

Every system in chemical equilibrium, under the influence of a change of any one of the factors of equilibrium, undergoes a transformation . . . [that produces a change] . . . in the opposite direction of the factor in question.

—HENRI LE CHÂTELIER (1850–1936)

CHAPTER

16

Chemical Equilibrium

In Chapter 15, we examined *how fast* a chemical reaction occurs. In this chapter, we examine *how far* a chemical reaction goes. The speed of a chemical reaction is determined by kinetics. The extent of a chemical reaction is determined by thermodynamics. Our focus is on describing how far a chemical reaction goes based on an experimentally measurable quantity called *the equilibrium constant*. A reaction with a large equilibrium constant proceeds nearly to completion—almost all the reactants react to form products. A reaction with a small equilibrium constant barely proceeds at all—almost all the reactants remain as reactants, hardly forming any products. For now, we simply accept the equilibrium constant as an experimentally measurable quantity and learn how to use it to predict and quantify the extent of a reaction. In Chapter 19, we will explore the reasons underlying the magnitude of equilibrium constants.



A developing fetus obtains oxygen from the mother's blood because the reaction between oxygen and fetal hemoglobin has a larger equilibrium constant than the reaction between oxygen and maternal hemoglobin.

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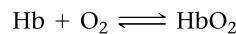
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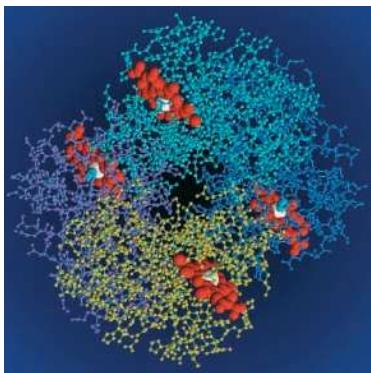
LEARNING OUTCOMES 720

16.1

Fetal Hemoglobin and Equilibrium

Have you ever wondered how a baby in the womb gets oxygen? Unlike you and me, a fetus does not breathe air. Yet, like you and me, a fetus needs oxygen. Where does that oxygen come from? After we are born, we inhale air into our lungs and that air diffuses into capillaries, where it comes into contact with our blood. Within our red blood cells, a protein called hemoglobin (Hb) reacts with oxygen according to the chemical equation:

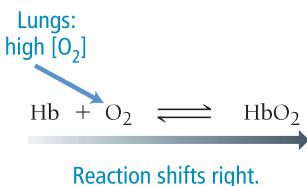




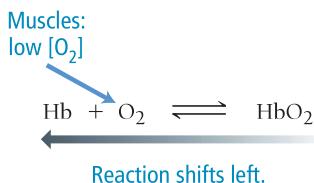
▲ Hemoglobin is the oxygen-carrying protein in red blood cells. Oxygen binds to iron atoms, which are depicted here in white.

The double arrows in this equation indicate that the reaction can occur in both the forward and reverse directions and can reach chemical *equilibrium*. We encountered this term in Chapters 12 and 14, and we define it more carefully in the next section. For now, understand that the relative concentrations of the reactants and products in a reaction at equilibrium are described by the *equilibrium constant*, *K*. A large value of *K* means that the reaction lies far to the right at equilibrium—a high concentration of products and a low concentration of reactants. A small value of *K* means that the reaction lies far to the left at equilibrium—a high concentration of reactants and a low concentration of products. In short, the value of *K* is a measure of how far a reaction proceeds—the larger the value of *K*, the more the reaction proceeds toward the products.

The equilibrium constant for the reaction between hemoglobin and oxygen is such that hemoglobin efficiently binds oxygen at typical lung oxygen concentrations, but it can also release oxygen under the appropriate conditions. Any system at equilibrium, including the hemoglobin–oxygen system, responds to changes in ways that maintain equilibrium. If any of the concentrations of the reactants or products change, the reaction shifts to counteract that change. For the hemoglobin system, as blood flows through the lungs where oxygen concentrations are high, the equilibrium shifts to the right—hemoglobin binds oxygen:



In our bodies, as blood flows out of the lungs and into muscles and organs where oxygen concentrations have been depleted (because muscles and organs use oxygen), the equilibrium shifts to the left—hemoglobin releases oxygen:

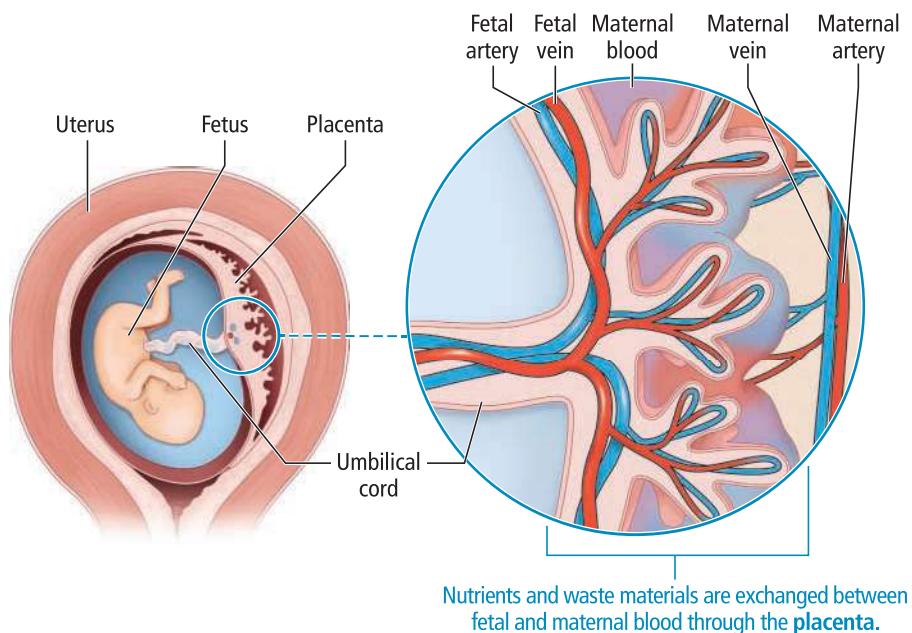


In other words, to maintain equilibrium, *hemoglobin binds oxygen when the surrounding oxygen concentration is high, but it releases oxygen when the surrounding oxygen concentration is low*. In this way, hemoglobin transports oxygen from the lungs to all parts of the body that use oxygen.

A fetus has its own circulatory system. The mother's blood never flows into the fetus's body, and the fetus cannot get any air in the womb. How, then, does the fetus get oxygen? The answer lies in the properties of fetal hemoglobin (HbF), which is slightly different from adult hemoglobin. Like adult hemoglobin, fetal hemoglobin is in equilibrium with oxygen:



However, the equilibrium constant for fetal hemoglobin is larger than the equilibrium constant for adult hemoglobin, meaning that the reaction tends to go farther in the direction of the product. Consequently, fetal hemoglobin loads oxygen at a lower oxygen concentration than does adult hemoglobin. In the placenta, fetal blood flows in close proximity to maternal blood. Although the two never mix, because of the different equilibrium constants, the maternal hemoglobin releases oxygen that the fetal hemoglobin then binds and carries into its own circulatory system (Figure 16.1►). Nature has evolved a chemical system through which the mother's hemoglobin can in effect *hand off* oxygen to the hemoglobin of the fetus.

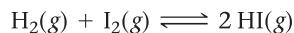


◀ FIGURE 16.1 Oxygen Exchange between the Maternal and Fetal Circulation In the placenta, the blood of the fetus comes into close proximity with the blood of the mother, although the two do not mix directly. Because the reaction of fetal hemoglobin with oxygen has a larger equilibrium constant than the reaction of maternal hemoglobin with oxygen, the fetus receives oxygen from the mother's blood.

16.2

The Concept of Dynamic Equilibrium

Recall from the previous chapter that reaction rates generally increase with increasing concentration of the reactants and decrease with decreasing concentration of the reactants (unless the reaction order is zero). With this in mind, consider the reaction between hydrogen and iodine:



In this reaction, H_2 and I_2 react to form 2 HI molecules, but the 2 HI molecules can also react to re-form H_2 and I_2 . A reaction such as this one—that can proceed in both the forward and reverse directions—is **reversible**. Suppose we begin with only H_2 and I_2 in a container (Figure 16.2a▶). What happens? Initially H_2 and I_2 begin to react to form HI (Figure 16.2b). However, as H_2 and I_2 react, their concentrations decrease, which in turn *decreases the rate of the forward reaction*. At the same time, HI begins to form. As the concentration of HI increases, the reverse reaction begins to occur at a faster and faster rate. Eventually the rate of the reverse reaction (which has been increasing) equals the rate of the forward reaction (which has been decreasing). At that point, **dynamic equilibrium** is reached (Figure 16.2c, d▶):

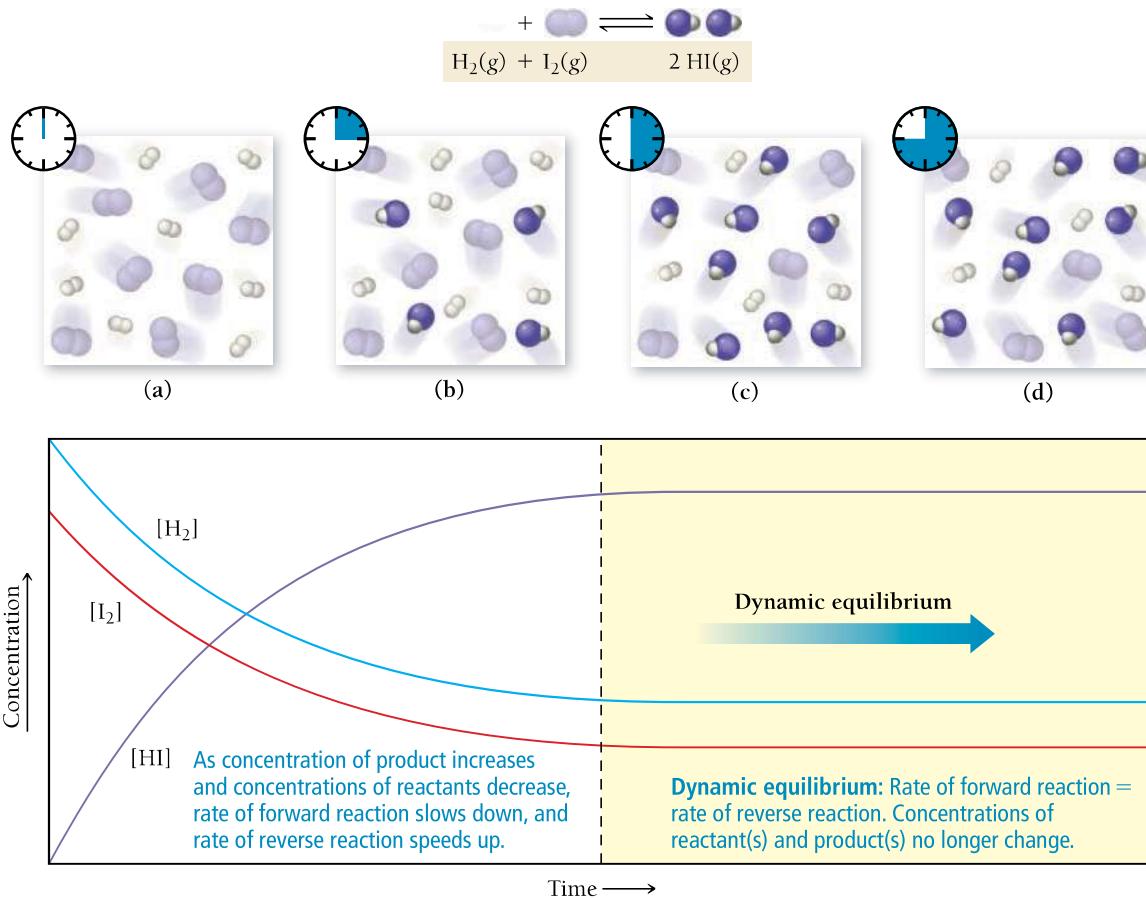
Dynamic equilibrium for a chemical reaction is the condition in which the rate of the forward reaction equals the rate of the reverse reaction.

Dynamic equilibrium is “dynamic” because the forward and reverse reactions are still occurring; however, they are occurring at the same rate. When dynamic equilibrium is reached, the concentrations of H_2 , I_2 , and HI no longer change. They remain constant because the reactants and products form at the same rate that they are depleted. Note that just because the concentrations of reactants and products no longer change at equilibrium *does not mean that the concentrations of reactants and products are equal to one another* at equilibrium. Some reactions reach equilibrium only after most of the reactants have formed products. Others reach equilibrium when only a small fraction of the reactants have formed products. It depends on the reaction.

Nearly all chemical reactions are at least theoretically reversible. In many cases, however, the reversibility is so small that it can be ignored.

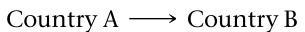
Dynamic Equilibrium

Equilibrium is reached in a chemical reaction when the concentrations of the reactants and products no longer change.

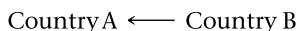


▲ FIGURE 16.2 Dynamic Equilibrium Equilibrium is reached in a chemical reaction when the concentrations of the reactants and products no longer change. The molecular images depict the progress of the reaction $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$. The graph shows the concentrations of H_2 , I_2 , and HI as a function of time. When the reaction reaches equilibrium, both the forward and reverse reactions continue, but at equal rates, so the concentrations of the reactants and products remain constant.

We can better understand dynamic equilibrium with a simple analogy. Imagine two neighboring countries (A and B) with a closed border between them (Figure 16.3►). Country A is overpopulated and Country B is underpopulated. One day, the border between the two countries opens, and people immediately begin to leave Country A for Country B:



The population of Country A goes down as the population of Country B goes up. As people leave Country A, however, the *rate* at which they leave slows down because as Country A becomes less populated, the pool of potential emigrants gets smaller. (In other words, the rate of emigration is directly proportional to the population—as the population decreases, the emigration rate goes down.) In contrast, as people move into Country B, it gets more crowded and some people begin to move from Country B to Country A:



Dynamic Equilibrium: An Analogy



Initial: Net movement from A to B



Equilibrium: Equal movement in both directions

▲ FIGURE 16.3 A Population Analogy for Chemical Equilibrium Because Country A is initially overpopulated, people migrate from Country A to Country B. As the population of Country A falls and that of Country B rises, the rate of migration from Country A to Country B decreases and the rate of migration from Country B to Country A increases. Eventually, the two rates become equal. Equilibrium has been reached.

As the population of Country B continues to grow, the rate of people moving out of Country B accelerates. Eventually, the *rate* of people moving out of Country A (which has been slowing down as people leave) equals the *rate* of people moving out of Country B (which has been increasing as Country B gets more crowded). Dynamic equilibrium has been reached:



Notice that when the two countries reach dynamic equilibrium, their populations no longer change because the number of people moving out of either country equals the number of people moving in. However, one country—because of its charm or the availability of good jobs or lower taxes, or for whatever other reason—may have a higher population than the other country, even when dynamic equilibrium is reached.

Similarly, when a chemical reaction reaches dynamic equilibrium, the rate of the forward reaction equals the rate of the reverse reaction, and the concentrations of reactants and products become *constant*. But the concentrations of reactants and products will not necessarily be *equal* at equilibrium, just as the populations of the two countries are not necessarily equal at equilibrium.

DYNAMIC EQUILIBRIUM Which statement does NOT generally apply to a chemical reaction in dynamic equilibrium?

- (a) The rates of the forward and reverse reactions are equal.
- (b) The concentrations of the reactants and products are constant.
- (c) The concentrations of the reactants and products are equal.

16.1
Cc

Conceptual Connection

ANSWER NOW!



WATCH NOW!**KEY CONCEPT VIDEO 16.3**

 The Equilibrium Constant
16.3 The Equilibrium Constant (*K*)

We have just seen that the *concentrations of reactants and products* are not equal at equilibrium—rather, the *rates of the forward and reverse reactions* are equal. So what about the concentrations? What can we know about them? The concentrations, as we can see by reexamining Figure 16.2, become constant; they don't change once equilibrium is reached (as long as the temperature is constant). We quantify the relative concentrations of reactants and products at equilibrium with a quantity called the *equilibrium constant (*K*)*. Consider an equation for a generic chemical reaction:

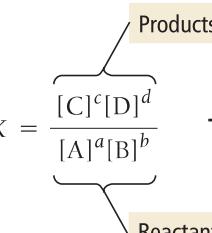


We distinguish between the equilibrium constant (*K*) and the Kelvin unit of temperature (K) by italicizing the equilibrium constant.

where A and B are reactants, C and D are products, and *a*, *b*, *c*, and *d* are the respective stoichiometric coefficients in the chemical equation. The **equilibrium constant (*K*)** for the reaction is defined as the ratio—*at equilibrium*—of the concentrations of the products raised to their stoichiometric coefficients divided by the concentrations of the reactants raised to their stoichiometric coefficients:

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

The Law of Mass Action



In this notation, [A] represents the molar concentration of A.

Why is *this* particular ratio of concentrations at equilibrium—and not some other ratio—defined as the equilibrium constant? *Because this particular ratio is always a constant when the reactants and products are at equilibrium* (at constant temperature). As we can see from the expression, the equilibrium constant *quantifies* the relative concentrations of reactants and products *at equilibrium*. The relationship between the balanced chemical equation and the expression of the equilibrium constant is the **law of mass action**.

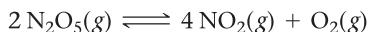
ANSWER NOW!
16.2
CC
 Conceptual Connection


THE LAW OF MASS ACTION According to the law of mass action, what is the correct expression for the equilibrium constant for the reaction $2A + B \rightleftharpoons 3C$?

- (a) $K = \frac{[C]}{[A][B]}$ (b) $K = \frac{3[C]}{2[A][B]}$ (c) $K = \frac{[A]^2[B]}{[C]^3}$ (d) $K = \frac{[C]^3}{[A]^2[B]}$

Expressing Equilibrium Constants for Chemical Reactions

To express an equilibrium constant for a chemical reaction, we examine the balanced chemical equation and apply the law of mass action. For example, suppose we want to express the equilibrium constant for the reaction:



The equilibrium constant is $[\text{NO}_2]$ raised to the fourth power multiplied by $[\text{O}_2]$ raised to the first power divided by $[\text{N}_2\text{O}_5]$ raised to the second power:

$$K = \frac{[\text{NO}_2]^4[\text{O}_2]}{[\text{N}_2\text{O}_5]^2}$$

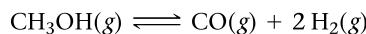
Notice that the *coefficients* in the chemical equation become the *exponents* in the expression of the equilibrium constant.

WATCH NOW!

INTERACTIVE WORKED EXAMPLE 16.1

EXAMPLE 16.1 Expressing Equilibrium Constants for Chemical Equations

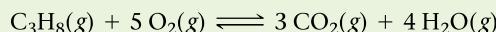
Express the equilibrium constant for the chemical equation:

**SOLUTION**

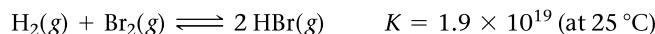
The equilibrium constant is the equilibrium concentrations of the products raised to their stoichiometric coefficients divided by the equilibrium concentrations of the reactants raised to their stoichiometric coefficients.

$$K = \frac{[\text{CO}][\text{H}_2]^2}{[\text{CH}_3\text{OH}]}$$

FOR PRACTICE 16.1 Express the equilibrium constant for the combustion of propane:

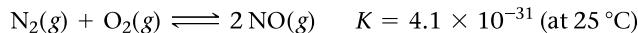
**The Significance of the Equilibrium Constant**

You now know how to express the equilibrium constant, but what does it mean? What, for example, does a large equilibrium constant ($K \gg 1$) imply about a reaction? A large equilibrium constant indicates that the numerator (which specifies the amounts of products at equilibrium) is larger than the denominator (which specifies the amounts of reactants at equilibrium). Therefore, when the equilibrium constant is large, the forward reaction is favored. For example, consider the reaction:



The equilibrium constant is large, indicating that the equilibrium point for the reaction lies far to the right—high concentrations of products, low concentrations of reactants (Figure 16.4►). Remember that the equilibrium constant says nothing about *how fast* a reaction reaches equilibrium, only *how far* the reaction has proceeded once equilibrium is reached. A reaction with a large equilibrium constant may be kinetically very slow and take a long time to reach equilibrium.

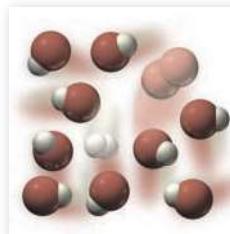
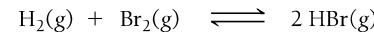
Conversely, what does a *small* equilibrium constant ($K \ll 1$) mean? It indicates that the reverse reaction is favored and that there will be more reactants than products when equilibrium is reached. For example, consider the reaction:



The equilibrium constant is very small, indicating that the equilibrium point for the reaction lies far to the left—high concentrations of reactants, low concentrations of products (Figure 16.5►). This is fortunate because N_2 and O_2 are the main components of air. If this equilibrium constant were large, much of the N_2 and O_2 in air would react to form NO, a toxic gas.

Summarizing the Significance of the Equilibrium Constant:

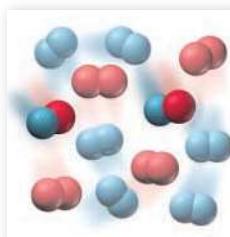
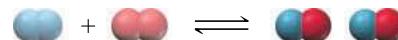
- $K \ll 1$ Reverse reaction is favored; forward reaction does not proceed very far.
- $K \approx 1$ Neither direction is favored; forward reaction proceeds about halfway.
- $K \gg 1$ Forward reaction is favored; forward reaction proceeds essentially to completion.



$$K = \frac{[\text{HBr}]^2}{[\text{H}_2][\text{Br}_2]} = \text{large number}$$

▲ FIGURE 16.4 The Meaning of a Large Equilibrium Constant

If the equilibrium constant for a reaction is large, the equilibrium point of the reaction lies far to the right—the concentration of products is large and the concentration of reactants is small.



$$K = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = \text{small number}$$

▲ FIGURE 16.5 The Meaning of a Small Equilibrium Constant

If the equilibrium constant for a reaction is small, the equilibrium point of the reaction lies far to the left—the concentration of products is small and the concentration of reactants is large.

