## Thermodynamics and Equilibrium

## Section Preview/ Specific Expectations

In this section, you will

- identify qualitatively entropy changes that are associated with physical and chemical processes
- describe how reactions have a tendency to achieve minimum energy and maximum entropy
- explain the effect of changes in enthalpy, entropy, and temperature on a chemical reaction
- communicate your understanding of the following terms: favourable change, entropy (S), second law of thermodynamics, free energy

Figure 7.4 A favourable endothermic reaction occurs when barium hydroxide is mixed with ammonium thiocyanate. If you removed the stopper in photograph (B), you would detect the characteristic odour of ammonia.

You can easily predict what will happen in a number of physical and chemical processes. What will happen if you let go of a pencil that you are holding tip-down on a table? What will you observe if you add a few drops of food colouring to some water in a glass? If a piece of paper starts to burn in a plentiful supply of air, what are the products of the reaction? How will an iron nail change if it is left outside? These are all examples of favourable (or spontaneous) changes. A favourable change is a change that has a natural tendency to happen under certain conditions.

## What Conditions Favour a Change?

What conditions determine whether or not a change is favourable? How are different conditions related to equilibrium, where forward and reverse changes occur at the same rate? The answers to these questions are linked to two important concepts in thermodynamics: enthalpy and entropy.

## Enthalpy and Favourable Changes

Energy is a key condition in favourable changes. For example, you know that a ball always rolls downhill. Its gravitational potential energy is lower at the bottom of the hill than at the top. For the ball to roll uphillan unfavourable (or non-spontaneous) change-you have to apply energy to the ball. Chemical reactions are similar. When products have less enthalpy than reactants, the reaction releases energy. Therefore, the reaction is exothermic. Are favourable changes those that are exothermic under certain conditions?

Certainly many favourable physical and chemical changes are exothermic. Some favourable changes, however, involve no release of energy. Others are actually endothermic. For example, a favourable endothermic chemical reaction occurs when barium hydroxide and ammonium thiocyanate are placed in an Erlenmeyer flask, as shown in Figure 7.4.

$$
\begin{array}{r}
\mathrm{Ba}(\mathrm{OH})_{2} \cdot 8 \mathrm{H}_{2} \mathrm{O}_{(\mathrm{s})}+2 \mathrm{NH}_{4} \mathrm{SCN}_{(\mathrm{s})} \rightarrow \mathrm{Ba}(\mathrm{SCN})_{2(\mathrm{aq})}+10 \mathrm{H}_{2} \mathrm{O}_{(\ell)}+2 \mathrm{NH}_{3(\mathrm{~g})} \\
\Delta H=+170 \mathrm{~kJ}
\end{array}
$$

When the flask is stoppered and the contents are shaken, the solids intermingle. The reaction produces a slush-like mixture. This favourable, but endothermic, reaction absorbs enough energy to freeze a thin layer of water under the flask.


## Temperature and Favourable Changes

Another condition that determines whether or not a particular reaction is favoured is temperature. Consider the reversible synthesis reaction between mercury and oxygen, and the decomposition of mercury(II) oxide.

$$
\mathrm{Hg}_{(\ell)}+\frac{1}{2} \mathrm{O}_{2(\mathrm{~g})} \rightleftharpoons \mathrm{HgO}_{(\mathrm{s})} \quad \Delta H= \pm 90.8 \mathrm{~kJ}
$$

From left to right, the reaction is exothermic. Therefore, the enthalpy change, $\Delta H$, is negative. If the enthalpy change was the only condition that determined whether a reaction is favourable, then the synthesis reaction would take place. The synthesis reaction does take place-but only at relatively moderate temperatures. Above $400^{\circ} \mathrm{C}$, the reverse reaction is favourable. The decomposition of $\mathrm{HgO}_{(s)}$ occurs. Thus, the direction in which this reaction proceeds depends on temperature. This is fundamentally different from the dependence of reaction rate on temperature that you learned about in Unit 3. The reaction between $\mathrm{Hg}_{(\ell)}, \mathrm{O}_{2(\mathrm{~g})}$, and $\mathrm{HgO}_{(\mathrm{s})}$ does not just change its rate with a change in temperature, it changes its direction.

