ}/1000 \text{ J})] = 22.0 \text{ kJ}$$

$\Delta G > 0$, so the reaction is nonspontaneous at the higher T .

Check The answer in part (b) seems reasonable based on our prediction in part (a). The arithmetic seems correct, given considerable rounding:

$$\Delta G \approx -200 \text{ kJ} - [(1200 \text{ K})(-200 \text{ J/K})/1000 \text{ J}] = +40 \text{ kJ}$$

FOLLOW-UP PROBLEM 20.6 A reaction is nonspontaneous at room temperature but is spontaneous at -40°C . What can you say about the signs and relative magnitudes of ΔH , ΔS , and $-T\Delta S$?

The Temperature at Which a Reaction Becomes Spontaneous

It would certainly be useful to know the temperature at which a reaction becomes spontaneous. This is the temperature at which a positive ΔG switches to a negative ΔG because of the changing magnitude of the $-T\Delta S$ term.

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

$$\Delta H = T\Delta S \quad \text{and} \quad T = \frac{\Delta H}{\Delta S}$$

Consider the reaction of copper(I) oxide with carbon:

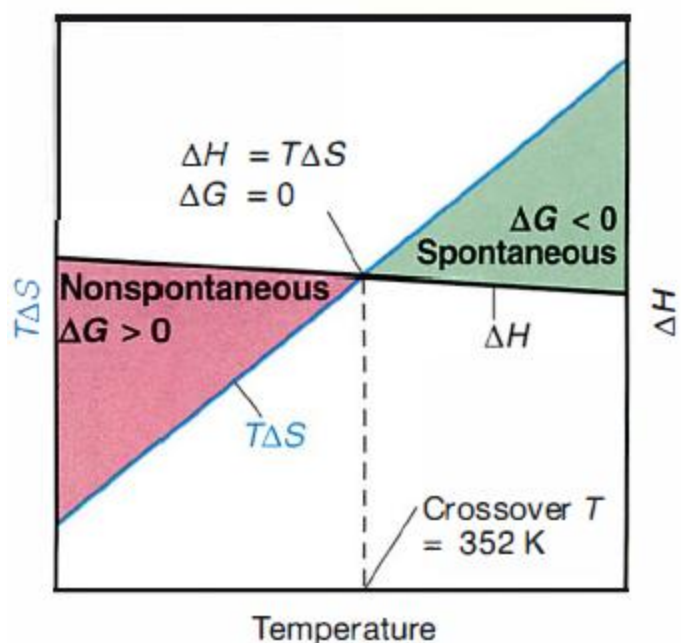


$\Delta S = 165 \text{ J/K}$, $\Delta H = 58.1 \text{ kJ}$. At the crossover temperature, $\Delta G = 0$, so

$$T = \frac{\Delta H}{\Delta S} = \frac{58.1 \text{ kJ} \times \frac{1000 \text{ J}}{1 \text{ kJ}}}{165 \text{ J/K}} = 352 \text{ K}$$

At any temperature above 352 K (79°C), the reaction occurs spontaneously.

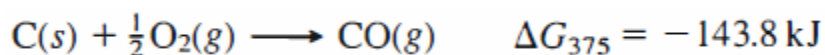
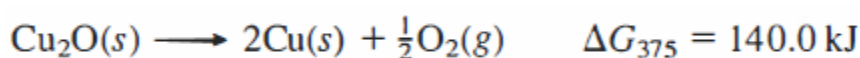
Figure 20.10 The effect of temperature on reaction spontaneity. The two terms that make up ΔG are plotted against T . The figure shows a relatively constant ΔH and a steadily increasing $T\Delta S$ (and thus more negative $-T\Delta S$) for the reaction between Cu_2O and C . At low T , the reaction is nonspontaneous ($\Delta G > 0$) because the positive ΔH term has a greater magnitude than the negative $T\Delta S$ term. At 352 K, $\Delta H = T\Delta S$, so $\Delta G = 0$. At any higher T , the reaction becomes spontaneous ($\Delta G < 0$) because the $-T\Delta S$ term dominates.