ANSWER NOW!

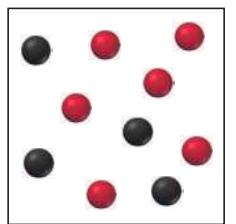
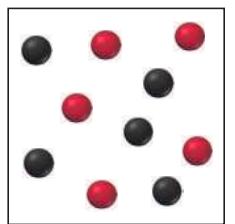
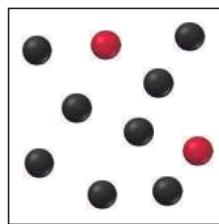


16.3 Cc

Conceptual Connection

THE MAGNITUDE OF THE EQUILIBRIUM CONSTANT

Consider the reaction $A(g) \rightleftharpoons B(g)$. The images shown here illustrate equilibrium mixtures of A (red) and B (black) at three different temperatures. At which temperature is the equilibrium constant the largest?

(a) T_1 (b) T_2 (c) T_3

ANSWER NOW!



16.4 Cc

Conceptual Connection

EQUILIBRIUM CONSTANTS AND EQUILIBRIUM CONCENTRATIONS

The equilibrium constant for the reaction $A(g) \rightleftharpoons B(g)$ is 10. A reaction mixture initially contains $[A] = 1.1\text{ M}$ and $[B] = 0.0\text{ M}$. Which statement is true at equilibrium?

- (a) The reaction mixture contains $[A] = 1.0\text{ M}$ and $[B] = 0.1\text{ M}$.
- (b) The reaction mixture contains $[A] = 0.1\text{ M}$ and $[B] = 1.0\text{ M}$.
- (c) The reaction mixture contains equal concentrations of A and B.



CHEMISTRY AND MEDICINE

Life and Equilibrium

Have you ever tried to define life? If you have, you probably know that a definition is elusive. How are living things different from nonliving things? You may try to define living things as those things that can move. But of course many living things do not move (most plants, for example), and some nonliving things, such as glaciers and Earth itself, do move. So motion is neither unique to nor definitive of life. You may try to define living things as those things that can reproduce. But again, many living things, such as mules or sterile humans, cannot reproduce; yet they are alive. In addition, some nonliving things, such as crystals, for example, reproduce (in some sense). So what is unique about living things?

One definition of life involves the concept of equilibrium—living things are not in equilibrium with their surroundings. Our body temperature, for example, is not the same as the temperature of our surroundings. If we jump into a

swimming pool, the acidity of our blood does not become the same as the acidity of the surrounding water. Living things, even the simplest ones, maintain some measure of disequilibrium with their environment.

We must add one more concept, however, to complete our definition of life with respect to equilibrium. A cup of hot water is in disequilibrium with its environment with respect to temperature, yet it is not alive. The cup of hot water has no control over its disequilibrium, however, and will slowly come to equilibrium with its environment. In contrast, living things—as long as they are alive—maintain and *control* their disequilibrium. Your body temperature, for example, is not only in disequilibrium with your surroundings—it is in controlled disequilibrium. Your body maintains your temperature within a specific range that is not in equilibrium with the surrounding temperature.

So, one criterion for life is that living things are in controlled disequilibrium with their environment. Maintaining disequilibrium is a main activity of living organisms, requiring energy obtained from their environment. Plants derive that energy from sunlight; animals eat plants (or other animals that have eaten plants), and thus they too ultimately derive their energy from the sun. A living thing comes into equilibrium with its surroundings only after it dies.



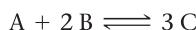
◀ What makes these cells alive?



Relationships between the Equilibrium Constant and the Chemical Equation

If a chemical equation is modified in some way, then the equilibrium constant for the equation changes because of the modification. The following three modifications are common:

- If you reverse the equation, invert the equilibrium constant.** For example, consider this equilibrium equation:



The expression for the equilibrium constant of this reaction is:

$$K_{\text{forward}} = \frac{[C]^3}{[A][B]^2}$$

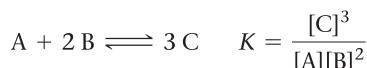
If you reverse the equation:



then, according to the law of mass action, the expression for the equilibrium constant becomes:

$$K_{\text{reverse}} = \frac{[A][B]^2}{[C]^3} = \frac{1}{K_{\text{forward}}}$$

- If you multiply the coefficients in the equation by a factor, raise the equilibrium constant to the same factor.** Consider again this chemical equation and corresponding expression for the equilibrium constant:



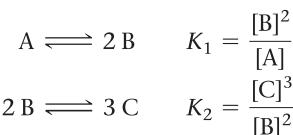
If you multiply the equation by n , you get:



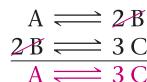
Applying the law of mass action, the expression for the equilibrium constant becomes:

$$K' = \frac{[C]^{3n}}{[A]^n[B]^{2n}} = \left(\frac{[C]^3}{[A][B]^2} \right)^n = K^n$$

- If you add two or more individual chemical equations to obtain an overall equation, multiply the corresponding equilibrium constants by each other to obtain the overall equilibrium constant.** Consider these two chemical equations and their corresponding equilibrium constant expressions:



The two equations sum as follows:



According to the law of mass action, the equilibrium constant for this overall equation is then:

$$K_{\text{overall}} = \frac{[C]^3}{[A]}$$

Notice that K_{overall} is the product of K_1 and K_2 :

$$\begin{aligned} K_{\text{overall}} &= K_1 \times K_2 \\ &= \frac{[B]^2}{[A]} \times \frac{[C]^3}{[B]^2} \\ &= \frac{[C]^3}{[A]} \end{aligned}$$

If n is a fractional quantity, raise K to the same fractional quantity.

Remember that $(x^a)^b = x^{ab}$.

ANSWER NOW!



16.5 Cc

Conceptual Connection

THE EQUILIBRIUM CONSTANT AND THE CHEMICAL EQUATION

The reaction $A(g) \rightleftharpoons 2 B(g)$ has an equilibrium constant of $K = 0.010$. What is the equilibrium constant for the reaction $B(g) \rightleftharpoons \frac{1}{2}A(g)$?

- (a) 1 (b) 10 (c) 100 (d) 0.0010

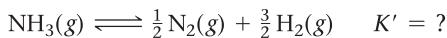
EXAMPLE 16.2

Manipulating the Equilibrium Constant to Reflect Changes in the Chemical Equation

Consider the chemical equation and equilibrium constant for the synthesis of ammonia at 25 °C:



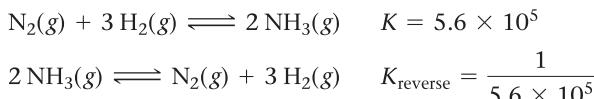
Calculate the equilibrium constant for the following reaction at 25 °C:



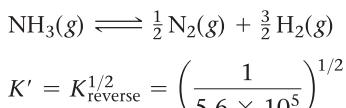
SOLUTION

You want to manipulate the given reaction and value of K to obtain the desired reaction and value of K' . You can see that the given reaction is the reverse of the desired reaction, and its coefficients are twice those of the desired reaction.

Begin by reversing the given reaction and taking the inverse of the value of K .



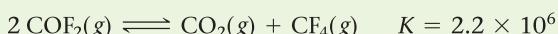
Next, multiply the reaction by $\frac{1}{2}$ and raise the equilibrium constant to the $\frac{1}{2}$ power.



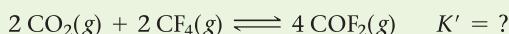
Calculate the value of K' .

$$K' = 1.3 \times 10^{-3}$$

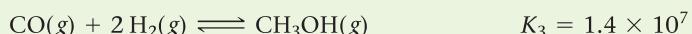
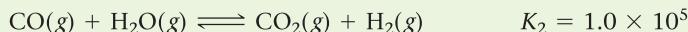
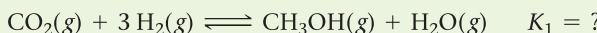
FOR PRACTICE 16.2 Consider the following chemical equation and equilibrium constant at 25 °C:



Calculate the equilibrium constant for the following reaction at 25 °C:



FOR MORE PRACTICE 16.2 Predict the equilibrium constant for the first reaction shown here given the equilibrium constants for the second and third reactions:



16.4

Expressing the Equilibrium Constant in Terms of Pressure

So far, we have expressed the equilibrium constant only in terms of the *concentrations* of the reactants and products. For gaseous reactions, the partial pressure of a particular gas is proportional to its concentration. Therefore, we can also express the equilibrium constant in terms of the *partial pressures* of the reactants and products. Consider the gaseous reaction:



From this point on, we designate K_c as the equilibrium constant with respect to concentration in molarity. For the reaction just given, we can express K_c using the law of mass action:

$$K_c = \frac{[\text{SO}_2]^2[\text{O}_2]}{[\text{SO}_3]^2}$$

We now designate K_p as the equilibrium constant with respect to partial pressures in atmospheres. *The expression for K_p takes the form of the expression for K_c , except that we use the partial pressure of each gas in place of its concentration.* For the SO_3 reaction, we write K_p as:

$$K_p = \frac{(P_{\text{SO}_2})^2 P_{\text{O}_2}}{(P_{\text{SO}_3})^2}$$

where P_A is simply the partial pressure of gas A in units of atmospheres.

Relationship Between K_p and K_c

Since the partial pressure of a gas in atmospheres is not the same as its concentration in molarity, the value of K_p for a reaction is not necessarily equal to the value of K_c . However, as long as the gases are behaving ideally, we can derive a relationship between the two constants. The concentration of an ideal gas A is the number of moles of A (n_A) divided by its volume (V) in liters:

$$[\text{A}] = \frac{n_A}{V}$$

From the ideal gas law, we can relate the quantity n_A/V to the partial pressure of A as follows:

$$P_A V = n_A R T$$

$$P_A = \frac{n_A}{V} R T$$

Since $[\text{A}] = n_A/V$, we can write:

$$P_A = [\text{A}] R T \quad \text{or} \quad [\text{A}] = \frac{P_A}{R T} \quad [16.1]$$

Now consider the following general equilibrium chemical equation:



According to the law of mass action, we write K_c as follows:

$$K_c = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

Substituting $[\text{X}] = P_{\text{X}}/RT$ for each concentration term, we get:

$$\begin{aligned} K_c &= \frac{\left(\frac{P_{\text{C}}}{RT}\right)^c \left(\frac{P_{\text{D}}}{RT}\right)^d}{\left(\frac{P_{\text{A}}}{RT}\right)^a \left(\frac{P_{\text{B}}}{RT}\right)^b} = \frac{P_{\text{C}}^c P_{\text{D}}^d \left(\frac{1}{RT}\right)^{c+d}}{P_{\text{A}}^a P_{\text{B}}^b \left(\frac{1}{RT}\right)^{a+b}} = \frac{P_{\text{C}}^c P_{\text{D}}^d}{P_{\text{A}}^a P_{\text{B}}^b} \left(\frac{1}{RT}\right)^{c+d-(a+b)} \\ &= K_p \left(\frac{1}{RT}\right)^{c+d-(a+b)} \end{aligned}$$

Rearranging,

$$K_p = K_c (RT)^{c+d-(a+b)}$$

Finally, if we let $\Delta n = c + d - (a + b)$, which is the sum of the stoichiometric coefficients of the gaseous products minus the sum of the stoichiometric coefficients of the gaseous reactants, we get the following general result:

$$K_p = K_c (RT)^{\Delta n} \quad [16.2]$$

Notice that if the total number of moles of gas is the same after the reaction as before, then $\Delta n = 0$, and K_p is equal to K_c .

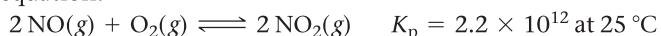
In the equation $K_p = K_c (RT)^{\Delta n}$, the quantity Δn represents the difference between the number of moles of gaseous products and gaseous reactants.

WATCH NOW!

INTERACTIVE WORKED EXAMPLE 16.3

EXAMPLE 16.3 Relating K_p and K_c 

Nitrogen monoxide, a pollutant in automobile exhaust, is oxidized to nitrogen dioxide in the atmosphere according to the equation:



Find K_c for this reaction.

SORT You are given K_p for the reaction and asked to find K_c .

GIVEN: $K_p = 2.2 \times 10^{12}$

FIND: K_c

STRATEGIZE Use Equation 16.2 to relate K_p and K_c .

EQUATION $K_p = K_c(RT)^{\Delta n}$

SOLVE Solve the equation for K_c .

SOLUTION

$$K_c = \frac{K_p}{(RT)^{\Delta n}}$$

$$\Delta n = 2 - 3 = -1$$

$$K_c = \frac{2.2 \times 10^{12}}{\left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 298 \text{ K}\right)^{-1}} \\ = 5.4 \times 10^{13}$$

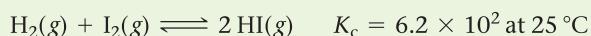
Calculate Δn .

Substitute the required quantities to calculate K_c . The temperature must be in kelvins. The units are dropped when reporting K_c , as described later in this section.

CHECK The easiest way to check this answer is to substitute it back into Equation 16.2 and confirm that you get the original value for K_p .

$$K_p = K_c(RT)^{\Delta n} \\ = 5.4 \times 10^{13} \left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 298 \text{ K}\right)^{-1} \\ = 2.2 \times 10^{12}$$

FOR PRACTICE 16.3 Consider the following reaction and corresponding value of K_c :



What is the value of K_p at this temperature?

Units of K

Throughout this book, we express concentrations and partial pressures within the equilibrium constant expression in units of molarity and atmospheres, respectively. When expressing the value of the equilibrium constant, however, we have not included the units. Formally, the values of concentration or partial pressure that we substitute into the equilibrium constant expression are ratios of the concentration or pressure to a reference concentration (exactly 1 M) or a reference pressure (exactly 1 atm).

For example, within the equilibrium constant expression, a pressure of 1.5 atm becomes:

$$\frac{1.5 \text{ atm}}{1 \text{ atm}} = 1.5$$

Similarly, a concentration of 1.5 M becomes:

$$\frac{1.5 \text{ M}}{1 \text{ M}} = 1.5$$

As long as concentration units are expressed in molarity for K_c and pressure units are expressed in atmospheres for K_p , we can skip this formality and enter the quantities directly into the equilibrium expression, dropping their corresponding units.

THE RELATIONSHIP BETWEEN K_p AND K_c

Under which circumstances are K_p and K_c equal for the reaction shown here?



- (a) If $a + b = c + d$.
- (b) If the reaction is reversible.
- (c) If the equilibrium constant is small.



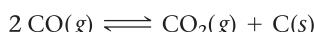
ANSWER NOW!



16.5

Heterogeneous Equilibria: Reactions Involving Solids and Liquids

Many chemical reactions involve pure solids or pure liquids as reactants or products. Consider, for example, the reaction:



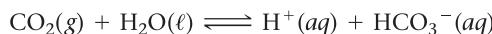
We might expect the expression for the equilibrium constant to be:

$$K_c = \frac{[\text{CO}_2][\text{C}]}{[\text{CO}]^2} \quad (\text{incorrect})$$

However, since carbon is a solid, its concentration is constant (if you double the amount of carbon its *concentration* remains the same). The concentration of a solid does not change because a solid does not expand to fill its container. Its concentration, therefore, depends only on its density, which is constant as long as *some* solid is present (Figure 16.6▼). Consequently, pure solids—those reactants or products labeled in the chemical equation with an (s)—are not included in the equilibrium expression (because their constant value is incorporated into the value of K). The correct equilibrium expression for this reaction is therefore:

$$K_c = \frac{[\text{CO}_2]}{[\text{CO}]^2}$$

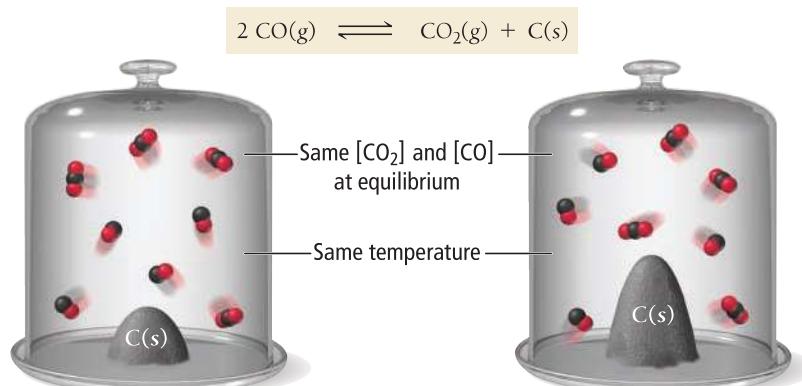
Similarly, the concentration of a pure liquid does not change. So, pure liquids—reactants or products labeled in the chemical equation with an (l)—are also excluded from the equilibrium expression. For example, consider the equilibrium expression for the reaction between carbon dioxide and water:



Since $\text{H}_2\text{O}(l)$ is pure liquid, it is omitted from the equilibrium expression:

$$K_c = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]}$$

A Heterogeneous Equilibrium



◀ FIGURE 16.6 Heterogeneous Equilibrium The concentration of solid carbon (the number of atoms per unit volume) is constant as long as some solid carbon is present. The same is true for pure liquids. For this reason, the concentrations of solids and pure liquids are not included in equilibrium constant expressions.

EXAMPLE 16.4 Writing Equilibrium Expressions for Reactions Involving a Solid or a Liquid

Write an expression for the equilibrium constant (K_c) for this chemical equation:

**SOLUTION**

Since $\text{CaCO}_3(s)$ and $\text{CaO}(s)$ are both solids, omit them from the equilibrium expression.

$$K_c = [\text{CO}_2]$$

FOR PRACTICE 16.4 Write an equilibrium expression (K_c) for the equation:



ANSWER NOW!



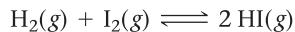
16.7 Cc Conceptual Connection

HETEROGENEOUS EQUILIBRIA, K_p AND K_c For which reaction does $K_p = K_c$?

- (a) $2 \text{ Na}_2\text{O}_2(s) + 2 \text{ CO}_2(g) \rightleftharpoons 2 \text{ Na}_2\text{CO}_3(s) + \text{O}(g)$
- (b) $\text{Fe}_2\text{O}_3(s) + 3 \text{ CO}(g) \rightleftharpoons 2 \text{ Fe}(s) + 3 \text{ CO}_2(g)$
- (c) $\text{NH}_4\text{NO}_3(s) \rightleftharpoons \text{N}_2\text{O}(g) + 2 \text{ H}_2\text{O}(g)$

16.6 Calculating the Equilibrium Constant from Measured Equilibrium Concentrations

The most direct way to obtain an experimental value for the equilibrium constant of a reaction is to measure the concentrations of the reactants and products in a reaction mixture at equilibrium. Consider the following reaction:



Since equilibrium constants depend on temperature, many equilibrium problems state the temperature even though it has no formal part in the calculation.

Suppose a mixture of H_2 and I_2 is allowed to come to equilibrium at 445 °C. The measured equilibrium concentrations are $[\text{H}_2] = 0.11 \text{ M}$, $[\text{I}_2] = 0.11 \text{ M}$, and $[\text{HI}] = 0.78 \text{ M}$. What is the value of the equilibrium constant at this temperature?

We can write the expression for K_c from the balanced equation:

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

To calculate the value of K_c , we substitute the correct equilibrium concentrations into the expression for K_c :

$$\begin{aligned} K_c &= \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} \\ &= \frac{(0.78)^2}{(0.11)(0.11)} \\ &= 5.0 \times 10^1 \end{aligned}$$

The concentrations within K_c should always be written in moles per liter (M); however, as noted in Section 16.4, we do not normally include the units when expressing the value of the equilibrium constant, so K_c is unitless.

For any reaction, the equilibrium *concentrations* of the reactants and products depend on the initial concentrations (and in general vary from one set of initial concentrations to another). However, the equilibrium *constant* is always the same at a given temperature, regardless of the initial concentrations. For example, Table 16.1 shows several different equilibrium concentrations of H_2 , I_2 , and HI , each from a different set of

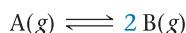
TABLE 16.1 ■ Initial and Equilibrium Concentrations for the Reaction
 $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$ at 445 °C

Initial Concentrations			Equilibrium Concentrations			Equilibrium Constant
[H ₂]	[I ₂]	[HI]	[H ₂]	[I ₂]	[HI]	$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$
0.50	0.50	0.0	0.11	0.11	0.78	$\frac{(0.78)^2}{(0.11)(0.11)} = 50$
0.0	0.0	0.50	0.055	0.055	0.39	$\frac{(0.39)^2}{(0.055)(0.055)} = 50$
0.50	0.50	0.50	0.165	0.165	1.17	$\frac{(1.17)^2}{(0.165)(0.165)} = 50$
1.0	0.50	0.0	0.53	0.033	0.934	$\frac{(0.934)^2}{(0.53)(0.033)} = 50$
0.50	1.0	0.0	0.033	0.53	0.934	$\frac{(0.934)^2}{(0.033)(0.53)} = 50$

initial concentrations. Notice that the equilibrium constant is always the same, regardless of the initial concentrations. Whether we start with only reactants or only products, the reaction reaches equilibrium concentrations at which the equilibrium constant is the same. No matter what the initial concentrations are, the reaction always goes in a direction that ensures that the equilibrium concentrations—when substituted into the equilibrium expression—give the same constant, K .

So far, we have calculated equilibrium constants from values of the equilibrium concentrations of all the reactants and products. In most cases, however, we need only know the initial concentrations of the reactant(s) and the equilibrium concentration of any *one* reactant or product. We can deduce the other equilibrium concentrations from the stoichiometry of the reaction.