## Temperature and Enthalpy Alone

## Cannot Explain Favourable Reactions

Temperature and enthalpy are not the only conditions that determine whether a change is favourable. Consider the process shown in Figure 7.5. A closed valve links two flasks together. The left flask contains an ideal gas. The right flask is evacuated. When the valve is opened, you expect the gas to diffuse into the evacuated flask until the pressure in both flasks is equal. You do not expect to see the reverse process-with all the gas molecules ending up in one of the flasks-unless work is done on the system.


Figure 7.5 If the gas is ideal, this favourable change involves no change in energy. Why must the gas be ideal?

The process shown in Figure 7.5 is certainly a favourable change. Yet no exchange of energy is involved. The condition that influences this change is called entropy. It is an important condition in all physical and chemical changes.

## Entropy and Favourable Changes

Entropy, $\boldsymbol{S}$, is the tendency toward randomness or disorder in a system. It is also a thermodynamic property that can be measured. It can be used to describe qualitative changes in energy.

An ordered arrangement of particles (atoms, ions, or molecules) has lower entropy (smaller disorder) than the same number of particles in random arrangements. Thus, the entropy of a pure substance depends on its state. The entropy of a system increases (becomes more disordered) with temperature, because the motion of particles becomes more chaotic at higher temperatures. See Figure 7.6 on the next page.


Figure 7.6 The entropy of the particles in a sample of matter increases as the matter changes state from solid to liquid to gas.

The mathematical definition of entropy describes the probability of a given arrangement of particles. A system of moving particles with low entropy probably has greater order than a similar system with higher entropy. Why say "probably"? Consider gas molecules in a container at room temperature. The gas molecules are moving rapidly, colliding with other molecules and the walls of the container. They have relatively large entropy. What if two different gases occupy the same container? It is possible, in principle, for the gases to separate so they are on opposite sides of the container. Given the huge number of particles, however, the probability of this happening is so close to zero that chemists say it will never happen. Nevertheless, it remains possible. The outcome is not certain.

As you know from Unit 3, chemists often use the terms "system" and "surroundings" to describe a chemical reaction. The system is the reaction itself-the reactants and products. The surroundings are everything else in the universe. According to the first law of thermodynamics (the law of conservation of energy) the algebraic sum of the energy changes in a system and its surroundings is zero. Unlike energy, entropy is not conserved. The total amount of entropy is increasing. This is part of the second law of thermodynamics: the total entropy of the universe is constantly increasing. The key word here is "total." If you are studying a system, you must add together changes in the entropy of the system, $\Delta S_{\text {sys }}$, and changes in the entropy of the surroundings, $\Delta S_{\text {surr }}$.

Consider what happens to you and your classmates (the particles in a "system") on your way to class. Initially, you and your classmates are in different places in the school, walking with different velocities toward the classroom. Going to class represents a relatively large amount of entropy. The final state of the system, when everyone is seated, represents a
smaller amount of entropy. Thus, the entropy of the system decreased. How, then, did the entropy of the universe increase?

The answer to this question involves changes to the surroundings. Each of you, on your way to class, metabolized energy. The movement and heat from your bodies added to the entropy of the air particles around you. In fact, the increase in the entropy of the surroundings was greater than the decrease in the entropy of the system. Therefore, the total entropy of the universe increased.

What does entropy have to do with favourable chemical changes and equilibrium systems? All favourable changes involve an increase in the total amount of entropy. Recall the endothermic reaction in Figure 7.4.
$\mathrm{Ba}(\mathrm{OH})_{2} \cdot 8 \mathrm{H}_{2} \mathrm{O}_{(\mathrm{s})}+2 \mathrm{NH}_{4} \mathrm{SCN}_{(\mathrm{s})} \rightarrow \mathrm{Ba}(\mathrm{SCN})_{2(\mathrm{aq})}+10 \mathrm{H}_{2} \mathrm{O}_{(\ell)}+2 \mathrm{NH}_{3(\mathrm{~g})}$ $\Delta H=+170 \mathrm{~kJ}$
The reaction is favourable, partly because the reactants are two solids and the products are a solution, water, and a gas. The products have a much larger entropy than the reactants. This helps to make the reaction favourable.

Now recall the reaction between mercury and oxygen. It favours the formation of HgO below about $400^{\circ} \mathrm{C}$, but the decomposition of HgO above $400^{\circ} \mathrm{C}$. This reaction highlights the importance of temperature to favourable change. Enthalpy, entropy, and temperature are linked in a concept called free energy.