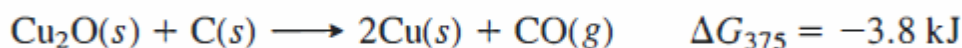
Coupling of Reactions to Drive a Nonspontaneous Change

When studying a multistep reaction, chemists often find that a nonspontaneous step is driven by a spontaneous step in a coupling of reactions.

- Look again at the reaction of copper(I) oxide with carbon. Previously, we found that the overall reaction becomes spontaneous above 352 K. Dividing the reaction into two steps, we find that, even at the slightly higher temperature of 375 K, decomposition of copper(I) oxide to its elements is not spontaneous:



Coupling these reactions allows the reaction with the larger negative ΔG to "drive" the one with the smaller positive ΔG .



- Many biochemical processes-including the syntheses of proteins, nucleic acids, and fatty acids have nonspontaneous steps. Coupling these steps to spontaneous ones is a life-sustaining strategy that is common to all organisms.

20.4 FREE ENERGY, EQUILIBRIUM, AND REACTION DIRECTION

The sign of ΔG allows us to predict reaction direction, and this can be related with the values of the reaction quotient (Q) and the equilibrium constant (K);

- If $Q/K < 1$, then $\ln Q/K < 0$: reaction proceeds to the right ($\Delta G < 0$).
- If $Q/K > 1$, then $\ln Q/K > 0$: reaction proceeds to the left ($\Delta G > 0$).
- If $Q/K = 1$, then $\ln Q/K = 0$: reaction is at equilibrium ($\Delta G = 0$).

In fact, ΔG and $\ln Q/K$ are proportional to each other and made equal through the constant RT :

$$\Delta G = RT \ln \frac{Q}{K} = RT \ln Q - RT \ln K$$

The equation says that ΔG depends on how different the ratio of concentrations, Q , is from the equilibrium ratio, K . By choosing standard-state values for Q , we obtain the standard free energy change (ΔG°). When all concentrations are 1 M (or all pressures 1 atm), ΔG equals ΔG° and Q equals 1:

$$\Delta G^\circ = RT \ln 1 - RT \ln K$$

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

This relationship allows us to calculate the standard free energy change of a reaction (ΔG°) from its equilibrium constant, or vice versa.

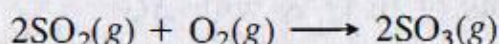
Table 20.2 shows the K values that correspond to a range of ΔG° values.

Of course, reactions do not usually begin with all components in their standard states. By substituting the relationship between ΔG° and K into the expression for ΔG , we obtain a relationship that applies to any starting concentrations:

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

Table 20.2 The Relationship Between ΔG° and K at 298 K

ΔG° (kJ)	K	Significance
200	9×10^{-36}	Essentially no forward reaction; reverse reaction goes to completion
100	3×10^{-18}	
50	2×10^{-9}	
10	2×10^{-2}	
1	7×10^{-1}	
0	1	Forward and reverse reactions proceed to same extent
-1	1.5	
-10	5×10^1	
-50	6×10^8	Forward reaction goes to completion; essentially no reverse reaction
-100	3×10^{17}	
-200	1×10^{35}	

SAMPLE PROBLEM 20.7 Calculating ΔG at Nonstandard Conditions**Problem** The oxidation of SO_2 , which we considered in Sample Problem 20.6,

is too slow at 298 K to be useful in the manufacture of sulfuric acid. To overcome this low rate, the process is conducted at an elevated temperature.

(a) Calculate K at 298 K and at 973 K. ($\Delta G_{298}^\circ = -141.6$ kJ/mol for reaction as written; using ΔH° and ΔS° values at 973 K, $\Delta G_{973}^\circ = -12.12$ kJ/mol for reaction as written.)

(b) In experiments to determine the effect of temperature on reaction spontaneity, two sealed containers are filled with 0.500 atm of SO_2 , 0.0100 atm of O_2 , and 0.100 atm of SO_3 and kept at 25°C and at 700°C. In which direction, if any, will the reaction proceed to reach equilibrium at each temperature?

(c) Calculate ΔG for the system in part (b) at each temperature.

Plan (a) We know ΔG° , T , and R , so we can calculate the K 's from Equation 20.12.