For example, consider the simple reaction:



Suppose that we have a reaction mixture in which the initial concentration of A is 1.00 M and the initial concentration of B is 0.00 M. When equilibrium is reached, the concentration of A is 0.75 M. Since [A] has changed by -0.25 M, we can deduce (based on the stoichiometry) that [B] must have changed by $2 \times (+0.25)$ M or +0.50 M. We summarize the initial conditions, the changes, and the equilibrium conditions in the following table:

	[A]	[B]
Initial	1.00	0.00
Change	-0.25	+2(0.25)
Equilibrium	0.75	0.50

We refer to this type of table as an ICE table (I = initial, C = change, E = equilibrium). To calculate the equilibrium constant, we use the balanced equation to write an expression for the equilibrium constant and then substitute the equilibrium concentrations from the ICE table:

$$K = \frac{[\text{B}]^2}{[\text{A}]} = \frac{(0.50)^2}{(0.75)} = 0.33$$

In Examples 16.5 and 16.6, we show the general procedure for solving these kinds of equilibrium problems in the left column and work two examples exemplifying the procedure in the center and right columns.

WATCH NOW!

INTERACTIVE WORKED EXAMPLE VIDEO 16.5

HOW TO: Find Equilibrium Constants from Experimental Concentration Measurements

To solve these types of problems, follow the given procedure.

1. Using the balanced equation as a guide, prepare an ICE table showing the known initial concentrations and equilibrium concentrations of the reactants and products.

Leave space in the middle of the table for determining the changes in concentration that occur during the reaction.

2. For the reactant or product whose concentration is known both initially and at equilibrium, calculate the change in concentration that occurs.

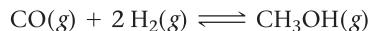
3. Use the change you calculated in step 2 and the stoichiometric relationships from the balanced chemical equation to determine the changes in concentration of all other reactants and products. Since reactants are consumed during the reaction, the changes in their concentrations are negative. Since products are formed, the changes in their concentrations are positive.

4. Sum each column for each reactant and product to determine the equilibrium concentrations.

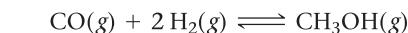
EXAMPLE 16.5

Finding Equilibrium Constants from Experimental Concentration Measurements

Consider the following reaction:



A reaction mixture at 780 °C initially contains $[\text{CO}] = 0.500 \text{ M}$ and $[\text{H}_2] = 1.00 \text{ M}$. At equilibrium, the CO concentration is found to be 0.15 M. What is the value of the equilibrium constant?



	[CO]	[H ₂]	[CH ₃ OH]
Initial	0.500	1.00	0.00
Change			
Equil	0.15		

EXAMPLE 16.6

Finding Equilibrium Constants from Experimental Concentration Measurements

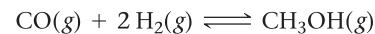
Consider the following reaction:



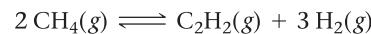
A reaction mixture at 1700 °C initially contains $[\text{CH}_4] = 0.115 \text{ M}$. At equilibrium, the mixture contains $[\text{C}_2\text{H}_2] = 0.035 \text{ M}$. What is the value of the equilibrium constant?



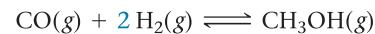
	[CH ₄]	[C ₂ H ₂]	[H ₂]
Initial	0.115	0.00	0.00
Change			
Equil		0.035	



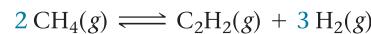
	[CO]	[H ₂]	[CH ₃ OH]
Initial	0.500	1.00	0.00
Change	-0.35		
Equil	0.15		



	[CH ₄]	[C ₂ H ₂]	[H ₂]
Initial	0.115	0.00	0.00
Change		+0.035	
Equil		0.035	



	[CO]	[H ₂]	[CH ₃ OH]
Initial	0.500	1.00	0.00
Change	-0.35	-2(0.35)	+0.35
Equil	0.15		



	[CH ₄]	[C ₂ H ₂]	[H ₂]
Initial	0.115	0.00	0.00
Change	-2(0.035)	+0.035	+3(0.035)
Equil		0.035	



	[CO]	[H ₂]	[CH ₃ OH]
Initial	0.500	1.00	0.00
Change	-0.35	-0.70	+0.35
Equil	0.15	0.30	0.35



	[CH ₄]	[C ₂ H ₂]	[H ₂]
Initial	0.115	0.00	0.00
Change	-0.070	+0.035	+0.105
Equil	0.045	0.035	0.105

- 5. Use the balanced equation to write an expression for the equilibrium constant and substitute the equilibrium concentrations to calculate K.**

$$K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2}$$

$$= \frac{0.35}{(0.15)(0.30)^2}$$

$$= 26$$

$$K_c = \frac{[\text{C}_2\text{H}_2][\text{H}_2]^3}{[\text{CH}_4]^2}$$

$$= \frac{(0.035)(0.105)^3}{(0.045)^2}$$

$$= 0.020$$

FOR PRACTICE 16.5 The reaction in Example 16.5 between CO and H₂ is carried out at a different temperature with initial concentrations of [CO] = 0.27 M and [H₂] = 0.49 M. At equilibrium, the concentration of CH₃OH is 0.11 M. Find the equilibrium constant at this temperature.

FOR PRACTICE 16.6 The reaction of CH₄ in Example 16.6 is carried out at a different temperature with an initial concentration of [CH₄] = 0.087 M. At equilibrium, the concentration of H₂ is 0.012 M. Find the equilibrium constant at this temperature.

16.7

The Reaction Quotient: Predicting the Direction of Change

When the reactants of a chemical reaction mix, they generally react to form products—we say that the reaction proceeds to the right (toward the products). The amount of products formed when a reaction reaches equilibrium depends on the magnitude of the equilibrium constant, as we have seen. However, what if a reaction mixture that is not at equilibrium contains both reactants *and products*? Can we predict the direction of change for such a mixture?

To gauge the progress of a reaction relative to equilibrium, we use a quantity called the *reaction quotient*. The definition of the reaction quotient takes the same form as the definition of the equilibrium constant, except that the reaction need not be at equilibrium. So, for the general reaction:



we define the **reaction quotient (Q_c)** as the ratio—at any point in the reaction—of the concentrations of the products raised to their stoichiometric coefficients divided by the concentrations of the reactants raised to their stoichiometric coefficients. For gases with amounts measured in atmospheres, the reaction quotient uses the partial pressures in place of concentrations and is called Q_p:

$$Q_c = \frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b} \quad Q_p = \frac{P_{\text{C}}^c P_{\text{D}}^d}{P_{\text{A}}^a P_{\text{B}}^b}$$

The difference between the reaction quotient and the equilibrium constant is that, at a given temperature, the equilibrium constant has only one value and it specifies the relative amounts of reactants and products *at equilibrium*. The reaction quotient, by contrast, depends on the current state of the reaction and has many different values as the reaction proceeds. For example, in a reaction mixture containing only reactants, the reaction quotient is zero (Q_c = 0):

$$Q_c = \frac{[0]^c[0]^d}{[\text{A}]^a[\text{B}]^b} = 0$$

In a reaction mixture containing only products, the reaction quotient is infinite (Q_c = ∞):

$$Q_c = \frac{[\text{C}]^c[\text{D}]^d}{[0]^a[0]^b} = \infty$$

In a reaction mixture containing both reactants and products, each at a concentration of 1 M, the reaction quotient is one (Q_c = 1):

$$Q_c = \frac{(1)^c(1)^d}{(1)^a(1)^b} = 1$$

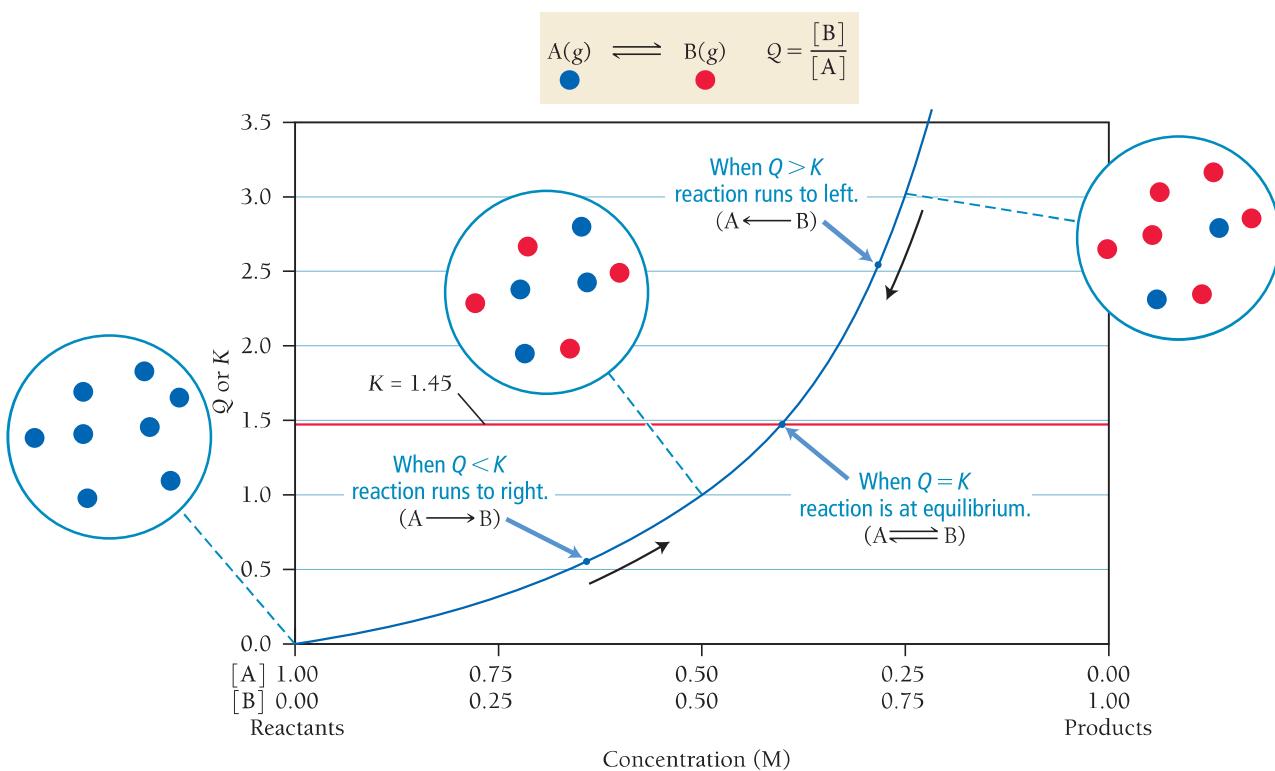
The reaction quotient is useful because *the value of Q relative to K is a measure of the progress of the reaction toward equilibrium. At equilibrium, the reaction quotient is equal to the*

WATCH NOW!

KEY CONCEPT VIDEO 16.7



The Reaction Quotient

Q, K, and the Direction of a Reaction

▲ FIGURE 16.7 Q , K , and the Direction of a Reaction The graph shows a plot of Q as a function of the concentrations of the reactants and products in a simple reaction $A \rightleftharpoons B$, in which $K = 1.45$ and the sum of the reactant and product concentrations is 1 M. The far left of the graph represents pure reactant, and the far right represents pure product. The midpoint of the graph represents an equal mixture of A and B. When Q is less than K , the reaction moves in the forward direction ($A \rightarrow B$). When Q is greater than K , the reaction moves in the reverse direction ($A \leftarrow B$). When Q is equal to K , the reaction is at equilibrium.

equilibrium constant. Figure 16.7▲ shows a plot of Q as a function of the concentrations of A and B for the simple reaction $A(g) \rightleftharpoons B(g)$, which has an equilibrium constant of $K = 1.45$. The following points are representative of three possible conditions:

Q	K	Predicted Direction of Reaction
0.55	1.45	To the right (toward products)
2.55	1.45	To the left (toward reactants)
1.45	1.45	No change (at equilibrium)

For the first set of values in the table, Q is less than K and must therefore get larger as the reaction proceeds toward equilibrium. Q becomes larger as the reactant concentration decreases and the product concentration increases—the reaction proceeds to the right. For the second set of values, Q is greater than K and must therefore get smaller as the reaction proceeds toward equilibrium. Q gets smaller as the reactant concentration increases and the product concentration decreases—the reaction proceeds to the left. In the third set of values, $Q = K$, implying that the reaction is at equilibrium—the reaction will not proceed in either direction.

Summarizing Direction of Change Predictions:

The reaction quotient (Q) relative to the equilibrium constant (K) is a measure of the progress of a reaction toward equilibrium.

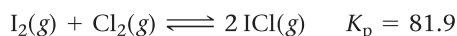
- $Q < K$ Reaction goes to the right (toward products).
- $Q > K$ Reaction goes to the left (toward reactants).
- $Q = K$ Reaction is at equilibrium.

WATCH NOW!

INTERACTIVE WORKED EXAMPLE 16.7

EXAMPLE 16.7 Predicting the Direction of a Reaction by Comparing Q and K 

Consider the reaction and its equilibrium constant at 25.0 °C:



A reaction mixture contains $P_{I_2} = 0.114$ atm, $P_{Cl_2} = 0.102$ atm, and $P_{ICl} = 0.355$ atm. Is the reaction mixture at equilibrium? If not, in which direction will the reaction proceed?

SOLUTION

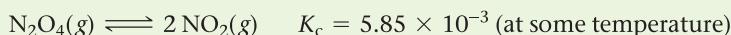
To determine the progress of the reaction relative to the equilibrium state, first calculate Q .

$$\begin{aligned} Q_p &= \left(\frac{P_{ICl}^2}{P_{I_2} P_{Cl_2}} \right) \\ &= \frac{(0.355)^2}{(0.114)(0.102)} \\ &= 10.8 \end{aligned}$$

Compare Q to K .

$$Q_p = 10.8; K_p = 81.9$$

Since $Q_p < K_p$, the reaction is not at equilibrium and will proceed to the right.

FOR PRACTICE 16.7 Consider the reaction and its equilibrium constant:

A reaction mixture contains $[NO_2] = 0.0255$ M and $[N_2O_4] = 0.0331$ M. Calculate Q_c and determine the direction in which the reaction will proceed.

Q AND K For the reaction $N_2O_4(g) \rightleftharpoons 2 NO_2(g)$, a reaction mixture at a certain temperature initially contains both N_2O_4 and NO_2 in their standard states, which means that $P_{N_2O_4} = 1$ atm and $P_{NO_2} = 1$ atm (see the definition of standard state in Section 7.9). If $K_p = 0.15$, which statement is true of the reaction mixture before any reaction occurs?

- (a) $Q = K$; the reaction is at equilibrium.
- (b) $Q < K$; the reaction will proceed to the right.
- (c) $Q > K$; the reaction will proceed to the left.

16.8**Cc**

Conceptual Connection

ANSWER NOW!

**16.8****Finding Equilibrium Concentrations**

In Section 16.6, we discussed how to calculate an equilibrium constant from the equilibrium concentrations of the reactants and products. Just as commonly, we will want to calculate equilibrium concentrations of reactants or products from the equilibrium constant. These kinds of calculations are important because they allow us to calculate the amount of a reactant or product at equilibrium. For example, in a synthesis reaction, we might want to know how much of the product forms when the reaction reaches equilibrium. Or for the hemoglobin–oxygen equilibrium discussed in Section 16.1, we might want to know the concentration of oxygenated hemoglobin present under certain oxygen concentrations within the lungs or muscles.

We divide these types of problems into two categories: (1) finding equilibrium concentrations when we know the equilibrium constant and all but one of the equilibrium concentrations of the reactants and products, and (2) finding equilibrium

WATCH NOW!

KEY CONCEPT VIDEO 16.8

Finding Equilibrium Concentrations from Initial Concentrations

concentrations when we know the equilibrium constant and only initial concentrations. The second category of problem is more difficult than the first. Let's examine each separately.

Finding Equilibrium Concentrations from the Equilibrium Constant and All but One of the Equilibrium Concentrations of the Reactants and Products

We can use the equilibrium constant to calculate the equilibrium concentration of one of the reactants or products, given the equilibrium concentrations of the others. To solve this type of problem, we follow our general problem-solving procedure.

WATCH NOW!

INTERACTIVE WORKED EXAMPLE 16.8

EXAMPLE 16.8

Consider the following reaction:



In an equilibrium mixture, the concentration of COF_2 is 0.255 M and the concentration of CF_4 is 0.118 M. What is the equilibrium concentration of CO_2 ?

SORT You are given the equilibrium constant of a chemical reaction, together with the equilibrium concentrations of the reactant and one product. You are asked to find the equilibrium concentration of the other product.

GIVEN: $[\text{COF}_2] = 0.255 \text{ M}$
 $[\text{CF}_4] = 0.118 \text{ M}$
 $K_c = 2.00$

FIND: $[\text{CO}_2]$

STRATEGIZE Calculate the concentration of the product using the given quantities and the expression for K_c .

CONCEPTUAL PLAN

$$\begin{array}{ccc} [\text{COF}_2], [\text{CF}_4], K_c & \longrightarrow & [\text{CO}_2] \\ & & K_c = \frac{[\text{CO}_2][\text{CF}_4]}{[\text{COF}_2]^2} \end{array}$$

SOLVE Solve the equilibrium expression for $[\text{CO}_2]$ and then substitute in the appropriate values to calculate it.

$$\begin{aligned} \text{SOLUTION} \quad & [\text{CO}_2] = K_c \frac{[\text{COF}_2]^2}{[\text{CF}_4]} \\ & [\text{CO}_2] = 2.00 \left(\frac{(0.255)^2}{0.118} \right) = 1.10 \text{ M} \end{aligned}$$

CHECK Check your answer by mentally substituting the given values of $[\text{COF}_2]$ and $[\text{CF}_4]$, as well as your calculated value for CO_2 , back into the equilibrium expression:

$$K_c = \frac{[\text{CO}_2][\text{CF}_4]}{[\text{COF}_2]^2}$$

$[\text{CO}_2]$ is roughly equal to 1. $[\text{COF}_2]^2 \approx 0.06$ and $[\text{CF}_4] \approx 0.12$. Therefore, K_c is approximately 2, as given in the problem.

FOR PRACTICE 16.8 Diatomic iodine $[\text{I}_2]$ decomposes at high temperature to form I atoms according to the reaction:



In an equilibrium mixture, the concentration of I_2 is 0.10 M. What is the equilibrium concentration of I?

FINDING EQUILIBRIUM CONCENTRATIONS For the reaction, $A(g) \rightleftharpoons 2B(g)$, $K_c = 4.0$. A reaction mixture at equilibrium contains $[A] = 1.0\text{ M}$. What is the concentration of B in the reaction mixture?

- (a) 0.50 M (b) 1.0 M (c) 2.0 M (d) 4.0 M



ANSWER NOW!



Finding Equilibrium Concentrations from the Equilibrium Constant and Initial Concentrations or Pressures

More commonly, we know the equilibrium constant and only initial concentrations of reactants and need to find the *equilibrium concentrations* of the reactants or products. These kinds of problems are generally more involved than those we just examined and require a specific procedure to solve them. The procedure has some similarities to the one used in Examples 16.5 and 16.6 in that we set up an ICE table showing the initial concentrations, the changes, and the equilibrium concentrations. However, unlike in Examples 16.5 and 16.6, here the changes in concentration are not known and are represented with the variable x .

For example, consider again the simple reaction:



Suppose that, as before (see Section 16.6), we have a reaction mixture in which the initial concentration of A is 1.0 M and the initial concentration of B is 0.00 M. However, now we know the equilibrium constant, $K = 0.33$, and want to find the equilibrium concentrations. We know that because $Q = 0$, the reaction proceeds to the right (toward the products). We set up the ICE table with the given initial concentrations and then represent the unknown change in $[A]$ with the variable x as follows:

	[A]	[B]	
Initial	1.0	0.00	
Change	$-x$	$+2x$	Represent changes from initial conditions with the variable x .
Equil	$1.0 - x$	$2x$	

Notice that, due to the stoichiometry of the reaction, the change in [B] must be $+2x$. As before, each *equilibrium* concentration is the sum of the two entries above it in the ICE table. In order to find the equilibrium concentrations of A and B, we must find the value of the variable x . Since we know the value of the equilibrium constant, we can use the equilibrium constant expression to set up an equation in which x is the only variable:

$$K = \frac{[B]^2}{[A]} = \frac{(2x)^2}{1.0 - x} = 0.33$$

or more simply:

$$\frac{4x^2}{1.0 - x} = 0.33$$

This equation is a *quadratic* equation—it contains the variable x raised to the second power. In general, we can solve quadratic equations with the quadratic formula (see Appendix IC), which we introduce in Example 16.10. If the quadratic equation is a perfect square, however, we can solve it by simpler means, as shown in Example 16.9. For both of these examples, we give the general procedure in the left column and apply the procedure to the two examples to the right. Later in this section, we see that quadratic equations can often be simplified by making some approximations based on our chemical knowledge.

WATCH NOW!
**INTERACTIVE WORKED
EXAMPLE VIDEO 16.9**

HOW TO: Find Equilibrium Concentrations from Initial Concentrations and the Equilibrium Constant

To solve these types of problems, follow the given procedure.

1. Using the balanced equation as a guide, prepare a table showing the known initial concentrations of the reactants and products.

Leave room in the table for the changes in concentrations and for the equilibrium concentrations.

2. Use the initial concentrations to calculate the reaction quotient (Q) for the initial concentrations. Compare Q to K to predict the direction in which the reaction proceeds.

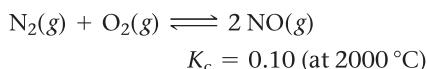
3. Represent the change in the concentration of one of the reactants or products with the variable x . Define the changes in the concentrations of the other reactants or products in terms of x . It is usually most convenient to let x represent the change in concentration of the reactant or product with the smallest stoichiometric coefficient.

4. Sum each column for each reactant and each product to determine the equilibrium concentrations in terms of the initial concentrations and the variable x .

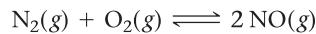
EXAMPLE 16.9

Finding Equilibrium Concentrations from Initial Concentrations and the Equilibrium Constant

Consider the reaction:



A reaction mixture at 2000 °C initially contains $[\text{N}_2] = 0.200 \text{ M}$ and $[\text{O}_2] = 0.200 \text{ M}$. Find the equilibrium concentrations of the reactants and product at this temperature.