## Free Energy and Equilibrium

Imagine a perfect engine-an engine without any friction between its moving parts. This engine would still be unable to convert all the energy in a fuel into useful work. The reason is that some energy, such as the energy of the hot exhaust, is used to increase the entropy of the surroundings. The term free energy means available energy. In a chemical change, free energy is a measure of the useful work that can be obtained from a reaction. Free energy is often called Gibbs free energy, and given the symbol $G$, in honour of Josiah Willard Gibbs (1839-1903). Gibbs, a professor of chemistry at Harvard University, developed the concept of free energy and the equations that describe it.

The change in the free energy of a system, $\Delta G$, at constant temperature is given by the equation $\Delta G=\Delta H-T \Delta S$. In this equation, as in most chemistry equations, the temperature, $T$, must be in Kelvin degrees. The symbol $\Delta H$ represents the change in enthalpy. The symbol $\Delta S$ represents the change in entropy.


The value of $\Delta G$ for a chemical reaction tells us whether the reaction is a source of useful energy. Such energy can be converted into another form, such as mechanical energy to drive machinery or electrical energy in a battery. The rest of the energy from the reaction enters the environment as heat. It increases the entropy of the surroundings.

## Biology <br> LINK

The concept of free energy appears in other areas of science, notably biology. Find out the meanings of the terms "exergonic" and "endergonic." How are these terms related to free energy?

The equation $\Delta G=\Delta H-T \Delta S$, and the sign of $\Delta G$, can help to explain why some chemical reactions are favourable at room temperature, why others are not, and how temperature affects the direction of a reaction. The change in the free energy of a chemical reaction is related to the direction of the reaction and to equilibrium as follows:

- When $\Delta G$ is negative, the forward reaction is favourable.
- When $\Delta G$ is zero, the reaction is at equilibrium.
- When $\Delta G$ is positive, the reaction is favourable in the reverse direction but not in the forward direction.

Exothermic reactions are often favourable because the sign of $\Delta H$ is negative. The equation shows that exothermic reactions are unfavourable only when $\Delta S$ is negative and the value of $-T \Delta S$ is large enough to make $\Delta G$ positive. This is what happens in the reaction between mercury and oxygen.

$$
\mathrm{Hg}_{(\ell)}+\frac{1}{2} \mathrm{O}_{2(\mathrm{~g})} \rightarrow \mathrm{HgO}_{(\mathrm{s})} \quad \Delta H=-90.8 \mathrm{~kJ}
$$

From left to right, the reaction is exothermic. There is a decrease in entropy because gas molecules react to form a solid. At temperatures greater than about $400^{\circ} \mathrm{C}(673 \mathrm{~K})$, the value of $-T \Delta S$ is positive and greater than 90.8 kJ . Thus, $\Delta G$ becomes positive. The forward reaction is no longer favourable, as experiments confirm.

In most reactions, the entropy of the system increases ( $S$ is positive), so the value of $-T \Delta S$ is negative. Therefore, most reactions tend to be more favourable at higher temperatures. At low temperatures, reactions are likely to be favourable only if they are highly exothermic.

## Section Summary

Table 7.1 shows how you can use the signs of $\Delta H$ and $\Delta S$ to determine whether a chemical reaction is favourable. It also shows how $\Delta H$ and $\Delta S$ may vary with temperature. Keep in mind that a favourable reaction may be fast or slow. Thermodynamics makes no prediction about the rate of a reaction, only whether or not it can take place. Also, before any reaction begins, the activation energy must be supplied.
Table 7.1 How the Signs of $\Delta H$ and $\Delta S$ Affect the Favourability of a Reaction