(b) To determine if a net reaction will occur at the given pressures, we calculate Q with the given partial pressures and compare it with each K from part (a). (c) Because these are not standard-state pressures, we calculate ΔG at each T from Equation 20.13 with the values of ΔG° (given) and Q [found in part (b)].

Solution (a) Calculating K at the two temperatures:

$$\Delta G^\circ = -RT \ln K \quad \text{so} \quad K = e^{-(\Delta G^\circ/RT)}$$

At 298 K, the exponent is

$$-(\Delta G^\circ/RT) = -\left(\frac{-141.6 \text{ kJ/mol} \times \frac{1000 \text{ J}}{1 \text{ kJ}}}{8.314 \text{ J/mol}\cdot\text{K} \times 298 \text{ K}}\right) = 57.2$$

So

$$K = e^{-(\Delta G^\circ/RT)} = e^{57.2} = 7 \times 10^{24}$$

At 973 K, the exponent is

$$-(\Delta G^\circ/RT) = -\left(\frac{-12.12 \text{ kJ/mol} \times \frac{1000 \text{ J}}{1 \text{ kJ}}}{8.314 \text{ J/mol}\cdot\text{K} \times 973 \text{ K}}\right) = 1.50$$

So

$$K = e^{-(\Delta G^\circ/RT)} = e^{1.50} = 4.5$$

(b) Calculating the value of Q :

$$Q = \frac{P_{\text{SO}_3}^2}{P_{\text{SO}_2}^2 \times P_{\text{O}_2}} = \frac{0.100^2}{0.500^2 \times 0.0100} = 4.00$$

Because $Q < K$ at both temperatures, the denominator will decrease and the numerator increase—more SO_3 will form—until Q equals K . However, the reaction will go far to the right at 298 K while approaching equilibrium, whereas it will move only slightly to the right at 973 K.

(c) Calculating ΔG , the nonstandard free energy change, at 298 K:

$$\Delta G_{298} = \Delta G^\circ + RT \ln Q$$

$$\begin{aligned}
 &= -141.6 \text{ kJ/mol} + \left(8.314 \text{ J/mol}\cdot\text{K} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \times 298 \text{ K} \times \ln 4.00 \right) \\
 &= -138.2 \text{ kJ/mol}
 \end{aligned}$$

Calculating ΔG at 973 K:

$$\begin{aligned}
 \Delta G_{973} &= \Delta G^\circ + RT \ln Q \\
 &= -12.12 \text{ kJ/mol} + \left(8.314 \text{ J/mol}\cdot\text{K} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \times 973 \text{ K} \times \ln 4.00 \right) \\
 &= -0.9 \text{ kJ/mol}
 \end{aligned}$$

Check Note that in parts (a) and (c) we made the energy units in free energy changes (kJ) consistent with those in R (J). Based on the rules for significant figures in addition and subtraction, we retain one digit to the right of the decimal place in part (c).

Comment For these starting gas pressures at 973 K, the process is barely spontaneous ($\Delta G = -0.9 \text{ kJ/mol}$), so why use a higher temperature? Like the synthesis of NH_3 (Section 17.6), this process is carried out at a higher temperature *with a catalyst* to attain a higher *rate*, even though the *yield* is greater at a lower temperature.

FOLLOW-UP PROBLEM 20.7 At 298 K, hypobromous acid (HBrO) dissociates in water with a K_a of 2.3×10^{-9} .

(a) Calculate ΔG° for the dissociation of HBrO .

(b) Calculate ΔG if $[\text{H}_3\text{O}^+] = 6.0 \times 10^{-4} \text{ M}$, $[\text{BrO}^-] = 0.10 \text{ M}$, and $[\text{HBrO}] = 0.20 \text{ M}$.

Another Look at the Meaning of Spontaneity

Consider the general reaction $\text{A} \leftrightarrow \text{B}$, for which $K = [\text{B}] / [\text{A}] > 1$; therefore, the reaction proceeds largely from left to right (Figure 20.12 A).