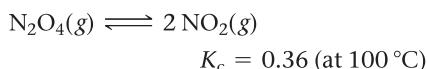


	[N ₂]	[O ₂]	[NO]
Initial	0.200	0.200	0.00
Change			
Equil			

EXAMPLE 16.10

Finding Equilibrium Concentrations from Initial Concentrations and the Equilibrium Constant

Consider the reaction:



A reaction mixture at 100 °C initially contains $[\text{NO}_2] = 0.100 \text{ M}$. Find the equilibrium concentrations of NO_2 and N_2O_4 at this temperature.



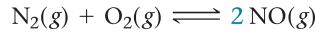
	[N ₂ O ₄]	[NO ₂]
Initial	0.00	0.100
Change		
Equil		

$$Q_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = \frac{(0.00)^2}{(0.200)(0.200)} = 0$$

$Q < K$; therefore, the reaction will proceed to the right.

$$Q_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{(0.100)^2}{0.00} = \infty$$

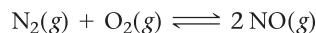
$Q > K$; therefore, the reaction will proceed to the left.



	[N ₂]	[O ₂]	[NO]
Initial	0.200	0.200	0.00
Change	-x	-x	+2x
Equil			



	[N ₂ O ₄]	[NO ₂]
Initial	0.00	0.100
Change	+x	-2x
Equil		



	[N ₂]	[O ₂]	[NO]
Initial	0.200	0.200	0.00
Change	-x	-x	+2x
Equil	0.200 - x	0.200 - x	2x



	[N ₂ O ₄]	[NO ₂]
Initial	0.00	0.100
Change	+x	-2x
Equil	x	0.100 - 2x

5. Substitute the expressions for the equilibrium concentrations (from step 4) into the expression for the equilibrium constant. Using the given value of the equilibrium constant, solve the expression for the variable x .

In some cases, such as Example 16.9, you can take the square root of both sides of the expression to solve for x . In other cases, such as Example 16.10, you must solve a quadratic equation to find x .

Remember the quadratic formula:

$$ax^2 + bx + c = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$K_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}$$

$$= \frac{(2x)^2}{(0.200 - x)(0.200 - x)}$$

$$0.10 = \frac{(2x)^2}{(0.200 - x)^2}$$

$$\sqrt{0.10} = \frac{2x}{0.200 - x}$$

$$\sqrt{0.10}(0.200 - x) = 2x$$

$$\sqrt{0.10}(0.200) - \sqrt{0.10}x = 2x$$

$$0.063 = 2x + \sqrt{0.10}x$$

$$0.063 = 2.3x$$

$$x = 0.027$$

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$

$$= \frac{(0.100 - 2x)^2}{x}$$

$$0.36 = \frac{0.0100 - 0.400x + 4x^2}{x}$$

$$0.36x = 0.0100 - 0.400x + 4x^2$$

$$4x^2 - 0.76x + 0.0100 = 0 \text{ (quadratic)}$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$= \frac{-(-0.76) \pm \sqrt{(-0.76)^2 - 4(4)(0.0100)}}{2(4)}$$

$$= \frac{0.76 \pm 0.65}{8}$$

$$x = 0.176 \text{ or } x = 0.014$$

6. Substitute x into the expressions for the equilibrium concentrations of the reactants and products (from step 4) and calculate the concentrations.

In cases where you solved a quadratic and have two values for x , choose the value for x that gives a physically realistic answer. For example, reject the value of x that results in any negative concentrations.

$$[\text{N}_2] = 0.200 - 0.027$$

$$= 0.173 \text{ M}$$

$$[\text{O}_2] = 0.200 - 0.027$$

$$= 0.173 \text{ M}$$

$$[\text{NO}] = 2(0.027)$$

$$= 0.054 \text{ M}$$

We reject the root $x = 0.176$ because it gives a negative concentration for NO_2 . Using $x = 0.014$, we get the following concentrations:

$$[\text{NO}_2] = 0.100 - 2x$$

$$= 0.100 - 2(0.014) = 0.072 \text{ M}$$

$$[\text{N}_2\text{O}_4] = x$$

$$= 0.014 \text{ M}$$

7. Check your answer by substituting the calculated equilibrium values into the equilibrium expression. The calculated value of K should match the given value of K .

Note that rounding errors could cause a difference in the least significant digit when comparing values of the equilibrium constant.

$$K_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}$$

$$= \frac{(0.054)^2}{(0.173)(0.173)} = 0.097$$

Since the calculated value of K_c matches the given value (to within one digit in the least significant figure), the answer is valid.

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{(0.072)^2}{0.014}$$

$$= 0.37$$

Since the calculated value of K_c matches the given value (to within one digit in the least significant figure), the answer is valid.

FOR PRACTICE 16.9

The reaction in Example 16.9 is carried out at a different temperature at which $K_c = 0.055$. This time, however, the reaction mixture starts with only the product, $[\text{NO}] = 0.0100 \text{ M}$, and no reactants. Find the equilibrium concentrations of N_2 , O_2 , and NO at equilibrium.

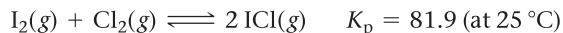
FOR PRACTICE 16.10

The reaction in Example 16.10 is carried out at the same temperature, but this time the reaction mixture initially contains only the reactant, $[\text{N}_2\text{O}_4] = 0.0250 \text{ M}$, and no NO_2 . Find the equilibrium concentrations of N_2O_4 and NO_2 .

When the initial conditions are given in terms of partial pressures (instead of concentrations) and the equilibrium constant is given as K_p instead of K_c , use the same procedure, but substitute partial pressures for concentrations, as shown in Example 16.11.

EXAMPLE 16.11**Finding Equilibrium Partial Pressures When You Are Given the Equilibrium Constant and Initial Partial Pressures**

Consider the reaction:

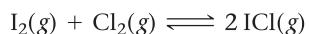


A reaction mixture at 25 °C initially contains $P_{I_2} = 0.100 \text{ atm}$, $P_{Cl_2} = 0.100 \text{ atm}$, and $P_{ICl} = 0.100 \text{ atm}$. Find the equilibrium partial pressures of I_2 , Cl_2 , and ICl at this temperature.

SOLUTION

Follow the procedure used in Examples 16.5 and 16.6 (using partial pressures in place of concentrations) to solve the problem.

- 1.** Using the balanced equation as a guide, prepare an ICE table showing the known initial partial pressures of the reactants and products.



	P_{I_2} (atm)	P_{Cl_2} (atm)	P_{ICl} (atm)
Initial	0.100	0.100	0.100
Change			
Equil			

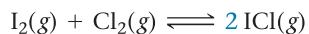
- 2.** Use the initial partial pressures to calculate the reaction quotient (Q). Compare Q to K to predict the direction in which the reaction will proceed.

$$Q_p = \frac{(P_{ICl})^2}{P_{I_2}P_{Cl_2}} = \frac{(0.100)^2}{(0.100)(0.100)} = 1$$

$$K_p = 81.9 \text{ (given)}$$

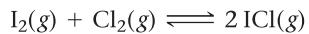
$Q < K$; therefore, the reaction will proceed to the right.

- 3.** Represent the change in the partial pressure of one of the reactants or products with the variable x . Define the changes in the partial pressures of the other reactants or products in terms of x .



	P_{I_2} (atm)	P_{Cl_2} (atm)	P_{ICl} (atm)
Initial	0.100	0.100	0.100
Change	$-x$	$-x$	$+2x$
Equil			

- 4.** Sum each column for each reactant and product to determine the equilibrium partial pressures in terms of the initial partial pressures and the variable x .



	P_{I_2} (atm)	P_{Cl_2} (atm)	P_{ICl} (atm)
Initial	0.100	0.100	0.100
Change	$-x$	$-x$	$+2x$
Equil	$0.100 - x$	$0.100 - x$	$0.100 + 2x$

- 5.** Substitute the expressions for the equilibrium partial pressures (from step 4) into the expression for the equilibrium constant. Use the given value of the equilibrium constant to solve the expression for the variable x .

$$K_p = \frac{(P_{ICl})^2}{P_{I_2}P_{Cl_2}} = \frac{(0.100 + 2x)^2}{(0.100 - x)(0.100 - x)}$$

$$81.9 = \frac{(0.100 + 2x)^2}{(0.100 - x)^2} \text{ (perfect square)}$$

$$\sqrt{81.9} = \frac{(0.100 + 2x)}{(0.100 - x)}$$

$$\sqrt{81.9}(0.100 - x) = 0.100 + 2x$$

$$\sqrt{81.9}(0.100) - \sqrt{81.9}x = 0.100 + 2x$$

$$\sqrt{81.9}(0.100) - 0.100 = 2x + \sqrt{81.9}x$$

$$0.805 = 11.05x$$

$$x = 0.0729$$

- 6.** Substitute x into the expressions for the equilibrium partial pressures of the reactants and products (from step 4) and calculate the partial pressures.

$$P_{I_2} = 0.100 - 0.0729 = 0.027 \text{ atm}$$

$$P_{Cl_2} = 0.100 - 0.0729 = 0.027 \text{ atm}$$

$$P_{ICl} = 0.100 + 2(0.0729) = 0.246 \text{ atm}$$

7. Check your answer by substituting the calculated equilibrium partial pressures into the equilibrium expression. The calculated value of K should match the given value of K .

$$K_p = \frac{(P_{\text{Cl}_1})^2}{P_{\text{I}_2} P_{\text{Cl}_2}} = \frac{(0.246)^2}{(0.027)(0.027)} = 83$$

Since the calculated value of K_p matches the given value (within the uncertainty indicated by the significant figures), the answer is valid.

FOR PRACTICE 16.11 The reaction between I_2 and Cl_2 in Example 16.11 is carried out at the same temperature, but with these initial partial pressures: $P_{\text{I}_2} = 0.150 \text{ atm}$, $P_{\text{Cl}_2} = 0.150 \text{ atm}$, $P_{\text{I}\text{Cl}} = 0.00 \text{ atm}$. Find the equilibrium partial pressures of all three substances.

Simplifying Approximations in Working Equilibrium Problems

For some equilibrium problems of the type shown in Examples 16.9, 16.10, and 16.11, we can make an approximation that simplifies the calculations without any significant loss of accuracy. For example, if the equilibrium constant is relatively small, the reaction will not proceed very far to the right. Therefore, if the initial reactant concentration is relatively large, we can make the assumption that x is small relative to the initial concentration of reactant.

To see how this approximation works, consider again the simple reaction $\text{A} \rightleftharpoons 2\text{B}$. Suppose that, as before, we have a reaction mixture in which the initial concentration of A is 1.0 M and the initial concentration of B is 0.0 M and that we want to find the equilibrium concentrations. However, suppose that in this case the equilibrium constant is much smaller, say $K = 3.3 \times 10^{-5}$. The ICE table is identical to the one we set up previously:

	[A]	[B]
Initial	1.0	0.0
Change	$-x$	$+2x$
Equil	$1.0 - x$	$2x$

Except for the value of K , we end up with the exact quadratic equation that we had before:

$$K = \frac{[\text{B}]^2}{[\text{A}]} = \frac{(2x)^2}{1.0 - x} = 3.3 \times 10^{-5}$$

or more simply:

$$\frac{4x^2}{1.0 - x} = 3.3 \times 10^{-5}$$

We can rearrange this quadratic equation into standard form and solve it using the quadratic formula. But since K is small, the reaction will not proceed very far toward products and, therefore, x will also be small. If x is much smaller than 1.0, then $(1.0 - x)$ (the quantity in the denominator) can be approximated by (1.0):

$$\frac{4x^2}{(1.0 - x)} = 3.3 \times 10^{-5}$$

This approximation greatly simplifies the equation, which we can then solve for x as follows:

$$\begin{aligned} \frac{4x^2}{1.0} &= 3.3 \times 10^{-5} \\ 4x^2 &= 3.3 \times 10^{-5} \\ x &= \sqrt{\frac{3.3 \times 10^{-5}}{4}} = 0.0029 \end{aligned}$$

We can check the validity of this approximation by comparing the calculated value of x to the number it was subtracted from. The ratio of x to the number it is subtracted from should be less than 0.05 (or 5%) for the approximation to be valid. In this case, we subtracted x from 1.0, and we calculate the ratio of the value of x to 1.0 as follows:

$$\frac{0.0029}{1.0} \times 100\% = 0.29\%$$

The approximation is therefore valid.

In Examples 16.12 and 16.13, we treat two nearly identical problems—the only difference is the initial concentration of the reactant. In Example 16.12, the initial concentration of the reactant is relatively large, the equilibrium constant is small, and the x is small approximation works well. In Example 16.13, however, the initial concentration of the reactant is much smaller, and even though the equilibrium constant is the same, the x is small approximation does not work (because the initial concentration is also small). In cases such as this, we have a couple of options to solve the problem. We can either solve the equation exactly (using the quadratic formula, for example), or we can use the *method of successive approximations*, which is introduced in Example 16.13. In this method, we essentially solve for x as if it were small, and then substitute the value obtained back into the equation (where x was initially neglected) to solve for x again. We repeat this process until the calculated value of x stops changing with each iteration, an indication that we have arrived at an acceptable value for x .

Note that the x is small approximation does not imply that x is zero. If that were the case, the reactant and product concentrations would not change from their initial values. The x is small approximation just means that when x is added or subtracted to another number, it does not change that number by very much. For example, we can calculate the value of the difference $1.0 - x$ when $x = 3.0 \times 10^{-4}$:

$$1.0 - x = 1.0 - 3.0 \times 10^{-4} = 0.9997 = 1.0$$

Since the value of 1.0 is known only to two significant figures, subtracting the small x does not change the value at all. This situation is similar to weighing yourself on a bathroom scale with and without a penny in your pocket. Unless your scale is unusually precise, removing the penny from your pocket will not change the reading on the scale. This does not imply that the penny is weightless, only that its weight is small when compared to your body weight. You can neglect the weight of the penny in reading your weight with no detectable loss in accuracy.

WATCH NOW!



INTERACTIVE WORKED EXAMPLE VIDEO 16.12

HOW TO: Determine Equilibrium Concentrations from Initial Concentrations and the Equilibrium Constant

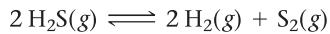
To solve these types of problems, follow the given procedure.

- Using the balanced equation as a guide, prepare a table showing the known initial concentrations of the reactants and products. (In these examples, you first calculate the concentration of H_2S from the given number of moles and volume.)

EXAMPLE 16.12

Finding Equilibrium Concentrations from Initial Concentrations in Cases with a Small Equilibrium Constant

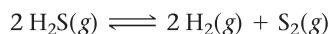
Consider the reaction for the decomposition of hydrogen disulfide:



$$K_c = 1.67 \times 10^{-7} \text{ at } 800^\circ\text{C}$$

A 0.500-L reaction vessel initially contains 0.0125 mol of H_2S at 800°C . Find the equilibrium concentrations of H_2 and S_2 .

$$[\text{H}_2\text{S}] = \frac{0.0125 \text{ mol}}{0.500 \text{ L}} = 0.0250 \text{ M}$$

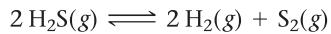


	[H_2S]	[H_2]	[S_2]
Initial	0.0250	0.00	0.00
Change			
Equil			

EXAMPLE 16.13

Finding Equilibrium Concentrations from Initial Concentrations in Cases with a Small Equilibrium Constant

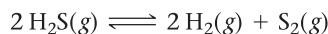
Consider the reaction for the decomposition of hydrogen disulfide:



$$K_c = 1.67 \times 10^{-7} \text{ at } 800^\circ\text{C}$$

A 0.500-L reaction vessel initially contains 1.25×10^{-4} mol of H_2S at 800°C . Find the equilibrium concentrations of H_2 and S_2 .

$$[\text{H}_2\text{S}] = \frac{1.25 \times 10^{-4} \text{ mol}}{0.500 \text{ L}} = 2.50 \times 10^{-4} \text{ M}$$



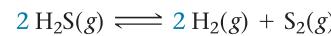
	[H_2S]	[H_2]	[S_2]
Initial	2.50×10^{-4}	0.00	0.00
Change			
Equil			

2. Use the initial concentrations to calculate the reaction quotient (Q). Compare Q to K to predict the direction in which the reaction proceeds.

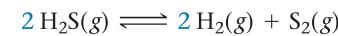
By inspection, $Q = 0$; the reaction proceeds to the right.

By inspection, $Q = 0$; the reaction proceeds to the right.

3. Represent the change in the concentration of one of the reactants or products with the variable x . Define the changes in the concentrations of the other reactants or products with respect to x .

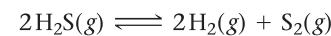


	[H ₂ S]	[H ₂]	[S ₂]
Initial	0.0250	0.00	0.00
Change	-2x	+2x	+x
Equil			

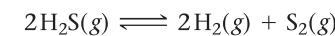


	[H ₂ S]	[H ₂]	[S ₂]
Initial	2.50×10^{-4}	0.00	0.00
Change	-2x	+2x	+x
Equil			

4. Sum each column for each reactant and product to determine the equilibrium concentrations in terms of the initial concentrations and the variable x .



	[H ₂ S]	[H ₂]	[S ₂]
Initial	0.0250	0.00	0.00
Change	-2x	+2x	+x
Equil	$0.0250 - 2x$	$2x$	x



	[H ₂ S]	[H ₂]	[S ₂]
Initial	2.50×10^{-4}	0.00	0.00
Change	-2x	+2x	+x
Equil	$2.50 \times 10^{-4} - 2x$	$2x$	x

5. Substitute the expressions for the equilibrium concentrations (from step 4) into the expression for the equilibrium constant. Use the given value of the equilibrium constant to solve the resulting equation for the variable x . In this case, the resulting equation is cubic in x . Although cubic equations can be solved, the solutions are not usually simple. However, since the equilibrium constant is small, we know that the reaction does not proceed very far to the right. Therefore, x is a small number and can be dropped from any quantities in which it is added to or subtracted from another number (as long as the number itself is not too small).

Check whether your approximation is valid by comparing the calculated value of x to the number it was added to or subtracted from. The ratio of the two numbers should be less than 0.05 (or 5%) for the approximation to be valid. If the approximation is not valid, proceed to step 5a.

$$K_c = \frac{[\text{H}_2]^2[\text{S}_2]}{[\text{H}_2\text{S}]^2}$$

$$= \frac{(2x)^2x}{(0.0250 - 2x)^2}$$

$$1.67 \times 10^{-7} = \frac{4x^3}{(0.0250 - 2x)^2}$$

$$1.67 \times 10^{-7} = \frac{4x^3}{(0.0250 - 2x)^2} \quad \text{x is small.}$$

$$1.67 \times 10^{-7} = \frac{4x^3}{6.25 \times 10^{-4}}$$

$$6.25 \times 10^{-4}(1.67 \times 10^{-7}) = 4x^3$$

$$x^3 = \frac{6.25 \times 10^{-4}(1.67 \times 10^{-7})}{4}$$

$$x = 2.97 \times 10^{-4}$$

Checking the x is small approximation:

$$\frac{2.97 \times 10^{-4}}{0.0250} \times 100\% = 1.19\%$$

The x is small approximation is valid; proceed to step 6.

$$K_c = \frac{[\text{H}_2]^2[\text{S}_2]}{[\text{H}_2\text{S}]^2}$$

$$= \frac{(2x)^2x}{(2.50 \times 10^{-4} - 2x)^2}$$

$$1.67 \times 10^{-7} = \frac{4x^3}{(2.50 \times 10^{-4} - 2x)^2}$$

$$1.67 \times 10^{-7} = \frac{4x^3}{(2.50 \times 10^{-4} - 2x)^2} \quad \text{x is small.}$$

$$1.67 \times 10^{-7} = \frac{4x^3}{6.25 \times 10^{-8}}$$

$$6.25 \times 10^{-8}(1.67 \times 10^{-7}) = 4x^3$$

$$x^3 = \frac{6.25 \times 10^{-8}(1.67 \times 10^{-7})}{4}$$

$$x = 1.38 \times 10^{-5}$$

Checking the x is small approximation:

$$\frac{1.38 \times 10^{-5}}{2.50 \times 10^{-4}} \times 100\% = 5.52\%$$

The approximation does not satisfy the <5% rule (although it is close).

Continued—

- 5a.** If the approximation is not valid, you can either solve the equation exactly (by hand or with your calculator) or use the method of successive approximations. In this example, the method of successive approximations is used.

Substitute the value obtained for x in step 5 back into the original cubic equation, but only at the exact spot where you assumed x was negligible, and then solve the equation for x again. Continue this procedure until the value of x you obtain from solving the equation is the same as the one that you substituted into the equation.

- 6.** Substitute x into the expressions for the equilibrium concentrations of the reactants and products (from step 4) and calculate the concentrations.

$$\begin{aligned} [\text{H}_2\text{S}] &= 0.0250 - 2(2.97 \times 10^{-4}) \\ &= 0.0244 \text{ M} \\ [\text{H}_2] &= 2(2.97 \times 10^{-4}) \\ &= 5.94 \times 10^{-4} \text{ M} \\ [\text{S}_2] &= 2.97 \times 10^{-4} \text{ M} \end{aligned}$$

- 7.** Check your answer by substituting the calculated equilibrium values into the equilibrium expression. The calculated value of K should match the given value of K . Note that the approximation method and rounding errors could cause a difference of up to about 5% when comparing values of the equilibrium constant.

$$K_c = \frac{(5.94 \times 10^{-4})(2.97 \times 10^{-4})}{(0.0244)^2} = 1.76 \times 10^{-7}$$

The calculated value of K is close enough to the given value when you consider the uncertainty introduced by the approximation. Therefore, the answer is valid.