| $\Delta \boldsymbol{H}$ | $\Delta \boldsymbol{S}$ | $-\boldsymbol{T} \Delta \boldsymbol{S}$ | Comments and examples |
| :---: | :---: | :---: | :--- |
| - | + | - | Both $\Delta H$ and $\Delta S$ favour the reaction. The <br> reaction is favourable at all temperatures. <br> Example: $\mathrm{OO}_{3(\mathrm{~g})} \rightarrow 3 \mathrm{O}_{2(\mathrm{~g})}$ |
| + | - | + | Neither $\Delta H$ nor $\Delta S$ favours the reaction. The <br> reaction is unfavourable at all temperatures. <br> Example: $3 \mathrm{O}_{2(\mathrm{~g})} \rightarrow 2 \mathrm{O}_{3(\mathrm{~g})}$ |
| - | - | + | $\Delta H$ is favourable, but $\Delta S$ is not. The reaction <br> is likely to be favourable at relatively <br> low temperatures. <br> Example: $\mathrm{Hg}_{(\ell)}+\frac{1}{2} \mathrm{O}_{2(\mathrm{~g})} \rightarrow \mathrm{HgO}_{(\mathrm{s})}$ |
| + | + | - | $\Delta S$ is favourable, but $\Delta H$ is not. The reaction <br> is likely to be favourable at higher temperatures. <br> Example: $\mathrm{HgO}_{(\mathrm{s})} \rightarrow \mathrm{Hg}_{(\ell)}+\frac{1}{2} \mathrm{O}_{2(\mathrm{~g})}$ |

Note that the entropy of a system cannot increase forever. Eventually, a maximum state of disorder is reached. When this happens, the system appears to have constant properties, even though changes are still taking place at the molecular level. We say that a chemical system is at equilibrium when it has constant observable properties. Therefore, equilibrium occurs when a system has reached its maximum entropy. In the next section, you will look more closely at the reactants and products of chemical systems and learn how equilibrium is measured.

## Section Review

( 1 K/U Explain the difference between a favourable chemical change and an unfavourable chemical change. Give two examples of each type of change.

2 (C) Write a short paragraph, or use a graphic organizer, to show the relationship among the following concepts: favourable chemical change, temperature, enthalpy, entropy, free energy.
(3) K/U In each process, how does the entropy of the system change?
(a) ice melting
(d) $\mathrm{HCl}_{(\mathrm{g})}+\mathrm{NH}_{3(\mathrm{~g})} \rightarrow \mathrm{NH}_{4} \mathrm{Cl}_{(\mathrm{s})}$
(b) water vapour condensing
(e) $\mathrm{CaCO}_{3(\mathrm{~s})} \rightarrow \mathrm{CaO}_{(\mathrm{s})}+\mathrm{CO}_{2(\mathrm{~g})}$
(c) sugar dissolving in water

4 K/U What is the sign of the entropy change in each chemical reaction?
(a) $\mathrm{N}_{2} \mathrm{O}_{4(\mathrm{~g})} \rightarrow 2 \mathrm{NO}_{2(\mathrm{~g})}$
(d) $\mathrm{N}_{2(\mathrm{~g})}+3 \mathrm{H}_{2(\mathrm{~g})} \rightarrow 2 \mathrm{NH}_{3(\mathrm{~g})}$
(b) $\mathrm{PCl}_{3(\mathrm{~g})}+\mathrm{Cl}_{2(\mathrm{~g})} \rightarrow \mathrm{PCl}_{5(\mathrm{~g})}$
(e) $\mathrm{S}_{(\mathrm{s})}+\mathrm{O}_{2(\mathrm{~g})} \rightarrow \mathrm{SO}_{2(\mathrm{~g})}$
(c) $2 \mathrm{Al}_{(\mathrm{s})}+\frac{3}{2} \mathrm{O}_{2(\mathrm{~g})} \rightarrow \mathrm{Al}_{2} \mathrm{O}_{3(\mathrm{~s})}$
(5) When water freezes, the phase change that occurs is exothermic.
$\mathrm{H}_{2} \mathrm{O}_{(\ell)} \rightarrow \mathrm{H}_{2} \mathrm{O}_{(\mathrm{s})} \quad \Delta H=-6.02 \mathrm{~kJ}$
Based on the change in enthalpy, you would expect that water would always freeze. Use the concepts of entropy and free energy to explain why this phase change is favourable only below $0^{\circ} \mathrm{C}$.

## The Equilibrium Constant

## Section Preview/ Specific Expectations

In this section, you will

- express your understanding of the law of chemical equilibrium as it applies to concentrations of reactants and products at equilibrium
- collect experimental data to determine an equilibrium constant for concentration
- solve equilibrium problems involving concentrations of reactants and products
- communicate your understanding of the following terms: law of chemical equilibrium, equilibrium constant ( $K_{c}$ ), ICE table

Chemists use both thermodynamics and rate to study chemical reactions. Thermodynamics determines whether a reaction will occur at a certain temperature and when equilibrium will be reached. The rate of a reaction determines the time it takes for a certain concentration of product to form. In this section, you will learn about the extent of a reaction: the relative concentrations of products to reactants at equilibrium.