- From pure A to the equilibrium point, $Q < K$ and the curved green arrow indicates the reaction is spontaneous ($\Delta G < 0$). From there on, the curved red arrow shows the reaction is nonspontaneous ($\Delta G > 0$).
- From pure B to the equilibrium point, $Q > K$ and the reaction is also spontaneous ($\Delta G < 0$), but not thereafter.
- In either case, **the free energy decreases as the reaction proceeds, until it reaches a minimum at the equilibrium mixture: $Q = K$ and $\Delta G = 0$.**
- For the overall reaction $\text{A} \leftrightarrow \text{B}$ (starting with all components in their standard states), $G^\circ_{\text{B}} < G^\circ_{\text{A}}$, so ΔG° is negative, which corresponds to $K > 1$. We call

this a *product favored reaction* because the final state of the system contains mostly product.

Now consider the opposite situation, a general reaction $C \leftrightarrow D$, for which $K = [D]/[C] < 1$: the reaction proceeds only slightly from left to right (Figure 20.12B).

- Here, too, whether we start with pure C or pure D, the reaction is spontaneous ($\Delta G < 0$) until the equilibrium point. But here, the equilibrium mixture contains mostly C (the reactant), so we say the reaction is *reactant favored*. In this case, $G_D^\circ > G_C^\circ$, so ΔG° is positive, which corresponds to $K < 1$.

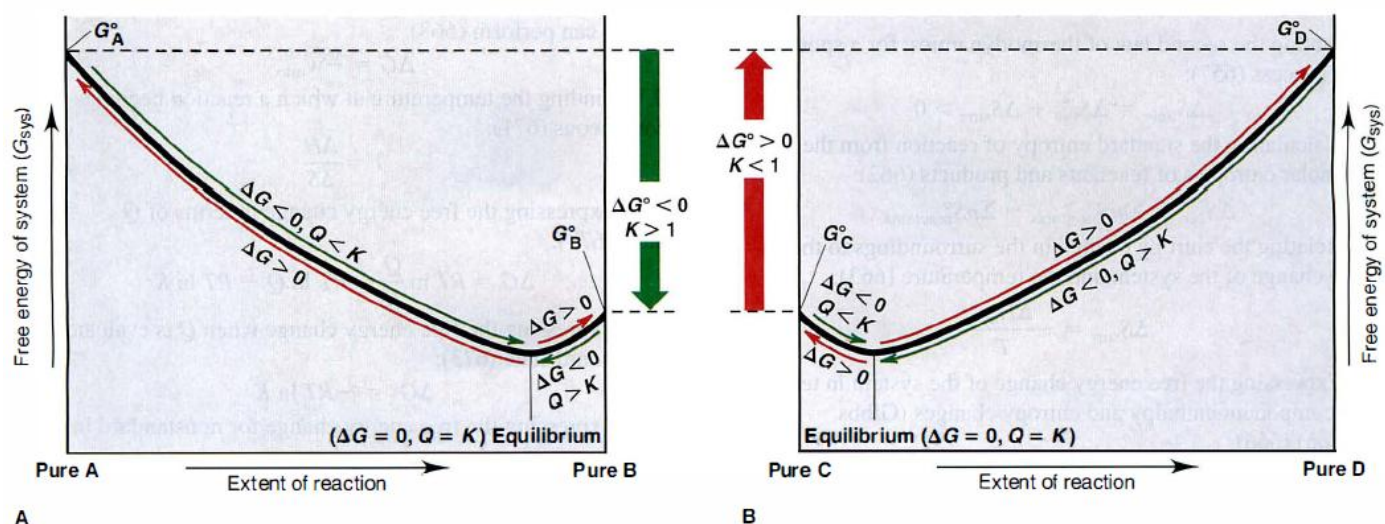


Figure 20.12 The relation between free energy and the extent of reaction. The free energy of the system is plotted against the extent of reaction. Each reaction proceeds spontaneously ($Q \neq K$ and $\Delta G < 0$; curved green arrows) from either pure reactants (A or C) or pure products (B or D) to the equilibrium mixture, at which point $\Delta G = 0$. The reaction from the equilibrium mixture to either pure reactants or products is nonspontaneous ($\Delta G > 0$; curved red arrows). A, For the product-favored reaction $A \leftrightarrow B$, $G_A^\circ > G_B^\circ$, so $\Delta G^\circ < 0$ and $K > 1$. B, For the reactant-favored reaction $C \leftrightarrow D$, $G_D^\circ > G_C^\circ$, so $\Delta G^\circ > 0$ and $K < 1$.