FOR PRACTICE 16.12

The reaction in Example 16.12 is carried out at the same temperature with the following initial concentrations: $[\text{H}_2\text{S}] = 0.100 \text{ M}$, $[\text{H}_2] = 0.100 \text{ M}$, and $[\text{S}_2] = 0.00 \text{ M}$. Find the equilibrium concentration of $[\text{S}_2]$.

$$1.67 \times 10^{-7} = \frac{4x^3}{(2.50 \times 10^{-4} - 2x)^2}$$

$$x = 1.38 \times 10^{-5}$$

$$\begin{aligned} 1.67 \times 10^{-7} &= \frac{4x^3}{(2.50 \times 10^{-4} - 2.76 \times 10^{-5})^2} \\ x &= 1.27 \times 10^{-5} \end{aligned}$$

If we substitute this value of x back into the cubic equation and solve it, we get $x = 1.28 \times 10^{-5}$, which is nearly identical to 1.27×10^{-5} . Therefore, we have arrived at the best approximation for x .

$$\begin{aligned} [\text{H}_2\text{S}] &= 2.50 \times 10^{-4} - 2(1.28 \times 10^{-5}) \\ &= 2.24 \times 10^{-4} \text{ M} \\ [\text{H}_2] &= 2(1.28 \times 10^{-5}) \\ &= 2.56 \times 10^{-5} \text{ M} \\ [\text{S}_2] &= 1.28 \times 10^{-5} \text{ M} \end{aligned}$$

$$K_c = \frac{(2.56 \times 10^{-5})^2(1.28 \times 10^{-5})}{(2.24 \times 10^{-4})^2} = 1.67 \times 10^{-7}$$

The calculated value of K is equal to the given value. Therefore, the answer is valid.

ANSWER NOW!



16.10

Cc
Conceptual Connection

THE X IS SMALL APPROXIMATION

For the generic reaction, $\text{A}(g) \rightleftharpoons \text{B}(g)$, consider each value of K and initial concentration of A . For which set of values does the x is small approximation most likely apply?

- (a) $K = 1.0 \times 10^{-5}$; $[\text{A}] = 0.250 \text{ M}$
 (b) $K = 1.0 \times 10^{-2}$; $[\text{A}] = 0.250 \text{ M}$
 (c) $K = 1.0 \times 10^{-5}$; $[\text{A}] = 0.00250 \text{ M}$
 (d) $K = 1.0 \times 10^{-2}$; $[\text{A}] = 0.00250 \text{ M}$

16.9

Le Châtelier's Principle: How a System at Equilibrium Responds to Disturbances

We have seen that a chemical system not in equilibrium tends to progress toward equilibrium and that the relative concentrations of the reactants and products at equilibrium are characterized by the equilibrium constant, K . What happens, however, when a chemical system already at equilibrium is disturbed? **Le Châtelier's principle** states that the chemical system responds to minimize the disturbance.

Le Châtelier's principle: When a chemical system at equilibrium is disturbed, the system shifts in a direction that minimizes the disturbance.

In other words, a system at equilibrium tends to maintain that equilibrium—it bounces back when disturbed.

We can understand Le Châtelier's principle by returning to our two neighboring countries analogy. Suppose the populations of Country A and Country B are at equilibrium. This means that the rate of people moving out of Country A and into Country B is equal to the rate of people moving into Country A and out of Country B, and the populations of the two countries are stable:



Now imagine disturbing the balance (Figure 16.8▼). Suppose there is a notable increase in the birthrate in Country B. What happens? After Country B becomes more crowded, the rate of people leaving Country B increases. The net flow of people is out of Country B and into Country A. Equilibrium is disturbed by the addition of more people to Country B, and people leave Country B in response. In effect, the system responded by shifting in the direction that minimized the disturbance.

On the other hand, what happens if there is a baby boom in Country A? As Country A gets more crowded, the rate of people leaving Country A increases. The net flow of people is out of Country A and into Country B. The number of people in Country A initially increases, and the system responds; people move out of Country A.

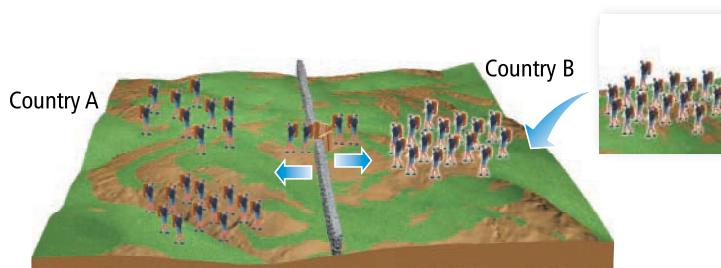
WATCH NOW!

KEY CONCEPT VIDEO 16.9

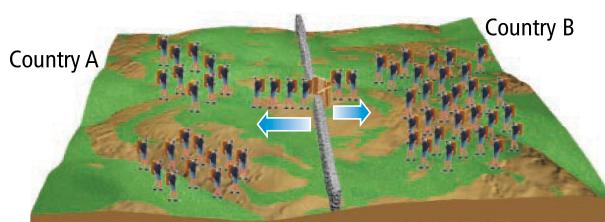


Pronounced "Le-sha-te-lyay."

Le Châtelier's Principle: An Analogy



Equilibrium is disturbed when the population in Country B grows.



System responds to minimize disturbance.

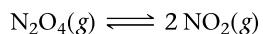
The two-country analogy should help you see the effects of disturbing a system in equilibrium—it should not be taken as an exact parallel.

◀ **FIGURE 16.8** A Population Analogy for Le Châtelier's Principle A baby boom in Country B shifts the equilibrium to the left. People leave Country B (because it has become too crowded) and migrate to Country A until equilibrium is reestablished.

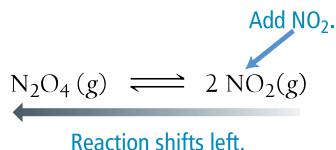
Chemical systems behave similarly: when their equilibrium is disturbed, they react to counter the disturbance. We can disturb a system in chemical equilibrium in several different ways, including changing the concentration of a reactant or product, changing the volume or pressure, and changing the temperature. We consider each of these separately.

The Effect of a Concentration Change on Equilibrium

Consider the following reaction in chemical equilibrium:



Suppose we disturb the equilibrium by adding NO_2 to the equilibrium mixture (Figure 16.9▼). In other words, we increase the concentration of NO_2 , the product. What happens? According to Le Châtelier's principle, the system shifts in a direction to minimize the disturbance. The reaction goes to the left (it proceeds in the reverse direction), consuming some of the added NO_2 and thus bringing its concentration back down, as shown graphically in Figure 16.10a►:



The reaction shifts to the left because the value of Q changes as follows:

- Before addition of NO_2 : $Q = K$.
- Immediately after addition of NO_2 : $Q > K$.
- Reaction shifts to the left to reestablish equilibrium.

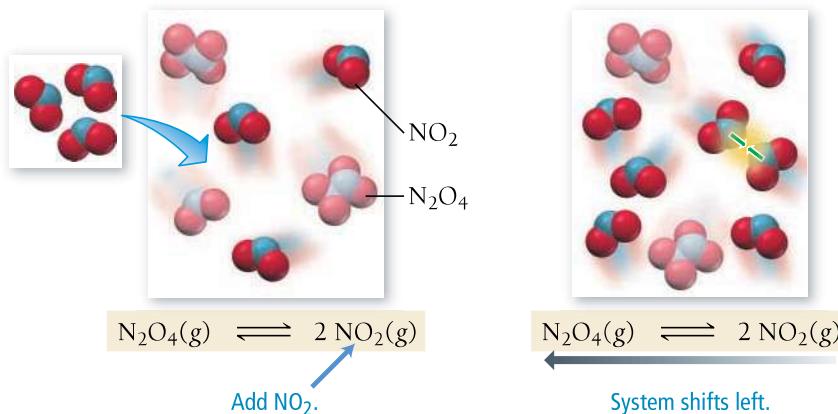
But what happens if we add extra N_2O_4 (the reactant), increasing its concentration? In this case, the reaction shifts to the right, consuming some of the added N_2O_4 and bringing its concentration back down, as shown graphically in Figure 16.10b►:

Le Châtelier's Principle: Changing Concentration

When you add more NO_2 to the reaction mixture...

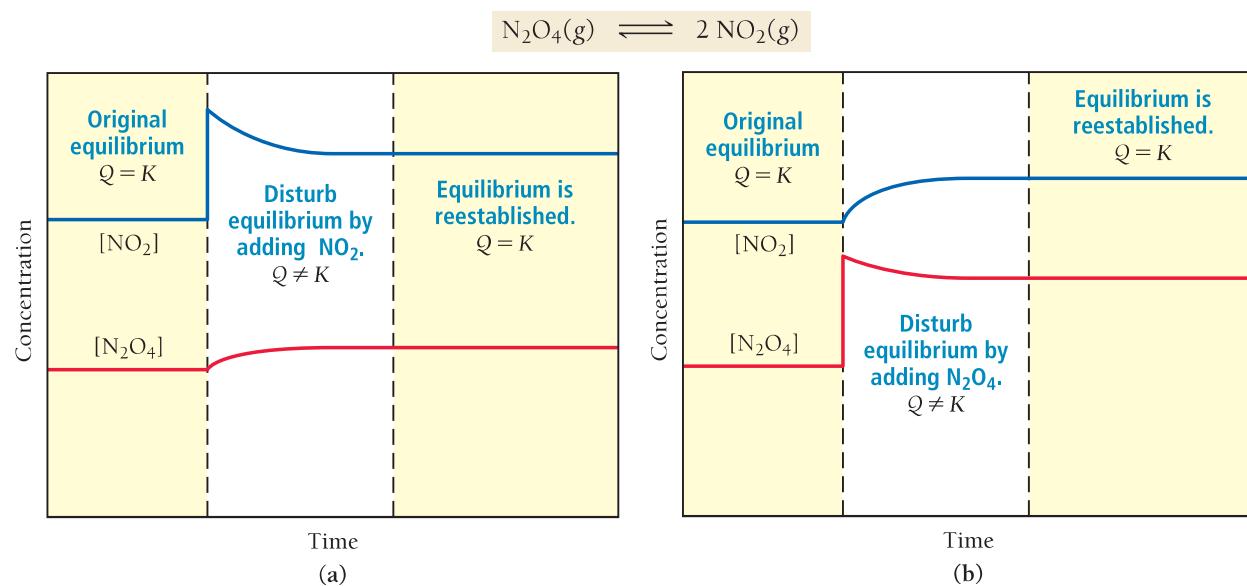
... equilibrium is disturbed...

...and the reaction shifts to the left, consuming some of the added NO_2 (and forming N_2O_4).

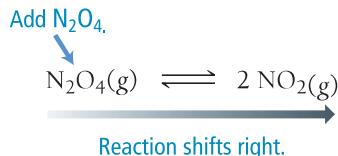


▲ FIGURE 16.9 Le Châtelier's Principle: The Effect of a Concentration Change Adding NO_2 causes the reaction to shift left, consuming some of the added NO_2 and forming more N_2O_4 .

Le Châtelier's Principle: Graphical Representation



▲ FIGURE 16.10 Le Châtelier's Principle: Changing Concentration The graph shows the concentrations of NO_2 and N_2O_4 for the reaction $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$ as a function of time in three distinct stages of the reaction: initially at equilibrium (left), upon disturbance of the equilibrium by addition of more NO_2 (a) or N_2O_4 (b) to the reaction mixture (center), and upon reestablishment of equilibrium (right).



The reaction shifts to the right because the value of Q changes as follows:

- Before addition of N_2O_4 : $Q = K$.
- Immediately after addition of N_2O_4 : $Q < K$.
- Reaction shifts to the right to reestablish equilibrium.

In both of these cases (either adding NO_2 or adding N_2O_4), the system shifts in a direction that minimizes the disturbance. Lowering the concentration of a reactant (which makes $Q > K$) causes the system to shift in the direction of the reactants to minimize the disturbance. Lowering the concentration of a product (which makes $Q < K$) causes the system to shift in the direction of products.

Summarizing the Effect of a Concentration Change on Equilibrium:

If a chemical system is at equilibrium:

- Increasing the concentration of one or more of the *reactants* (which makes $Q < K$) causes the reaction to *shift to the right* (in the direction of the products).
- Increasing the concentration of one or more of the *products* (which makes $Q > K$) causes the reaction to *shift to the left* (in the direction of the reactants).
- Decreasing the concentration of one or more of the *reactants* (which makes $Q > K$) causes the reaction to *shift to the left* (in the direction of the reactants).
- Decreasing the concentration of one or more of the *products* (which makes $Q < K$) causes the reaction to *shift to the right* (in the direction of the products).

WATCH NOW!

INTERACTIVE WORKED EXAMPLE 16.14

EXAMPLE 16.14 The Effect of a Concentration Change on Equilibrium

Consider the following reaction at equilibrium:

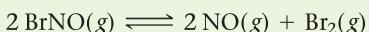


What is the effect of adding additional CO_2 to the reaction mixture? What is the effect of adding additional CaCO_3 ?

SOLUTION

Adding additional CO_2 increases the concentration of CO_2 and causes the reaction to shift to the left. Adding additional CaCO_3 , however, does *not* increase the concentration of CaCO_3 because CaCO_3 is a solid and therefore has a constant concentration. Thus, adding additional CaCO_3 has no effect on the position of the equilibrium. (Note that, as we saw in Section 16.5, solids are not included in the equilibrium expression.)

FOR PRACTICE 16.14 Consider the following reaction in chemical equilibrium:



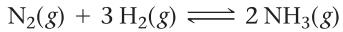
What is the effect of adding additional Br_2 to the reaction mixture? What is the effect of adding additional BrNO ?

The Effect of a Volume (or Pressure) Change on Equilibrium

In considering the effect of a change in volume, we are assuming that the change in volume is carried out at constant temperature.

How does a system in chemical equilibrium respond to a volume change? Recall from Chapter 6 that changing the volume of a gas (or a gas mixture) results in a change in pressure. Remember also that pressure and volume are inversely related: a *decrease* in volume causes an *increase* in pressure, and an *increase* in volume causes a *decrease* in pressure. So, if the volume of a reaction mixture at chemical equilibrium is changed, the pressure changes and the system shifts in a direction to minimize that change.

For example, consider the following reaction at equilibrium in a cylinder equipped with a moveable piston:



What happens if we push down on the piston, lowering the volume and raising the pressure (Figure 16.11►)? How can the chemical system respond to bring the pressure back down? Look carefully at the reaction coefficients. If the reaction shifts to the right, 4 mol of gas particles are converted to 2 mol of gas particles. From the ideal gas law ($PV = nRT$), we know that decreasing the number of moles of a gas (n) results in a lower pressure (P). Therefore, the system shifts to the right, decreasing the number of gas molecules and bringing the pressure back down, minimizing the disturbance.

Consider the same reaction mixture at equilibrium again. What happens if, this time, we pull *up* on the piston, *increasing* the volume (Figure 16.11b►)? The higher volume results in a lower pressure and the system responds to bring the pressure back up. It does this by shifting to the left, converting 2 mol of gas particles into 4 mol of gas particles, increasing the pressure and minimizing the disturbance.

Consider again the same reaction mixture at equilibrium. What happens if, this time, we keep the volume the same but increase the pressure by *adding an inert gas* to the mixture? Although the overall pressure of the mixture increases, the partial pressures of the reactants and products do not change. Consequently, there is no effect, and the reaction does not shift in either direction.

Summarizing the Effect of Volume Change on Equilibrium:

If a chemical system is at equilibrium:

- *Decreasing* the volume causes the reaction to shift in the direction that has *the fewer moles of gas particles*.
- *Increasing* the volume causes the reaction to shift in the direction that has *the greater number of moles of gas particles*.

- If a reaction has an equal number of moles of gas on both sides of the chemical equation, then a change in volume produces no effect on the equilibrium.
- Adding an inert gas to the mixture at a fixed volume has no effect on the equilibrium.

Le Châtelier's Principle: Changing Pressure

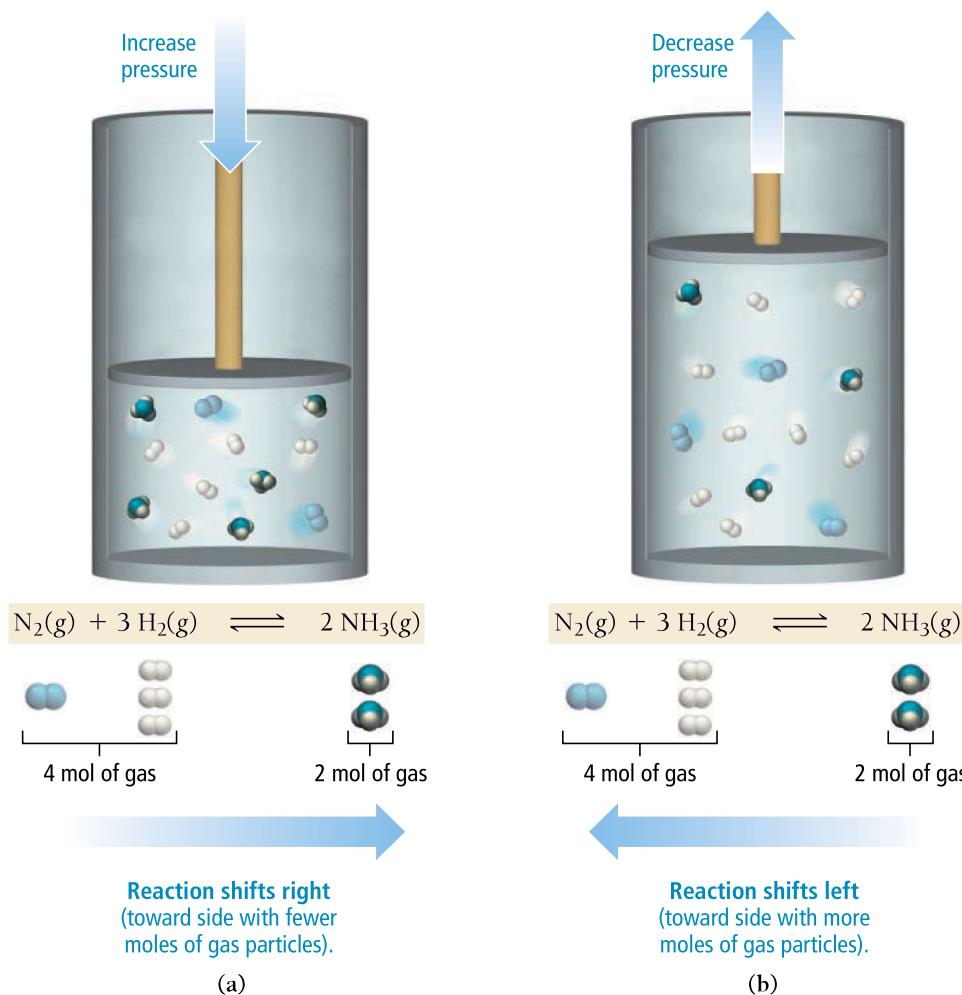
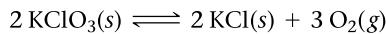


FIGURE 16.11 Le Châtelier's Principle: The Effect of a Pressure Change (a) Decreasing the volume increases the pressure, causing the reaction to shift to the right (fewer moles of gas, lower pressure). (b) Increasing the volume reduces the pressure, causing the reaction to shift to the left (more moles of gas, higher pressure).

EXAMPLE 16.15 The Effect of a Volume Change on Equilibrium

Consider the following reaction at chemical equilibrium:

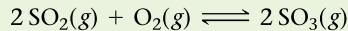


What is the effect of decreasing the volume of the reaction mixture? Increasing the volume of the reaction mixture? Adding an inert gas at constant volume?

SOLUTION

The chemical equation has 3 mol of gas on the right and zero moles of gas on the left. Decreasing the volume of the reaction mixture increases the pressure and causes the reaction to shift to the left (toward the side with fewer moles of gas particles). Increasing the volume of the reaction mixture decreases the pressure and causes the reaction to shift to the right (toward the side with more moles of gas particles.) Adding an inert gas has no effect.

FOR PRACTICE 16.15 Consider the following reaction at chemical equilibrium:



What is the effect of decreasing the volume of the reaction mixture? Increasing the volume of the reaction mixture?

In considering the effect of a change in temperature, we are assuming that the heat is added (or removed) at constant pressure.

The Effect of a Temperature Change on Equilibrium

When a system at equilibrium is disturbed by a change in concentration or a change in volume, the equilibrium shifts to counter the change, but *the equilibrium constant does not change*. In other words, changes in volume or concentration generally change Q , not K , and the system responds by shifting so that Q becomes equal to K . In contrast, a change in temperature changes the actual value of the equilibrium constant. Nonetheless, we can use Le Châtelier's principle to predict the effects of a temperature change.

If we increase the temperature of a reaction mixture at equilibrium, the reaction shifts in the direction that tends to decrease the temperature and vice versa. Recall from Chapter 7 that an exothermic reaction (negative ΔH) emits heat:

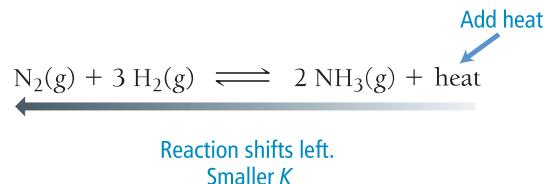


We can think of heat as a product in an exothermic reaction. In an endothermic reaction (positive ΔH), the reaction absorbs heat:



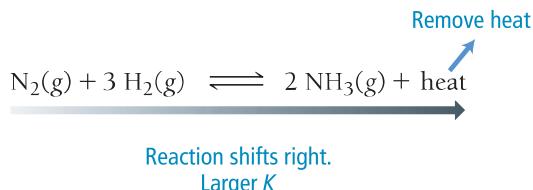
We can think of heat as a reactant in an endothermic reaction.

At constant pressure, raising the temperature of an *exothermic* reaction—think of this as adding heat—is similar to adding more product, causing the reaction to shift left. For example, the reaction of nitrogen with hydrogen to form ammonia is exothermic:

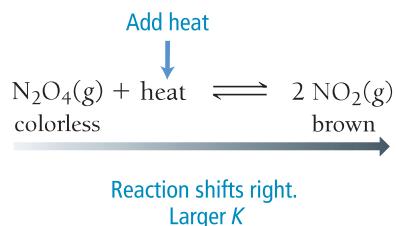


Raising the temperature of an equilibrium mixture of these three gases causes the reaction to shift left, absorbing some of the added heat and forming less products and more reactants. Note that, unlike adding additional NH_3 to the reaction mixture (which does *not* change the value of the equilibrium constant), *changing the temperature does change the value of the equilibrium constant*. The new equilibrium mixture will have more reactants and fewer products and therefore a smaller value of K .