## Opposing Rates and the Law of Chemical Equilibrium

In 1864, two Norwegian chemists, Cato Guldberg and Peter Waage, summarized their experiments on chemical equilibrium in the law of chemical equilibrium: At equilibrium, there is a constant ratio between the concentrations of the products and reactants in any change. Figure 7.7 shows how the law of chemical equilibrium applies to one chemical system. Chemists have studied this system extensively. It involves the reversible reaction between two gases: dinitrogen tetroxide, which is colourless, and nitrogen dioxide, which is dark brown.

$$
\begin{gathered}
\mathrm{N}_{2} \mathrm{O}_{4(\mathrm{~g})} \rightleftharpoons 2 \mathrm{NO}_{2(\mathrm{~g})} \\
\text { colourless } \quad \text { brown }
\end{gathered}
$$

By observing the intensity of the brown colour in the mixture, chemists can determine the concentration of nitrogen dioxide.


Figure 7.7 As this system nears equilibrium, the rate of the forward reaction decreases and the rate of the reverse reaction increases. At equilibrium, the macroscopic properties of this system are constant. Changes at the molecular level take place at equal rates.

Dinitrogen tetroxide gas is produced by vaporizing dinitrogen tetroxide liquid. Dinitrogen tetroxide liquid boils at $21^{\circ} \mathrm{C}$. If a small quantity is placed in a sealed flask at $100^{\circ} \mathrm{C}$, it vaporizes, filling the flask with dinitrogen tetroxide gas.

Suppose that the initial concentration of $\mathrm{N}_{2} \mathrm{O}_{4(\mathrm{~g})}$ is $0.0200 \mathrm{~mol} / \mathrm{L}$. The initial concentration of $\mathrm{NO}_{2(\mathrm{~g})}$ is zero. The initial rate of the forward reaction, $k_{\mathrm{f}}$, is relatively large, while the initial rate of the reverse reaction, $k_{\mathrm{r}}$, is zero. The initial conditions correspond to the first exchange in the ExpressLab on page 325, where the reactant cylinder was full and the product cylinder was empty. As the reaction proceeds, the rate of the forward reaction decreases because the concentration of $\mathrm{N}_{2} \mathrm{O}_{4(\mathrm{~g})}$ decreases. At the same time, the rate of the reverse reaction increases because the concentration of $\mathrm{NO}_{2(\mathrm{~g})}$ increases. At equilibrium, $k_{\mathrm{f}}=k_{\mathrm{r}}$. There are no further changes in the relative amounts of $\mathrm{N}_{2} \mathrm{O}_{4}$ and $\mathrm{NO}_{2}$.

## The Equilibrium Constant

From other experiments involving the reaction between nitrogen tetroxide and nitrogen dioxide, chemists know that both the forward and reverse reactions involve elementary steps. Thus, you can write rate equations for the reactions.
Forward reaction: $\mathrm{N}_{2} \mathrm{O}_{4(\mathrm{~g})} \rightarrow 2 \mathrm{NO}_{2(\mathrm{~g})} \quad$ Reverse reaction: $2 \mathrm{NO}_{2(\mathrm{~g})} \rightarrow \mathrm{N}_{2} \mathrm{O}_{4(\mathrm{~g})}$
Forward rate: $\quad k_{f}\left[\mathrm{~N}_{2} \mathrm{O}_{4}\right] \quad$ Reverse rate: $k_{\mathrm{f}}\left[\mathrm{NO}_{2}\right]^{2}$
At equilibrium,

$$
\begin{aligned}
\text { Foward rate } & =\text { Reverse rate } \\
k_{\mathrm{f}}\left[\mathrm{~N}_{2} \mathrm{O}_{4}\right] & =k_{\mathrm{r}}\left[\mathrm{NO}_{2}\right]^{2}
\end{aligned}
$$

The ratio of rate constants is another constant. The forward rate constant, $k_{\mathrm{f}}$, divided by the reverse rate constant, $k_{\mathrm{r}}$, is called the equilibrium
constant, $K_{\text {eq }}$.

$$
\frac{k_{\mathrm{f}}}{k_{\mathrm{r}}}=K_{\mathrm{eq}}=\frac{\left[\mathrm{NO}_{2}\right]^{2}}{\left[\mathrm{~N}_{2} \mathrm{O}_{4}\right]}
$$

You can write rate equations for these reactions because they are elementary mechanisms. Guldberg and Waage, however, showed that similar results are found for any reaction, regardless of the mechanism. For any general equilibrium equation, let $\mathrm{P}, \mathrm{Q}, \mathrm{R}$, and S represent chemical formulas and $a, b, c$, and $d$ represent their respective coefficients in the chemical equation.

$$
a \mathrm{P}+b \mathrm{Q} \rightleftharpoons c \mathrm{R}+d \mathrm{~S}
$$

Recall that molar concentrations are indicated by square brackets. The equilibrium expression is usually expressed in terms of molar concentrations. Thus, the subscript "c" is usually used instead of "eq" in the equilibrium constant.

$$
K_{\mathrm{c}}=\frac{[\mathrm{R}]^{c}[\mathrm{~S}]^{d}}{[\mathrm{P}]^{a}[\mathrm{Q}]^{b}}
$$

This equilibrium expression depends only on the stoichiometry of the reaction. By convention, chemists always write the concentrations of the products in the numerator and the concentrations of the reactants in the denominator. Each concentration term is raised to the power of the coefficient in the chemical equation. The terms are multiplied, never added.

The following Sample Problem shows how to find the equilibrium expression for a reaction. In this chapter, you will use equilibrium expressions for homogeneous reactions (mostly reactions between gases). In Chapters 8 and 9, you will learn how to use equilibrium expressions for heterogeneous systems.

## CONCEPT CHECK

How did the ExpressLab on page 325 model a reaction approaching equilibrium? How did it model the situation when equilibrium was reached?

## Sample Problem

## Writing Equilibrium Expressions

## Problem

One of the steps in the production of sulfuric acid involves the catalytic oxidation of sulfur dioxide.

$$
2 \mathrm{SO}_{2(\mathrm{~g})}+\mathrm{O}_{2(\mathrm{~g})} \rightarrow 2 \mathrm{SO}_{3(\mathrm{~g})}
$$

Write the equilibrium expression.

## What Is Required?

You need to find an expression for $K_{\mathrm{c}}$.

## What Is Given?

You know the balanced chemical equation.

## Plan Your Strategy

The expression for $K_{\mathrm{c}}$ is a fraction. The concentration of the product is in the numerator, and the concentrations of the reactants are in the denominator. Each concentration term must be raised to the power of the coefficient in the balanced equation.

## Act on Your Strategy

$K_{\mathrm{C}}=\frac{\left[\mathrm{SO}_{3}\right]^{2}}{\left[\mathrm{SO}_{2}\right]^{2}\left[\mathrm{O}_{2}\right]}$

## Check Your Solution

The square brackets indicate concentrations. The product is in the numerator, and each term is raised to the power of the coefficient in the chemical equation. The coefficient or power of 1 is not written, thus following chemistry conventions.

## Practice Problems

Write the equilibrium expression for each homogeneous reaction.

1. The reaction between ethanol and ethanoic acid to form ethyl ethanoate and water:

$$
\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OH}_{(\ell)}+\mathrm{CH}_{3} \mathrm{COOH}_{(\ell)} \rightleftharpoons \mathrm{CH}_{3} \mathrm{CHOOCH}_{2} \mathrm{CH}_{3(\ell)}+\mathrm{H}_{2} \mathrm{O}_{(\ell)}
$$

2. The reaction between nitrogen gas and oxygen gas at high temperatures:
$\mathrm{N}_{2(\mathrm{~g})}+\mathrm{O}_{2(\mathrm{~g})} \rightleftharpoons 2 \mathrm{NO}_{(\mathrm{g})}$
3. The reaction between hydrogen gas and oxygen gas to form water vapour:
$2 \mathrm{H}_{2(\mathrm{~g})}+\mathrm{O}_{2(\mathrm{~g})} \rightleftharpoons 2 \mathrm{H}_{2} \mathrm{O}_{(\mathrm{g})}$
4. The reduction-oxidation equilibrium of iron and iodine ions in aqueous solution:
$2 \mathrm{Fe}^{3+}{ }_{(\text {aq) }}+2 \mathrm{I}^{-}($aq $) ~ \rightleftharpoons 2 \mathrm{Fe}^{2+}{ }_{(\text {aq })}+\mathrm{I}_{2(\mathrm{aq})}$
Note: You will learn about reduction-oxidation reactions in the next unit.
5. The oxidation of ammonia (one of the reactions in the production of nitric acid):
$4 \mathrm{NH}_{3(\mathrm{~g})}+5 \mathrm{O}_{2(\mathrm{~g})} \rightleftharpoons 4 \mathrm{NO}_{(\mathrm{g})}+6 \mathrm{H}_{2} \mathrm{O}_{(\mathrm{g})}$