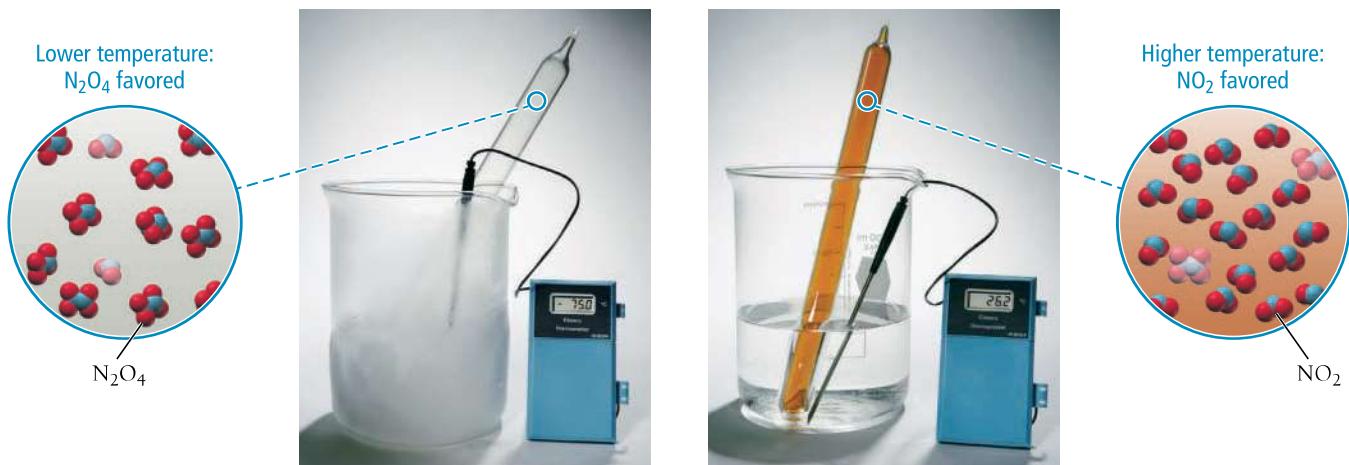
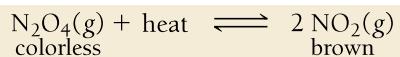
Conversely, lowering the temperature causes the reaction to shift right, releasing heat and producing more products because the value of K has increased:



In contrast, for an *endothermic* reaction, raising the temperature (adding heat) causes the reaction to shift right to absorb the added heat. For example, the following reaction is endothermic:



Le Châtelier's Principle: Changing Temperature

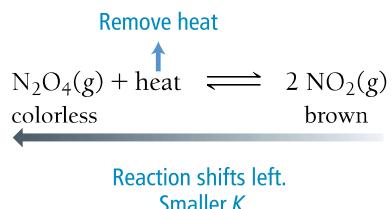


▲ FIGURE 16.12 Le Châtelier's Principle: The Effect of a Temperature Change

Because the reaction is endothermic, raising the temperature causes a shift to the right, toward the formation of brown NO_2 .

On the one hand, raising the temperature of an equilibrium mixture of these two gases causes the reaction to shift right, absorbing some of the added heat and producing more products because the value of K has increased. Because N_2O_4 is colorless and NO_2 is brown, the effects of changing the temperature of this reaction are easily seen (Figure 16.12▲).

On the other hand, lowering the temperature (removing heat) of a reaction mixture of these two gases causes the reaction to shift left, releasing heat, forming less products, and lowering the value of K :



Summarizing the Effect of a Temperature Change on Equilibrium:

In an *exothermic* chemical reaction, heat is a product.

- Increasing the temperature causes an exothermic reaction to *shift left* (in the direction of the reactants); the value of the equilibrium constant decreases.
- Decreasing the temperature causes an exothermic reaction to *shift right* (in the direction of the products); the value of the equilibrium constant increases.

In an *endothermic* chemical reaction, heat is a reactant.

- Increasing the temperature causes an endothermic reaction to *shift right* (in the direction of the products); the equilibrium constant increases.
- Decreasing the temperature causes an endothermic reaction to *shift left* (in the direction of the reactants); the equilibrium constant decreases.

Adding heat favors the endothermic direction. Removing heat favors the exothermic direction.

EXAMPLE 16.16 The Effect of a Temperature Change on Equilibrium

The following reaction is endothermic:



What is the effect of increasing the temperature of the reaction mixture? Decreasing the temperature?

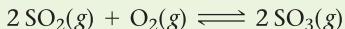
SOLUTION

Since the reaction is endothermic, we can think of heat as a reactant:



Raising the temperature is like adding a reactant, causing the reaction to shift to the right. Lowering the temperature is equivalent to removing a reactant, causing the reaction to shift to the left.

FOR PRACTICE 16.16 The following reaction is exothermic:



What is the effect of increasing the temperature of the reaction mixture? Decreasing the temperature?

ANSWER NOW!



16.11 Cc

Conceptual Connection

LE CHÂTELIER'S PRINCIPLE

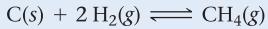
Consider the exothermic reaction $2 \text{NO}(g) + \text{Cl}_2(g) \rightleftharpoons 2 \text{NOCl}(g)$. Which change causes a reaction mixture at equilibrium to shift right?

- (a) Adding NOCl to the reaction mixture.
- (b) Increasing the volume of the reaction vessel at constant temperature.
- (c) Increasing the temperature of the reaction vessel.
- (d) None of the above.

QUIZ YOURSELF NOW!

Self-Assessment Quiz

- Q1.** What is the correct expression for the equilibrium constant (K_c) for the reaction between carbon and hydrogen gas to form methane shown here?



MISSED THIS? Read Section 16.3; Watch KCV 16.3

- | | |
|---|---|
| a) $K_c = \frac{[\text{CH}_4]}{[\text{H}_2]}$ | b) $K_c = \frac{[\text{CH}_4]}{[\text{C}][\text{H}_2]}$ |
| c) $K_c = \frac{[\text{CH}_4]}{[\text{C}][\text{H}_2]^2}$ | d) $K_c = \frac{[\text{CH}_4]}{[\text{H}_2]^2}$ |

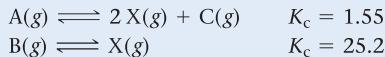
- Q2.** The equilibrium constant for the reaction shown here is $K_c = 1.0 \times 10^3$. A reaction mixture at equilibrium contains $[A] = 1.0 \times 10^{-3}$ M. What is the concentration of B in the mixture?



MISSED THIS? Read Section 16.3; Watch KCV 16.3

- a) 1.0×10^{-3} M
- b) 1.0 M
- c) 2.0 M
- d) 1.0×10^3 M

- Q3.** Use the data shown here to find the equilibrium constant (K_c) for the reaction $\text{A}(g) \rightleftharpoons 2 \text{B}(g) + \text{C}(g)$.



MISSED THIS? Read Section 16.3

- a) 984
- b) 26.8
- c) 6.10×10^{-4}
- d) 2.44×10^{-3}

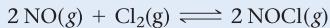
- Q4.** The reaction shown here has a $K_p = 4.5 \times 10^2$ at 825 K. Find K_c for the reaction at this temperature.



MISSED THIS? Read Section 16.4; Watch IWE 16.3

- a) 0.098
- b) 2.1×10^6
- c) 6.6
- d) 4.5×10^{-2}

- Q5.** Consider the reaction between NO and Cl_2 to form NOCl:



A reaction mixture at a certain temperature initially contains only $[\text{NO}] = 0.50$ M and $[\text{Cl}_2] = 0.50$ M. After the reaction comes to equilibrium, the concentration of NOCl is 0.30 M. Find the value of the equilibrium constant (K_c) at this temperature.

MISSED THIS? Read Section 16.6; Watch IWE 16.5

- a) 11
- b) 4.3
- c) 6.4
- d) 0.22

- Q6.** For the reaction $2 \text{A}(g) \rightleftharpoons \text{B}(g)$, the equilibrium constant is $K_p = 0.76$. A reaction mixture initially contains 2.0 atm of each gas ($P_A = 2.0$ atm and $P_B = 2.0$ atm). Which statement is true of the reaction mixture?

MISSED THIS? Read Section 16.7; Watch KCV 16.7, IWE 16.7

- a) The reaction mixture is at equilibrium.
- b) The reaction mixture will proceed toward products.
- c) The reaction mixture will proceed toward reactants.
- d) It is not possible to determine from the information given the future direction of the reaction mixture.

- Q7.** Consider the reaction between iodine gas and chlorine gas to form iodine monochloride:



A reaction mixture at 298 K initially contains $P_{I_2} = 0.25 \text{ atm}$ and $P_{Cl_2} = 0.25 \text{ atm}$. What is the partial pressure of iodine monochloride when the reaction reaches equilibrium?

MISSED THIS? Read Section 16.8; Watch KCV 16.8, IWE 16.9

- a) 0.18 atm b) 0.64 atm c) 0.41 atm d) 2.3 atm

- Q8.** Consider the reaction of A to form B:

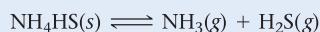


A reaction mixture at 298 K initially contains $[A] = 0.50 \text{ M}$. What is the concentration of B when the reaction reaches equilibrium?

MISSED THIS? Read Section 16.8; Watch KCV 16.8, IWE 16.12

- a) $9.0 \times 10^{-6} \text{ M}$ b) 0.060 M
c) 0.030 M d) $4.5 \times 10^{-6} \text{ M}$

- Q9.** The decomposition of NH_4HS is endothermic:

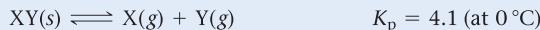


Which change to an equilibrium mixture of this reaction results in the formation of more H_2S ?

MISSED THIS? Read Section 16.9; Watch KCV 16.9, IWE 16.14

- a) a decrease in the volume of the reaction vessel (at constant temperature)
b) an increase in the amount of NH_4HS in the reaction vessel
c) an increase in temperature
d) all of the above

- Q10.** The solid XY decomposes into gaseous X and Y:

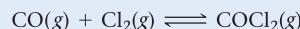


If the reaction is carried out in a 22.4-L container, which initial amounts of X and Y result in the formation of solid XY?

MISSED THIS? Read Section 16.7; Watch KCV 16.7, IWE 16.7

- a) 5 mol X; 0.5 mol Y b) 2.0 mol X; 2.0 mol Y
c) 1 mol X; 1 mol Y d) none of the above

- Q11.** What is the effect of adding helium gas (at constant volume) to an equilibrium mixture of the reaction:



MISSED THIS? Read Section 16.9

- a) The reaction shifts toward the products.
b) The reaction shifts toward the reactants.
c) The reaction does not shift in either direction.
d) The reaction slows down.

- Q12.** The reaction $\text{X}_2(g) \rightleftharpoons 2 \text{X}(g)$ occurs in a closed reaction vessel at constant volume and temperature. Initially, the vessel contains only X_2 at a pressure of 1.55 atm. After the reaction reaches equilibrium, the total pressure is 2.85 atm. What is the value of the equilibrium constant, K_p , for the reaction?

MISSED THIS? Read Section 16.6; Watch IWE 16.5

- a) 27 b) 10 c) 5.2 d) 32

Answers: 1. (d) 2. (b) 3. (d) 4. (a) 5. (c) 6. (b) 7. (c)

8. (d) 9. (c) 10. (d) 11. (c) 12. (a)

CHAPTER 16 IN REVIEW

TERMS

Section 16.2

reversible (685)
dynamic equilibrium (685)

Section 16.3

equilibrium constant (K) (688)
law of mass action (688)

Section 16.7

reaction quotient (Q_c) (699)

Section 16.9

Le Châtelier's principle (711)

CONCEPTS

The Equilibrium Constant (16.1)

- The relative concentrations of the reactants and the products at equilibrium are expressed by the equilibrium constant, K .
- The equilibrium constant measures how far a reaction proceeds toward products: a large K (greater than 1) indicates a high concentration of products at equilibrium, and a small K (less than 1) indicates a low concentration of products at equilibrium.

Dynamic Equilibrium (16.2)

- Most chemical reactions are reversible; they can proceed in either the forward or the reverse direction.
- When a chemical reaction is in dynamic equilibrium, the rate of the forward reaction equals the rate of the reverse reaction, so the net concentrations of reactants and products do not change. However, this does *not* imply that the concentrations of the reactants and the products are equal at equilibrium.

The Equilibrium Constant Expression (16.3)

- The equilibrium constant expression is given by the law of mass action and is equal to the concentrations of the products, raised to their stoichiometric coefficients, divided by the concentrations of the reactants, raised to their stoichiometric coefficients.
- When the equation for a chemical reaction is reversed, multiplied, or added to another equation, K must be modified accordingly.

The Equilibrium Constant, K (16.4)

- The equilibrium constant can be expressed in terms of concentrations (K_c) or in terms of partial pressures (K_p). These two constants are related by Equation 16.2. Concentration must always be expressed in units of molarity for K_c . Partial pressures must always be expressed in units of atmospheres for K_p .

States of Matter and the Equilibrium Constant (16.5)

The equilibrium constant expression contains only partial pressures or concentrations of reactants and products that exist as gases or solutes dissolved in solution. Pure liquids and solids are not included in the expression for the equilibrium constant.

Calculating K (16.6)

- We can calculate the equilibrium constant from equilibrium concentrations or partial pressures by substituting measured values into the expression for the equilibrium constant (as obtained from the law of mass action).
- In most cases, we can calculate the equilibrium concentrations of the reactants and products—and therefore the value of the equilibrium constant—from the initial concentrations of the reactants and products and the equilibrium concentration of *just one* reactant or product.

The Reaction Quotient, Q (16.7)

- The reaction quotient, Q , is the ratio of the concentrations (or partial pressures) of products raised to their stoichiometric coefficients to the concentrations of reactants raised to their stoichiometric coefficients *at any point in the reaction*.

- Like K , Q can be expressed in terms of concentrations (Q_c) or partial pressures (Q_p).
- At equilibrium, Q is equal to K ; therefore, we can determine the direction in which a reaction proceeds by comparing Q to K . If $Q < K$, the reaction moves in the direction of the products; if $Q > K$, the reaction moves in the reverse direction.

Finding Equilibrium Concentrations (16.8)

- There are two general types of problems in which K is given and we can determine one (or more) equilibrium concentrations:
 - We are given K and all but one equilibrium concentration.
 - We are given K and *only* initial concentrations.
- We solve the first type by rearranging the law of mass action and substituting the given values.
- We solve the second type by creating an ICE table and using a variable x to represent the change in concentration.

Le Châtelier's Principle (16.9)

- When a system at equilibrium is disturbed—by a change in the amount of a reactant or product, a change in volume, or a change in temperature—the system shifts in the direction that minimizes the disturbance.

EQUATIONS AND RELATIONSHIPS

Expression for the Equilibrium Constant, K_c (16.3)



$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \quad (\text{equilibrium concentrations only})$$

Relationship between the Equilibrium Constant and the Chemical Equation (16.3)

- If you reverse the equation, invert the equilibrium constant.
- If you multiply the coefficients in the equation by a factor, raise the equilibrium constant to the same factor.
- If you add two or more individual chemical equations to obtain an overall equation, multiply the corresponding equilibrium constants by each other to obtain the overall equilibrium constant.

Expression for the Equilibrium Constant, K_p (16.4)



$$K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b} \quad (\text{equilibrium partial pressures only})$$

Relationship between the Equilibrium Constants, K_c and K_p (16.4)

$$K_p = K_c (RT)^{\Delta n}$$

The Reaction Quotient, Q_c (16.7)



$$Q_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \quad (\text{concentrations at any point in the reaction})$$

The Reaction Quotient, Q_p (16.7)



$$Q_p = \frac{P_C^c P_D^d}{P_A^a P_B^b} \quad (\text{partial pressures at any point in the reaction})$$

Relationship of Q to the Direction of the Reaction (16.7)

$Q < K$ Reaction goes to the right.

$Q > K$ Reaction goes to the left.

$Q = K$ Reaction is at equilibrium.

LEARNING OUTCOMES

Chapter Objectives	Assessment
Write equilibrium constant expressions for chemical equations (16.2, 16.3)	Example 16.1 For Practice 16.1 Exercises 21–26
Predict how changes in the chemical equation affect the equilibrium constant (16.3)	Example 16.2 For Practice 16.2 For More Practice 16.2 Exercises 27–30
Write equilibrium constants in terms of partial pressures (K_p) or concentrations (K_c) (16.4)	Example 16.3 For Practice 16.3 Exercises 31–32

Write equilibrium constants for chemical equations that contain solids and pure liquids (16.5)	Example 16.4 For Practice 16.4 Exercises 33–34
Calculate equilibrium constants from experimental concentration measurements (16.6)	Examples 16.5, 16.6 For Practices 16.5, 16.6 Exercises 35–46
Predict the direction of a reaction by comparing the reaction quotient (Q_c) to the equilibrium constant (K_c) (16.7)	Example 16.7 For Practice 16.7 Exercises 47–50
Calculate unknown equilibrium concentrations from known equilibrium constants and all but one of the reactant and product equilibrium concentrations (16.8)	Example 16.8 For Practice 16.8
Calculate unknown equilibrium concentrations from known equilibrium constants and initial concentrations or pressures (16.8)	Examples 16.9–16.11 For Practices 16.9–16.11 Exercises 51–60
Calculate unknown equilibrium concentrations from known equilibrium constants and initial concentration or pressures in cases with a relatively small equilibrium constant (16.8)	Examples 16.12, 16.13 For Practice 16.12, 16.13 Exercises 61–62
Predict the effect of a concentration change on equilibrium (16.9)	Example 16.14 For Practices 16.14 Exercises 63–66
Predict the effect of a volume or pressure change on equilibrium (16.9)	Example 16.15 For Practice 16.15 Exercises 67–68
Predict the effect of a temperature change on equilibrium (16.9)	Example 16.16 For Practice 16.16 Exercises 69–72

EXERCISES

Mastering Chemistry provides end-of-chapter exercises, feedback-enriched tutorial problems, animations, and interactive activities to encourage problem-solving practice and deeper understanding of key concepts and topics.

REVIEW QUESTIONS

- How does a developing fetus get oxygen in the womb?
- What is dynamic equilibrium? Why is it called *dynamic*?
- Give the general expression for the equilibrium constant of the following generic reaction:

$$aA + bB \rightleftharpoons cC + dD$$
- What is the significance of the equilibrium constant? What does a large equilibrium constant tell us about a reaction? A small one?
- What happens to the value of the equilibrium constant for a reaction if the reaction equation is reversed? Multiplied by a constant?
- If two reactions sum to an overall reaction, and the equilibrium constants for the two reactions are K_1 and K_2 , what is the equilibrium constant for the overall reaction?
- Explain the difference between K_c and K_p . For a given reaction, how are the two constants related?
- What units should be used when expressing concentrations or partial pressures in the equilibrium constant? What are the units of K_p and K_c ? Explain.
- Why are the concentrations of solids and liquids omitted from equilibrium expressions?
- Does the value of the equilibrium constant depend on the initial concentrations of the reactants and products? Do the equilibrium concentrations of the reactants and products depend on their initial concentrations? Explain.
- Explain how you might deduce the equilibrium constant for a reaction in which you know the initial concentrations of the reactants and products and the equilibrium concentration of only one reactant or product.
- What is the definition of the reaction quotient (Q) for a reaction? What does Q measure?
- What is the value of Q when each reactant and product is in its standard state? (See Section 7.9 for the definition of standard states.)
- In what direction will a reaction proceed for each condition:
 - $Q < K$;
 - $Q > K$; and
 - $Q = K$
- Many equilibrium calculations involve finding the equilibrium concentrations of reactants and products given their initial concentrations and the equilibrium constant. Outline the general procedure used in solving these kinds of problems.
- In equilibrium problems involving equilibrium constants that are small relative to the initial concentrations of reactants, we can often assume that the quantity x (which represents how far the reaction proceeds toward products) is small. When this assumption is made, we can ignore the quantity x when it is subtracted from a large number but not when it is multiplied by a large number. In other words, $2.5 - x \approx 2.5$, but $2.5x \neq 2.5$. Explain why we can ignore a small x in the first case but not in the second.
- What happens to a chemical system at equilibrium when that equilibrium is disturbed?
- What is the effect of a change in concentration of a reactant or product on a chemical reaction initially at equilibrium?
- What is the effect of a change in volume on a chemical reaction (that includes gaseous reactants or products) initially at equilibrium?
- What is the effect of a temperature change on a chemical reaction initially at equilibrium? How does the effect differ for an exothermic reaction compared to an endothermic one?

PROBLEMS BY TOPIC

Equilibrium and the Equilibrium Constant Expression

21. Write an expression for the equilibrium constant of each chemical equation.

MISSED THIS? Read Section 16.3; Watch KCV 16.3

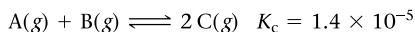
- $\text{SbCl}_5(g) \rightleftharpoons \text{SbCl}_3(g) + \text{Cl}_2(g)$
- $2 \text{BrNO}(g) \rightleftharpoons 2 \text{NO}(g) + \text{Br}_2(g)$
- $\text{CH}_4(g) + 2 \text{H}_2\text{S}(g) \rightleftharpoons \text{CS}_2(g) + 4 \text{H}_2(g)$
- $2 \text{CO}(g) + \text{O}_2(g) \rightleftharpoons 2 \text{CO}_2(g)$

22. Find and fix each mistake in the equilibrium constant expressions.

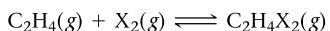
- $2 \text{H}_2\text{S}(g) \rightleftharpoons 2 \text{H}_2(g) + \text{S}_2(g) \quad K = \frac{[\text{H}_2][\text{S}_2]}{[\text{H}_2\text{S}]}$
- $\text{CO}(g) + \text{Cl}_2(g) \rightleftharpoons \text{COCl}_2(g) \quad K = \frac{[\text{CO}][\text{Cl}_2]}{[\text{COCl}_2]}$

23. When this reaction comes to equilibrium, will the concentrations of the reactants or products be greater? Does the answer to this question depend on the initial concentrations of the reactants and products?