## The Equilibrium Constant and Temperature

Adding a chemical that is involved in a reaction at equilibrium increases the rate at which this chemical reacts. The rate, however, decreases as the concentration of the added chemical decreases. Eventually, equilibrium is re-established with the same equilibrium constant. For a given system at equilibrium, the value of the equilibrium constant depends only on temperature. Changing the temperature of a reacting mixture changes the rate of the forward and reverse reactions by different amounts, because the forward and reverse reactions have different activation energies. A reacting mixture at one temperature has an equilibrium constant whose value changes if the mixture is allowed to reach equilibrium at a different temperature.

The numerical value of the equilibrium constant does not depend on whether the starting point involves reactants or products. These are just labels that chemists use to identify particular chemicals in the reaction mixture. Also, at a given temperature, the value of $K_{\mathrm{c}}$ does not depend on the starting concentrations. The reaction gives the same ratio of products and reactants according to the equilibrium law. Remember, however, that $K_{\mathrm{c}}$ is calculated using concentration values when the system is at equilibrium.

## Sample Problem

## Calculating an Equilibrium Constant

## Problem

A mixture of nitrogen and chlorine gases was kept at a certain temperature in a 5.0 L reaction flask.

$$
\mathrm{N}_{2(\mathrm{~g})}+3 \mathrm{Cl}_{2(\mathrm{~g})} \rightleftharpoons 2 \mathrm{NCl}_{3(\mathrm{~g})}
$$

When the equilibrium mixture was analyzed, it was found to contain 0.0070 mol of $\mathrm{N}_{2(\mathrm{~g})}, 0.0022 \mathrm{~mol}$ of $\mathrm{Cl}_{2(\mathrm{~g})}$, and 0.95 mol of $\mathrm{NCl}_{3(\mathrm{~g})}$.

Calculate the equilibrium constant for this reaction.

## What Is Required?

You need to calculate the value of $K_{\mathrm{c}}$.

## What Is Given?

You have the balanced chemical equation and the amount of each substance at equilibrium.

## Plan Your Strategy

Step 1 Calculate the molar concentration of each compound at equilibrium.
Step 2 Write the equilibrium expression. Then substitute the equilibrium molar concentrations into the expression.

## Act on Your Strategy

Step 1 The reaction takes place in a 5.0 L flask. Calculate the molar concentrations at equilibrium.
$\left[\mathrm{N}_{2}\right]=\frac{0.0070 \mathrm{~mol}}{5.0 \mathrm{~L}}=1.4 \times 10^{-3} \mathrm{~mol} / \mathrm{L}$

## PROBLEM TIP

Notice that units are not included when using or calculating the value of $K_{c}$. This is the usual practice. The units do not help you check your solution.

$$
\begin{aligned}
& {\left[\mathrm{Cl}_{2}\right]=\frac{0.0022 \mathrm{~mol}}{5.0 \mathrm{~L}}=1.9 \times 10^{-1} \mathrm{~mol} / \mathrm{L}} \\
& {\left[\mathrm{NCl}_{3}\right]=\frac{0.95 \mathrm{~mol}}{5.0 \mathrm{~L}}=1.9 \times 10^{-1} \mathrm{~mol} / \mathrm{L}}
\end{aligned}
$$

Step 2 Write the equilibrium expression. Substitute the equilibrium molar concentrations into the expression.

$$
\begin{aligned}
K_{\mathrm{C}} & =\frac{\left[\mathrm{NCl}_{3}\right]^{2}}{\left[\mathrm{~N}_{2}\right]\left[\mathrm{Cl}_{2}\right]^{3}} \\
& =\frac{\left(1.9 \times 10^{-1}\right)^{2}}{\left(1.4 \times 10^{-3}\right) \times\left(4.4 \times 10^{-4}\right)^{3}} \\
& =3.0 \times 10^{11}
\end{aligned}
$$

## Check Your Solution

The equilibrium expression has the product terms in the numerator and the reactant terms in the denominator. The exponents in the equilibrium expression match the corresponding coefficients in the chemical equation. The molar concentrations at equilibrium were substituted into the expression.