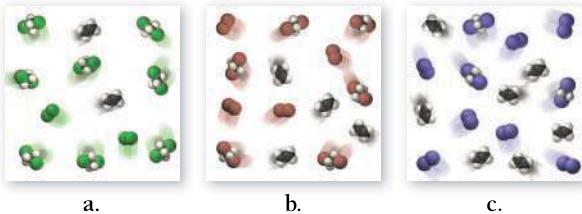
MISSED THIS? Read Section 16.3; Watch KCV 16.3



24. Ethene (C_2H_4) can be halogenated by this reaction:

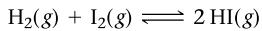


where X_2 can be Cl_2 (green), Br_2 (brown), or I_2 (purple). Examine the three figures representing equilibrium concentrations in this reaction at the same temperature for the three different halogens. Rank the equilibrium constants for the three reactions from largest to smallest.



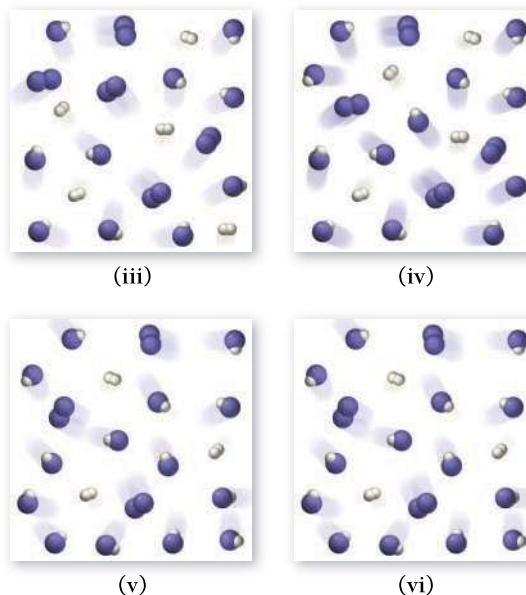
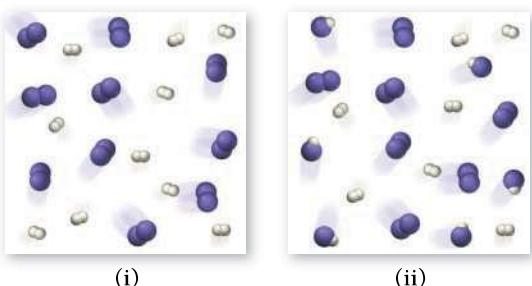
25. H_2 and I_2 are combined in a flask and allowed to react according to the reaction:

MISSED THIS? Read Section 16.3; Watch KCV 16.3



Examine the figures (sequential in time) and answer the questions:

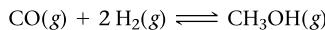
- Which figure represents the point at which equilibrium is reached?
- How would the series of figures change in the presence of a catalyst?
- Would there be different amounts of reactants and products in the final figure (vi) in the presence of a catalyst?



26. A chemist trying to synthesize a particular compound attempts two different synthesis reactions. The equilibrium constants for the two reactions are 23.3 and 2.2×10^4 at room temperature. However, upon carrying out both reactions for 15 minutes, the chemist finds that the reaction with the smaller equilibrium constant produces more of the desired product. Explain how this might be possible.

27. This reaction has an equilibrium constant of $K_p = 2.26 \times 10^4$ at 298 K.

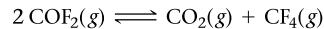
MISSED THIS? Read Section 16.3



Calculate K_p for each reaction and predict whether reactants or products will be favored at equilibrium.

- $\text{CH}_3\text{OH}(g) \rightleftharpoons \text{CO}(g) + 2 \text{H}_2(g)$
- $\frac{1}{2}\text{CO}(g) + \text{H}_2(g) \rightleftharpoons \frac{1}{2}\text{CH}_3\text{OH}(g)$
- $2 \text{CH}_3\text{OH}(g) \rightleftharpoons 2 \text{CO}(g) + 4 \text{H}_2(g)$

28. This reaction has an equilibrium constant of $K_p = 2.2 \times 10^6$ at 298 K.

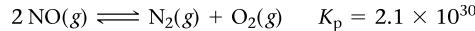


Calculate K_p for each reaction and predict whether reactants or products will be favored at equilibrium.

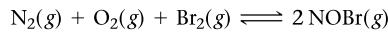
- $\text{COF}_2(g) \rightleftharpoons \frac{1}{2}\text{CO}_2(g) + \frac{1}{2}\text{CF}_4(g)$
- $6 \text{COF}_2(g) \rightleftharpoons 3 \text{CO}_2(g) + 3 \text{CF}_4(g)$
- $2 \text{CO}_2(g) + 2 \text{CF}_4(g) \rightleftharpoons 4 \text{COF}_2(g)$

29. Consider the reactions and their respective equilibrium constants:

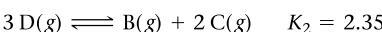
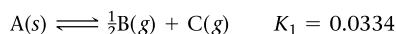
MISSED THIS? Read Section 16.3



Use these reactions and their equilibrium constants to predict the equilibrium constant for the following reaction:



30. Use the reactions and their equilibrium constants to predict the equilibrium constant for the reaction $2 \text{A}(s) \rightleftharpoons 3 \text{D}(g)$.



K_p , K_c , and Heterogeneous Equilibria

31. Calculate K_c for each reaction.

MISSED THIS? Read Section 16.4; Watch IWE 16.3

- $I_2(g) \rightleftharpoons 2 I(g)$ $K_p = 6.26 \times 10^{-22}$ (at 298 K)
- $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3 H_2(g)$ $K_p = 7.7 \times 10^{24}$ (at 298 K)
- $I_2(g) + Cl_2(g) \rightleftharpoons 2 ICl(g)$ $K_p = 81.9$ (at 298 K)

32. Calculate K_p for each reaction.

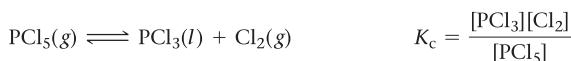
- $N_2O_4(g) \rightleftharpoons 2 NO_2(g)$ $K_c = 5.9 \times 10^{-3}$ (at 298 K)
- $N_2(g) + 3 H_2(g) \rightleftharpoons 2 NH_3(g)$ $K_c = 3.7 \times 10^8$ (at 298 K)
- $N_2(g) + O_2(g) \rightleftharpoons 2 NO(g)$ $K_c = 4.10 \times 10^{-31}$ (at 298 K)

33. Write an equilibrium expression for each chemical equation involving one or more solid or liquid reactants or products.

MISSED THIS? Read Section 16.4

- $CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$
- $2 KClO_3(s) \rightleftharpoons 2 KCl(s) + 3 O_2(g)$
- $HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$
- $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

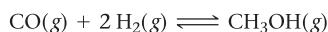
34. Find and fix the mistake in the equilibrium expression.



Relating the Equilibrium Constant to Equilibrium Concentrations and Equilibrium Partial Pressures

35. Consider the reaction:

MISSED THIS? Read Section 16.6



An equilibrium mixture of this reaction at a certain temperature has $[CO] = 0.105\text{ M}$, $[H_2] = 0.114\text{ M}$, and $[CH_3OH] = 0.185\text{ M}$. What is the value of the equilibrium constant (K_c) at this temperature?

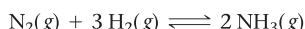
36. Consider the reaction:



An equilibrium mixture of this reaction at a certain temperature has $[NH_3] = 0.278\text{ M}$ and $[H_2S] = 0.355\text{ M}$. What is the value of the equilibrium constant (K_c) at this temperature?

37. Consider the reaction:

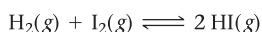
MISSED THIS? Read Section 16.6; Watch IWE 16.5



Complete the table. Assume that all concentrations are equilibrium concentrations in M.

T (K)	[N ₂]	[H ₂]	[NH ₃]	K _c
500	0.115	0.105	0.439	_____
575	0.110	_____	0.128	9.6
775	0.120	0.140	_____	0.0584

38. Consider the following reaction:

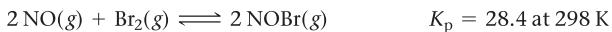


Complete the table. Assume that all concentrations are equilibrium concentrations in M.

T (°C)	[H ₂]	[I ₂]	[HI]	K _c
25	0.0355	0.0388	0.922	_____
340	_____	0.0455	0.387	9.6
445	0.0485	0.0468	_____	50.2

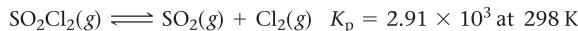
39. Consider the reaction:

MISSED THIS? Read Section 16.8; Watch IWE 16.8



In a reaction mixture at equilibrium, the partial pressure of NO is 108 torr and that of Br₂ is 126 torr. What is the partial pressure of NOBr in this mixture?

40. Consider the reaction:



In a reaction at equilibrium, the partial pressure of SO₂ is 137 torr and that of Cl₂ is 285 torr. What is the partial pressure of SO₂Cl₂ in this mixture?

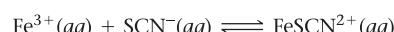
41. For the reaction A(g) \rightleftharpoons 2 B(g), a reaction vessel initially contains only A at a pressure of $P_A = 1.32\text{ atm}$. At equilibrium, $P_A = 0.25\text{ atm}$. Calculate the value of K_p . (Assume no changes in volume or temperature.)

MISSED THIS? Read Section 16.6; Watch IWE 16.5

42. For the reaction 2 A(g) \rightleftharpoons B(g) + 2 C(g), a reaction vessel initially contains only A at a pressure of $P_A = 255\text{ mmHg}$. At equilibrium, $P_A = 55\text{ mmHg}$. Calculate the value of K_p . (Assume no changes in volume or temperature.)

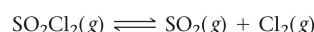
43. Consider the reaction:

MISSED THIS? Read Section 16.6; Watch IWE 16.5



A solution is made containing an initial $[Fe^{3+}]$ of $1.0 \times 10^{-3}\text{ M}$ and an initial $[SCN^-]$ of $8.0 \times 10^{-4}\text{ M}$. At equilibrium, $[FeSCN^{2+}] = 1.7 \times 10^{-4}\text{ M}$. Calculate the value of the equilibrium constant (K_c).

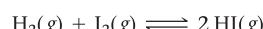
44. Consider the reaction:



A reaction mixture is made containing an initial $[SO_2Cl_2]$ of 0.020 M . At equilibrium, $[Cl_2] = 1.2 \times 10^{-2}\text{ M}$. Calculate the value of the equilibrium constant (K_c).

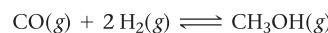
45. Consider the reaction:

MISSED THIS? Read Section 16.6; Watch IWE 16.5



A reaction mixture in a 3.67-L flask at a certain temperature initially contains 0.763 g H₂ and 96.9 g I₂. At equilibrium, the flask contains 90.4 g HI. Calculate the equilibrium constant (K_c) for the reaction at this temperature.

46. Consider the reaction:



A reaction mixture in a 5.19-L flask at a certain temperature contains 26.9 g CO and 2.34 g H₂. At equilibrium, the flask contains 8.65 g CH₃OH. Calculate the equilibrium constant (K_c) for the reaction at this temperature.

The Reaction Quotient and Reaction Direction

47. Consider the reaction:

MISSED THIS? Read Section 16.7; Watch KCV 16.7, IWE 16.7



At a certain temperature, $K_c = 8.5 \times 10^{-3}$. A reaction mixture at this temperature containing solid NH₄HS has $[NH_3] = 0.166\text{ M}$ and $[H_2S] = 0.166\text{ M}$. Will more of the solid decompose as equilibrium is reached?

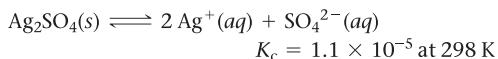
48. Consider the reaction:



A reaction mixture contains 0.112 atm of H_2 , 0.055 atm of S_2 , and 0.445 atm of H_2S . Is the reaction mixture at equilibrium? If not, in what direction will the reaction proceed?

49. Silver sulfate dissolves in water according to the reaction:

MISSED THIS? Read Section 16.7; Watch KCV 16.7, IWE 16.7



A 1.5-L solution contains 6.55 g of dissolved silver sulfate. If additional solid silver sulfate is added to the solution, will it dissolve?

50. Nitrogen dioxide dimerizes according to the reaction:

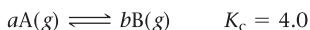


A 2.25-L container contains 0.055 mol of NO_2 and 0.082 mol of N_2O_4 at 298 K. Is the reaction at equilibrium? If not, in what direction will the reaction proceed?

Finding Equilibrium Concentrations from Initial Concentrations and the Equilibrium Constant

51. Consider the reaction and the associated equilibrium constant:

MISSED THIS? Read Section 16.8; Watch KCV 16.8, IWE 16.9



Find the equilibrium concentrations of A and B for each value of a and b . Assume that the initial concentration of A in each case is 1.0 M and that no B is present at the beginning of the reaction.

- a. $a = 1; b = 1$ b. $a = 2; b = 2$ c. $a = 1; b = 2$

52. Consider the reaction and the associated equilibrium constant:



Find the equilibrium concentrations of A, B, and C for each value of a , b , and c . Assume that the initial concentrations of A and B are each 1.0 M and that no product is present at the beginning of the reaction.

- a. $a = 1; b = 1; c = 2$
 b. $a = 1; b = 1; c = 1$
 c. $a = 2; b = 1; c = 1$ (set up equation for x ; don't solve)

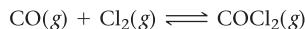
53. For the reaction shown here, $K_c = 0.513$ at 500 K.

MISSED THIS? Read Section 16.8; Watch KCV 16.8, IWE 16.9



If a reaction vessel initially contains an N_2O_4 concentration of 0.0500 M at 500 K, what are the equilibrium concentrations of N_2O_4 and NO_2 at 500 K?

54. For the reaction shown here, $K_c = 255$ at 1000 K.



If a reaction mixture initially contains a CO concentration of 0.1500 M and a Cl_2 concentration of 0.175 M at 1000 K, what are the equilibrium concentrations of CO, Cl_2 , and COCl_2 at 1000 K?

55. Consider the reaction:

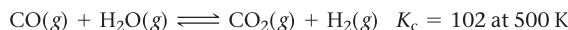
MISSED THIS? Read Section 16.8; Watch KCV 16.8, IWE 16.9



$$K_c = 4.0 \times 10^3 \text{ at } 1500 \text{ K}$$

If a mixture of solid nickel(II) oxide and 0.20 M carbon monoxide comes to equilibrium at 1500 K, what is the equilibrium concentration of CO_2 ?

56. Consider the reaction:



If a reaction mixture initially contains 0.110 M CO and 0.110 M H_2O , what will the equilibrium concentration of each of the reactants and products be?

57. Consider the reaction:

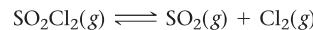
MISSED THIS? Read Section 16.8; Watch KCV 16.8, IWE 16.12



$$K_c = 1.8 \times 10^{-5} \text{ at } 25^\circ\text{C}$$

If a solution initially contains 0.210 M $\text{HC}_2\text{H}_3\text{O}_2$, what is the equilibrium concentration of H_3O^+ at 25°C ?

58. Consider the reaction:

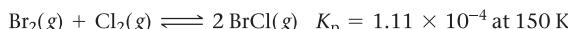


$$K_c = 2.99 \times 10^{-7} \text{ at } 227^\circ\text{C}$$

If a reaction mixture initially contains 0.175 M SO_2Cl_2 , what is the equilibrium concentration of Cl_2 at 227°C ?

59. Consider the reaction:

MISSED THIS? Read Section 16.8; Watch KCV 16.8, IWE 16.12



A reaction mixture initially contains a Br_2 partial pressure of 755 torr and a Cl_2 partial pressure of 735 torr at 150 K. Calculate the equilibrium partial pressure of BrCl .

60. Consider the reaction:

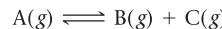


$$K_p = 0.0611 \text{ at } 2000 \text{ K}$$

A reaction mixture initially contains a CO partial pressure of 1344 torr and a H_2O partial pressure of 1766 torr at 2000 K. Calculate the equilibrium partial pressures of each of the products.

61. Consider the reaction:

MISSED THIS? Read Section 16.8; Watch KCV 16.8, IWE 16.9, 16.12



Find the equilibrium concentrations of A, B, and C for each value of K_c . Assume that the initial concentration of A in each case is 1.0 M and that the reaction mixture initially contains no products. Make any appropriate simplifying assumptions.

- a. $K_c = 1.0$
 b. $K_c = 0.010$
 c. $K_c = 1.0 \times 10^{-5}$

62. Consider the reaction:



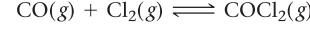
Find the equilibrium partial pressures of A and B for each value of K_p . Assume that the initial partial pressure of B in each case is 1.0 atm and that the initial partial pressure of A is 0.0 atm. Make any appropriate simplifying assumptions.

- a. $K_p = 1.0$
 b. $K_p = 1.0 \times 10^{-4}$
 c. $K_p = 1.0 \times 10^5$

Le Châtelier's Principle

63. Consider this reaction at equilibrium:

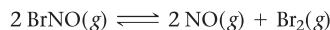
MISSED THIS? Read Section 16.9; Watch KCV 16.9, IWE 16.14



Predict whether the reaction will shift left, shift right, or remain unchanged after each disturbance.

- a. COCl_2 is added to the reaction mixture.
 b. Cl_2 is added to the reaction mixture.
 c. COCl_2 is removed from the reaction mixture.

- 64.** Consider this reaction at equilibrium:

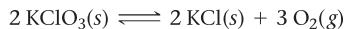


Predict whether the reaction will shift left, shift right, or remain unchanged after each disturbance.

- NO is added to the reaction mixture.
- BrNO is added to the reaction mixture.
- Br₂ is removed from the reaction mixture.

- 65.** Consider this reaction at equilibrium:

MISSED THIS? Read Section 16.9; Watch KCV 16.9, IWE 16.14



Predict whether the reaction will shift left, shift right, or remain unchanged after each disturbance.

- O₂ is removed from the reaction mixture.
- KCl is added to the reaction mixture.
- KClO₃ is added to the reaction mixture.
- O₂ is added to the reaction mixture.

- 66.** Consider this reaction at equilibrium:



Predict whether the reaction will shift left, shift right, or remain unchanged after each disturbance.

- C is added to the reaction mixture.
- H₂O is condensed and removed from the reaction mixture.
- CO is added to the reaction mixture.
- H₂ is removed from the reaction mixture.

- 67.** Each reaction is allowed to come to equilibrium, and then the volume is changed as indicated. Predict the effect (shift right, shift left, or no effect) of the indicated volume change.

MISSED THIS? Read Section 16.9; Watch KCV 16.9

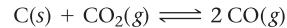
- I₂(g) \rightleftharpoons 2 I(g) (volume is increased)
- 2 H₂S(g) \rightleftharpoons 2 H₂(g) + S₂(g) (volume is decreased)
- I₂(g) + Cl₂(g) \rightleftharpoons 2 ICl(g) (volume is decreased)

- 68.** Each reaction is allowed to come to equilibrium, and then the volume is changed as indicated. Predict the effect (shift right, shift left, or no effect) of the indicated volume change.

- CO(g) + H₂O(g) \rightleftharpoons CO₂(g) + H₂(g) (volume is decreased)
- PCl₃(g) + Cl₂(g) \rightleftharpoons PCl₅(g) (volume is increased)
- CaCO₃(s) \rightleftharpoons CaO(s) + CO₂(g) (volume is increased)

- 69.** This reaction is endothermic.

MISSED THIS? Read Section 16.9; Watch KCV 16.9



Predict the effect (shift right, shift left, or no effect) of increasing and decreasing the reaction temperature. How does the value of the equilibrium constant depend on temperature?

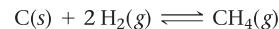
- 70.** This reaction is exothermic.



Predict the effect (shift right, shift left, or no effect) of increasing and decreasing the reaction temperature. How does the value of the equilibrium constant depend on temperature?

- 71.** Coal, which is primarily carbon, can be converted to natural gas, primarily CH₄, by the exothermic reaction:

MISSED THIS? Read Section 16.9; Watch KCV 16.9, IWE 16.14



Which disturbance will favor CH₄ at equilibrium?

- adding more C to the reaction mixture
- adding more H₂ to the reaction mixture
- raising the temperature of the reaction mixture
- lowering the volume of the reaction mixture
- adding a catalyst to the reaction mixture
- adding neon gas to the reaction mixture

- 72.** Coal can be used to generate hydrogen gas (a potential fuel) by the endothermic reaction:



If this reaction mixture is at equilibrium, predict whether each disturbance will result in the formation of additional or less hydrogen gas, or have no effect on the quantity of hydrogen gas.

- adding more C to the reaction mixture
- adding more H₂O to the reaction mixture
- raising the temperature of the reaction mixture
- increasing the volume of the reaction mixture
- adding a catalyst to the reaction mixture
- adding an inert gas to the reaction mixture

CUMULATIVE PROBLEMS

- 73.** Carbon monoxide replaces oxygen in oxygenated hemoglobin according to the reaction:

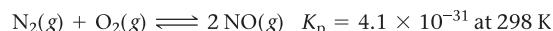


- Use the reactions and associated equilibrium constants at body temperature given here to find the equilibrium constant for the reaction just shown.



- Suppose that an air mixture becomes polluted with carbon monoxide at a level of 0.10% (by volume). Assuming that the air contains 20.0% oxygen and that the oxygen and carbon monoxide ratios that dissolve in the blood are identical to the ratios in the air, what is the ratio of HbCO to HbO₂ in the bloodstream? Comment on the toxicity of carbon monoxide.

- 74.** Nitrogen monoxide is a pollutant in the lower atmosphere that irritates the eyes and lungs and leads to the formation of acid rain. Nitrogen monoxide forms naturally in atmosphere according to the endothermic reaction:

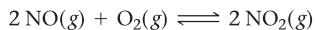


Use the ideal gas law to calculate the concentrations of nitrogen and oxygen present in air at a pressure of 1.0 atm and a temperature of 298 K. Assume that nitrogen composes 78% of air by volume and that oxygen composes 21% of air. Find the “natural” equilibrium concentration of NO in air in units of molecules/cm³. How would you expect this concentration to change in an automobile engine in which combustion is occurring?

- 75.** The reaction $\text{CO}_2(g) + \text{C}(s) \rightleftharpoons 2 \text{CO}(g)$ has $K_p = 5.78$ at 1200 K.
- Calculate the total pressure at equilibrium when 4.45 g of CO_2 is introduced into a 10.0-L container and heated to 1200 K in the presence of 2.00 g of graphite.
 - Repeat the calculation of part a in the presence of 0.50 g of graphite.
- 76.** A mixture of water and graphite is heated to 600 K. When the system comes to equilibrium, it contains 0.13 mol of H_2 , 0.13 mol of CO, 0.43 mol of H_2O , and some graphite. Some O_2 is added to the system, and a spark is applied so that the H_2 reacts completely with the O_2 . Find the amount of CO in the flask when the system returns to equilibrium.
- 77.** At 650 K, the reaction $\text{MgCO}_3(s) \rightleftharpoons \text{MgO}(s) + \text{CO}_2(g)$ has $K_p = 0.026$. A 10.0-L container at 650 K has 1.0 g of $\text{MgO}(s)$ and CO_2 at $P = 0.0260$ atm. The container is then compressed to a volume of 0.100 L. Find the mass of MgCO_3 that is formed.
- 78.** A system at equilibrium contains $\text{I}_2(g)$ at a pressure of 0.21 atm and $\text{I}(g)$ at a pressure of 0.23 atm. The system is then compressed to half its volume. Find the pressure of each gas when the system returns to equilibrium.
- 79.** Consider the exothermic reaction:
- $$\text{C}_2\text{H}_4(g) + \text{Cl}_2(g) \rightleftharpoons \text{C}_2\text{H}_4\text{Cl}_2(g)$$
- If you were trying to maximize the amount of $\text{C}_2\text{H}_4\text{Cl}_2$ produced, which tactic might you try? Assume that the reaction mixture reaches equilibrium.
- increasing the reaction volume
 - removing $\text{C}_2\text{H}_4\text{Cl}_2$ from the reaction mixture as it forms
 - lowering the reaction temperature
 - adding Cl_2
- 80.** Consider the endothermic reaction:
- $$\text{C}_2\text{H}_4(g) + \text{I}_2(g) \rightleftharpoons \text{C}_2\text{H}_4\text{I}_2(g)$$
- If you were trying to maximize the amount of $\text{C}_2\text{H}_4\text{I}_2$ produced, which tactic might you try? Assume that the reaction mixture reaches equilibrium.
- decreasing the reaction volume
 - removing I_2 from the reaction mixture
 - raising the reaction temperature
 - adding C_2H_4 to the reaction mixture
- 81.** Consider the reaction:
- $$\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2 \text{HI}(g)$$
- A reaction mixture at equilibrium at 175 K contains $P_{\text{H}_2} = 0.958$ atm, $P_{\text{I}_2} = 0.877$ atm, and $P_{\text{HI}} = 0.020$ atm. A second reaction mixture, also at 175 K, contains $P_{\text{H}_2} = P_{\text{I}_2} = 0.621$ atm and $P_{\text{HI}} = 0.101$ atm. Is the second reaction at equilibrium? If not, what will be the partial pressure of HI when the reaction reaches equilibrium at 175 K?
- 82.** Consider the reaction:
- $$2 \text{H}_2\text{S}(g) + \text{SO}_2(g) \rightleftharpoons 3 \text{S}(s) + 2 \text{H}_2\text{O}(g)$$
- A reaction mixture initially containing 0.500 M H_2S and 0.500 M SO_2 contains 0.0011 M H_2O at equilibrium at a certain temperature. A second reaction mixture at the same temperature initially contains $[\text{H}_2\text{S}] = 0.250$ M and $[\text{SO}_2] = 0.325$ M. Calculate the equilibrium concentration of H_2O in the second mixture at this temperature.
- 83.** Ammonia can be synthesized according to the reaction:
- $$\text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g) \quad K_p = 5.3 \times 10^{-5} \text{ at } 725 \text{ K}$$
- A 200.0-L reaction container initially contains 1.27 kg of N_2 and 0.310 kg of H_2 at 725 K. Assuming ideal gas behavior, calculate the mass of NH_3 (in g) present in the reaction mixture at equilibrium. What is the percent yield of the reaction under these conditions?
- 84.** Hydrogen can be extracted from natural gas according to the reaction:
- $$\text{CH}_4(g) + \text{CO}_2(g) \rightleftharpoons 2 \text{CO}(g) + 2 \text{H}_2(g) \quad K_p = 4.5 \times 10^2 \text{ at } 825 \text{ K}$$
- An 85.0-L reaction container initially contains 22.3 kg of CH_4 and 55.4 kg of CO_2 at 825 K. Assuming ideal gas behavior, calculate the mass of H_2 (in g) present in the reaction mixture at equilibrium. What is the percent yield of the reaction under these conditions?
- 85.** The system described by the reaction $\text{CO}(g) + \text{Cl}_2(g) \rightleftharpoons \text{COCl}_2(g)$ is at equilibrium at a given temperature when $P_{\text{CO}} = 0.30$ atm, $P_{\text{Cl}_2} = 0.10$ atm, and $P_{\text{COCl}_2} = 0.60$ atm. An additional pressure of $\text{Cl}_2(g) = 0.40$ atm is added. Find the pressure of CO when the system returns to equilibrium.
- 86.** A reaction vessel at 27 °C contains a mixture of SO_2 ($P = 3.00$ atm) and O_2 ($P = 1.00$ atm). When a catalyst is added, this reaction takes place: $2 \text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{SO}_3(g)$. At equilibrium, the total pressure is 3.75 atm. Find the value of K_c .
- 87.** At 70 K, CCl_4 decomposes to carbon and chlorine. The K_p for the decomposition is 0.76. Find the starting pressure of CCl_4 at this temperature that will produce a total pressure of 1.0 atm at equilibrium.
- 88.** The equilibrium constant for the reaction $\text{SO}_2(g) + \text{NO}_2(g) \rightleftharpoons \text{SO}_3(g) + \text{NO}(g)$ is $K_c = 3.0$. Find the amount of NO_2 that must be added to 2.4 mol of SO_2 in order to form 1.2 mol of SO_3 at equilibrium.
- 89.** A sample of $\text{CaCO}_3(s)$ is introduced into a sealed container of volume 0.654 L and heated to 1000 K until equilibrium is reached. The K_p for the reaction $\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$ is 3.9×10^{-2} at this temperature. Calculate the mass of $\text{CaO}(s)$ that is present at equilibrium.
- 90.** An equilibrium mixture contains N_2O_4 ($P = 0.28$ atm) and NO_2 ($P = 1.1$ atm) at 350 K. The volume of the container is doubled at constant temperature. Write a balanced chemical equation for the reaction and calculate the equilibrium pressures of the two gases when the system reaches a new equilibrium.
- 91.** Carbon monoxide and chlorine gas react to form phosgene:
- $$\text{CO}(g) + \text{Cl}_2(g) \rightleftharpoons \text{COCl}_2(g) \quad K_p = 3.10 \text{ at } 700 \text{ K}$$
- If a reaction mixture initially contains 215 torr of CO and 245 torr of Cl_2 , what is the mole fraction of COCl_2 when equilibrium is reached?
- 92.** Solid carbon can react with gaseous water to form carbon monoxide gas and hydrogen gas. The equilibrium constant for the reaction at 700.0 K is $K_p = 1.60 \times 10^{-3}$. If a 1.55-L reaction vessel initially contains 145 torr of water at 700.0 K in contact with excess solid carbon, find the percent by mass of hydrogen gas of the gaseous reaction mixture at equilibrium.

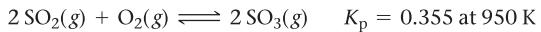
CHALLENGE PROBLEMS

- 93.** Consider the reaction:



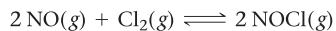
- a. A reaction mixture at 175 K initially contains 522 torr of NO and 421 torr of O₂. At equilibrium, the total pressure in the reaction mixture is 748 torr. Calculate K_p at this temperature.
 b. A second reaction mixture at 175 K initially contains 255 torr of NO and 185 torr of O₂. What is the equilibrium partial pressure of NO₂ in this mixture?

- 94.** Consider the reaction:



A 2.75-L reaction vessel at 950 K initially contains 0.100 mol of SO₂ and 0.100 mol of O₂. Calculate the total pressure (in atmospheres) in the reaction vessel when equilibrium is reached.

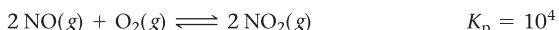
- 95.** Nitric oxide reacts with chlorine gas according to the reaction:



$$K_p = 0.27 \text{ at } 700 \text{ K}$$

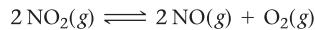
A reaction mixture initially contains equal partial pressures of NO and Cl₂. At equilibrium, the partial pressure of NOCl is 115 torr. What were the initial partial pressures of NO and Cl₂?

- 96.** At a given temperature, a system containing O₂(g) and some oxides of nitrogen can be described by these reactions:



A pressure of 1 atm of N₂O₄(g) is placed in a container at this temperature. Predict which, if any, component (other than N₂O₄) will be present at a pressure greater than 0.2 atm at equilibrium.

- 97.** A sample of pure NO₂ is heated to 337 °C, at which temperature it partially dissociates according to the equation:



At equilibrium the density of the gas mixture is 0.520 g/L at 0.750 atm. Calculate K_c for the reaction.

- 98.** When N₂O₅(g) is heated, it dissociates into N₂O₃(g) and O₂(g) according to the reaction:



$$K_c = 7.75 \text{ at a given temperature}$$

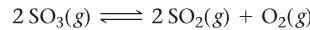
The N₂O₃(g) dissociates to give N₂O(g) and O₂(g) according to the reaction:



$$K_c = 4.00 \text{ at the same temperature}$$

When 4.00 mol of N₂O₅(g) is heated in a 1.00-L reaction vessel to this temperature, the concentration of O₂(g) at equilibrium is 4.50 mol/L. Find the concentrations of all the other species in the equilibrium system.

- 99.** A sample of SO₃ is introduced into an evacuated sealed container and heated to 600 K. The following equilibrium is established:



The total pressure in the system is 3.0 atm, and the mole fraction of O₂ is 0.12. Find K_p.

CONCEPTUAL PROBLEMS

- 100.** A reaction A(g) \rightleftharpoons B(g) has an equilibrium constant of 1.0×10^{-4} . For which of the initial reaction mixtures is the *x is small* approximation most likely to apply?

- a. [A] = 0.0010 M; [B] = 0.00 M
- b. [A] = 0.00 M; [B] = 0.10 M
- c. [A] = 0.10 M; [B] = 0.10 M
- d. [A] = 0.10 M; [B] = 0.00 M

- 101.** The reaction A(g) \rightleftharpoons 2 B(g) has an equilibrium constant of K_c = 1.0 at a given temperature. If a reaction vessel contains equal initial amounts (in moles) of A and B, does the direction in which the reaction proceeds depend on the volume of the reaction vessel? Explain.

- 102.** A particular reaction has an equilibrium constant of K_p = 0.50. A reaction mixture is prepared in which all the reactants and products are in their standard states. In which direction does the reaction proceed?

- 103.** Consider the reaction:



Each of the entries in the following table represents equilibrium partial pressures of A and B under different initial conditions. What are the values of *a* and *b* in the reaction?

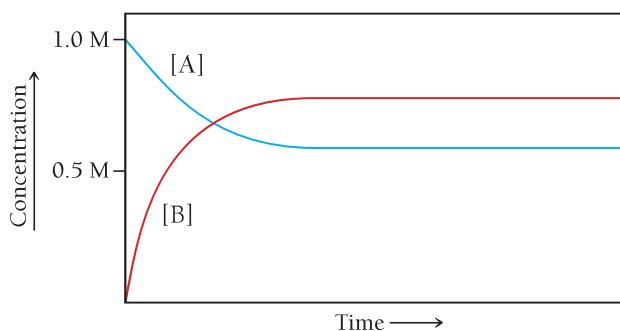
P _A (atm)	P _B (atm)
4.0	2.0
2.0	1.4
1.0	1.0
0.50	0.71
0.25	0.50

- 104.** Consider the simple one-step reaction:



Since the reaction occurs in a single step, the forward reaction has a rate of $k_{\text{for}}[A]$ and the reverse reaction has a rate of $k_{\text{rev}}[B]$. What happens to the rate of the forward reaction when we increase the concentration of A? How does this explain the reason behind Le Châtelier's principle?

- 105.** Consider the reaction: $A(g) \rightleftharpoons 2 B(g)$. The graph plots the concentrations of A and B as a function of time at a constant temperature. What is the equilibrium constant for this reaction at this temperature?



QUESTIONS FOR GROUP WORK

Discuss these questions with the group and record your consensus answer.

- 106.** The reactions shown here can be combined to make the overall reaction $C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g)$ by reversing some and/or dividing all the coefficients by a number. As a group, determine how the reactions need to be modified to sum to the overall process. Then have each group member determine the value of K for one of the reactions to be combined. Finally, combine all the values of K to determine the value of K for the overall reaction.

- a. $C(s) + O_2(g) \longrightarrow CO_2(g) \quad K = 1.363 \times 10^{69}$
- b. $2 H_2(g) + O_2(g) \longrightarrow 2 H_2O(g) \quad K = 1.389 \times 10^{80}$
- c. $2 CO(g) + O_2(g) \longrightarrow 2 CO_2(g) \quad K = 1.477 \times 10^{90}$

- 107.** Consider the reaction: $N_2(g) + 3 H_2(g) \longrightarrow 2 NH_3(g)$.
- Write the equilibrium constant expression for this reaction. If some hydrogen is added, before the reaction shifts,
 - How will the numerator and denominator of the expression in part a compare to the value at equilibrium?
 - Will Q be larger or smaller than K ? Why?
 - Will the reaction have to shift forward or backward to retain equilibrium? Explain.
 - Are your answers above consistent with Le Châtelier's principle? Explain.

Active Classroom Learning

- 108.** For the reaction $A \longrightarrow B$, the ratio of products to reactants at equilibrium is always the same number, no matter how much A or B is initially present. Interestingly, in contrast, the ratio of products to reactants for the reaction $C \longrightarrow 2 D$ does depend on how much of C and D you have initially. Explain this observation. Which ratio is independent of the starting amounts of C and D? Answer in complete sentences.

- 109.** Solve each of the expressions for x using the quadratic formula and the x is small approximation. In which of the following expressions is the x is small approximation valid?

- a. $x^2/(0.2 - x) = 1.3 \times 10^4$
- b. $x^2/(0.2 - x) = 1.3$
- c. $x^2/(0.2 - x) = 1.3 \times 10^{-4}$
- d. $x^2/(0.01 - x) = 1.3 \times 10^{-4}$

In a complete sentence, describe the factor(s) that tend to make the x is small approximation valid in an expression.

- 110.** Have each group member explain to the group what happens if a system at equilibrium is subject to one of the following changes and why:

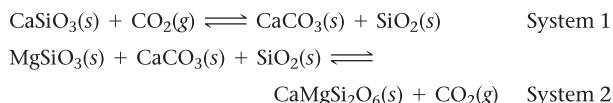
- a. the concentration of a reactant is increased
- b. a solid product is added
- c. the volume is decreased
- d. the temperature is raised



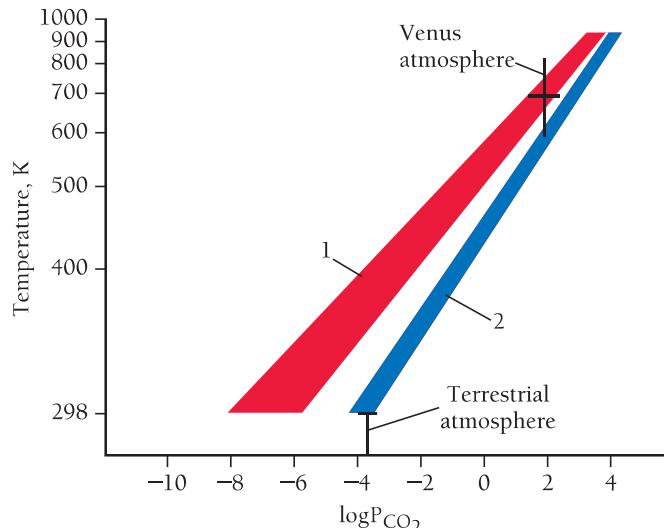
DATA INTERPRETATION AND ANALYSIS

Chemical Equilibrium on Venus

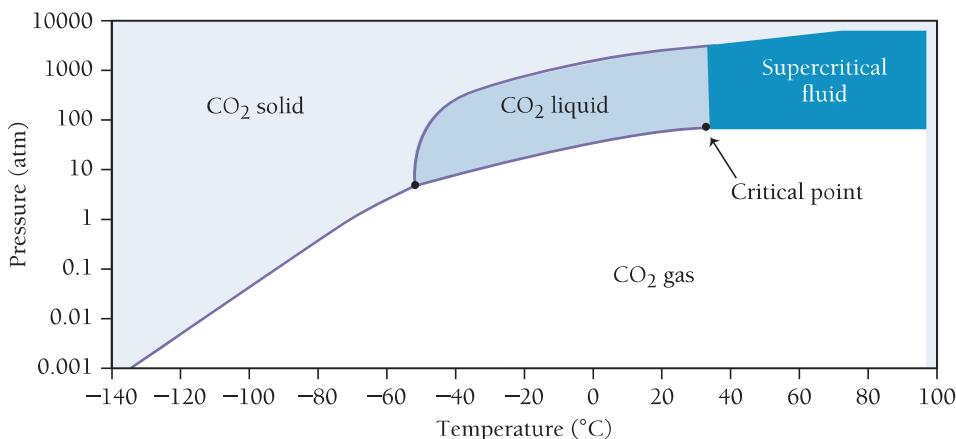
- 111.** The atmosphere of the planet Venus is almost entirely composed of carbon dioxide (about 96.5% carbon dioxide). The carbon dioxide on Venus might be in equilibrium with carbonate ions in minerals on the planet's crust. Two possible equilibrium systems involve $CaSiO_3$ and $MgSiO_3$:



The first graph shows the expected pressures of carbon dioxide (in atm) at different temperatures for each of these equilibrium systems. (Note that both axes on this graph are logarithmic.) The second graph is a phase diagram for carbon dioxide. Examine the graphs and answer the questions.



▲ Carbon Dioxide Partial Pressures for Systems 1 and 2



▲ Carbon Dioxide Phase Diagram

- a. The partial pressure of carbon dioxide on the surface of Venus is 91 atm. What is the value of the equilibrium constant (K_p) if the Venusian carbon dioxide is in equilibrium according to system 1? According to system 2?
- b. The approximate temperature on the surface of Venus is about 740 K. What is the approximate carbon dioxide concentration for system 1 at this temperature? For system 2? (Use a point at approximately the middle of each colored band, which represents the range of possible values, to estimate the carbon dioxide concentration.)
- c. Use the partial pressure of carbon dioxide on the surface of Venus given in part a to determine which of the two equilibrium systems is more likely to be responsible for the carbon dioxide on the surface of Venus.
- d. From the carbon dioxide phase diagram, determine the minimum pressure required for supercritical carbon dioxide to form. If the partial pressure of carbon dioxide on the surface of Venus was higher in the distant past, could supercritical carbon dioxide have existed on the surface of Venus?

Cc ANSWERS TO CONCEPTUAL CONNECTIONS

Dynamic Equilibrium

- 16.1** (c) For a chemical reaction in dynamic equilibrium, the concentrations of the reactants and products are generally *not* equal.

The Law of Mass Action

- 16.2** (d) The equilibrium constant is defined as the ratio—*at equilibrium*—of the concentrations of the products raised to their stoichiometric coefficients divided by the concentrations of the reactants raised to their stoichiometric coefficients.

The Magnitude of the Equilibrium Constant

- 16.3** (c) The equilibrium constant is largest for temperature T₃ (because the reaction mixture has the most products relative to reactants at that temperature).

Equilibrium Constants and Equilibrium Concentrations

- 16.4** (b) The reaction mixture will contain [A] = 0.1 M and [B] = 1.0 M so that [B]/[A] = 10.

The Equilibrium Constant and the Chemical Equation

- 16.5** (b) The reaction is reversed and divided through by two. Therefore, you invert the equilibrium constant and take the square root of the result. $K = (1/0.010)^{1/2} = 10$.

The Relationship between K_p and K_c

- 16.6** (a) When $a + b = c + d$, the quantity Δn is zero so that $K_p = K_c(RT)^0$. Since $(RT)^0$ is equal to 1, $K_p = K_c$.

Heterogeneous Equilibria, K_p , and K_c

- 16.7** (b) Since Δn for gaseous reactants and products is zero, $K_p = K_c$.

Q and K

- 16.8** (c) Because N₂O₄ and NO₂ are both in their standard states, they each have a partial pressure of 1.0 atm. Consequently, $Q_p = 1$. Since $K_p = 0.15$, $Q_p > K_p$, and the reaction proceeds to the left.

Finding Equilibrium Concentrations

- 16.9** (c) $K_c = \frac{[B]^2}{[A]}$
 $[B] = \sqrt{[A]K_c} = \sqrt{1.0 \times 4.0} = 2.0$

The x is small Approximation

- 16.10** (a) The *x is small* approximation is most likely to apply to a reaction with a small equilibrium constant and an initial concentration of reactant that is not too small. The bigger the equilibrium constant and the smaller the initial concentration of reactant, the less likely that the *x is small* approximation will apply.

Le Châtelier's Principle

- 16.11** (d) None of the changes listed here causes the reaction to shift right. They all cause the reaction to shift left.