## Practice Problems

6. The following reaction took place in a sealed flask at $250^{\circ} \mathrm{C}$.
$\mathrm{PCl}_{5(\mathrm{~g})} \rightleftharpoons \mathrm{PCl}_{3(\mathrm{~g})}+\mathrm{Cl}_{2(\mathrm{~g})}$
At equilibrium, the gases in the flask had the following concentrations: $\left[\mathrm{PCl}_{5}\right]=1.2 \times 10^{-2} \mathrm{~mol} / \mathrm{L},\left[\mathrm{PCl}_{3}\right]=1.5 \times 10^{-2} \mathrm{~mol} / \mathrm{L}$, and $\left[\mathrm{Cl}_{2}\right]=1.5 \times 10^{-2} \mathrm{~mol} / \mathrm{L}$. Calculate the value of $K_{\mathrm{c}}$ at $250^{\circ} \mathrm{C}$.
7. Iodine and bromine react to form iodine monobromide, IBr .
$\mathrm{I}_{2(\mathrm{~g})}+\mathrm{Br}_{2(\mathrm{~g})} \rightleftharpoons 2 \mathrm{IBr}_{(\mathrm{g})}$
At $250^{\circ} \mathrm{C}$, an equilibrium mixture in a 2.0 L flask contained 0.024 mol of $\mathrm{I}_{2(\mathrm{~g})}$, 0.050 mol of $\mathrm{Br}_{2(\mathrm{~g})}$, and 0.38 mol of $\mathrm{IBr}_{(\mathrm{g})}$. What is the value of $K_{\mathrm{C}}$ for the reaction at $250^{\circ} \mathrm{C}$ ?
8. At high temperatures, carbon dioxide gas decomposes into carbon monoxide and oxygen gas. At equilibrium, the gases have the following concentrations: $\left[\mathrm{CO}_{2(\mathrm{~g})}\right]=1.2 \mathrm{~mol} / \mathrm{L},\left[\mathrm{CO}_{(\mathrm{g})}\right]=0.35 \mathrm{~mol} / \mathrm{L}$, and $\left[\mathrm{O}_{2(\mathrm{~g})}\right]=0.15 \mathrm{~mol} / \mathrm{L}$. Determine $K_{\mathrm{c}}$ at the temperature of the reaction.
9. Hydrogen sulfide is a pungent, poisonous gas. At 1400 K , an equilibrium mixture was found to contain $0.013 \mathrm{~mol} / \mathrm{L}$ hydrogen, $0.046 \mathrm{~mol} / \mathrm{L}$ sulfur in the form of $\mathrm{S}_{2(\mathrm{~g})}$, and $0.18 \mathrm{~mol} / \mathrm{L}$ hydrogen sulfide. Calculate the equilibrium constant, at 1400 K , for the following reaction.
$2 \mathrm{H}_{2} \mathrm{~S}_{(\mathrm{g})} \rightleftharpoons 2 \mathrm{H}_{2(\mathrm{~g})}+\mathrm{S}_{2(\mathrm{~g})}$
10. Methane, ethyne, and hydrogen form the following equilibrium mixture.
$2 \mathrm{CH}_{4(\mathrm{~g})} \rightleftharpoons \mathrm{C}_{2} \mathrm{H}_{2(\mathrm{~g})}+3 \mathrm{H}_{2(\mathrm{~g})}$
While studying this reaction mixture, a chemist analyzed a 4.0 L sealed flask at $1700^{\circ} \mathrm{C}$. The chemist found 0.46 mol of $\mathrm{CH}_{4(\mathrm{~g})}, 0.64 \mathrm{~mol}$ of $\mathrm{C}_{2} \mathrm{H}_{2(\mathrm{~g})}$, and 0.92 mol of $\mathrm{H}_{2(\mathrm{~g})}$. What is the value of $K_{\mathrm{c}}$ for the reaction at $1700^{\circ} \mathrm{C}$ ?
