14.9 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.

Pronounced "Le-sha-te-lyay"

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.

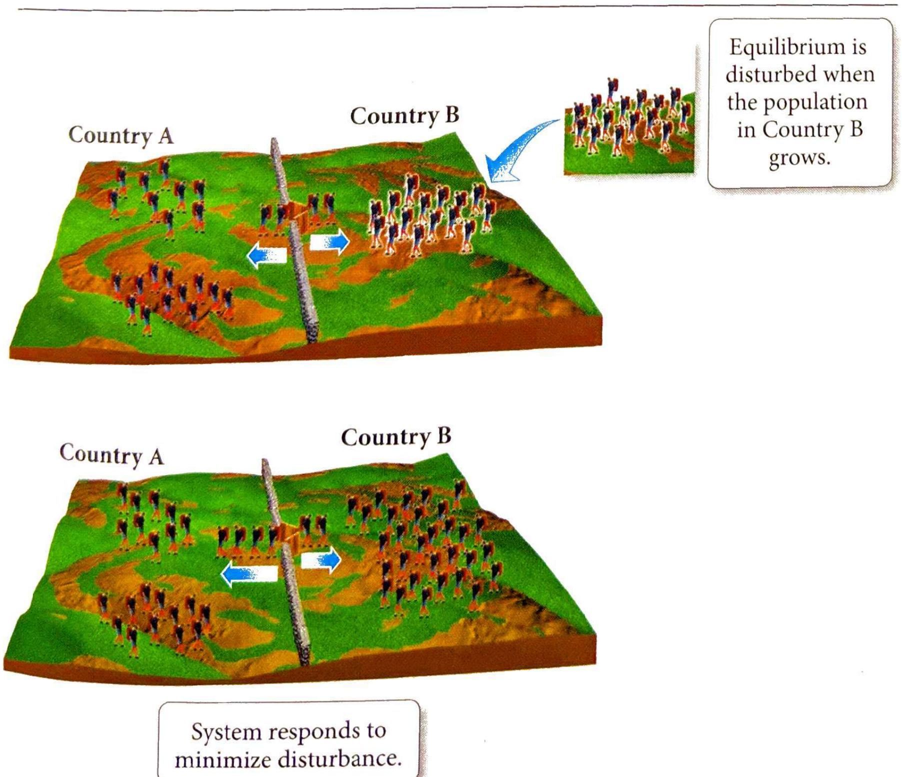
$$\text{Country A} \rightleftharpoons \text{Country B}$$

Now imagine disturbing the balance (Figure 14.8 ▼). 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 instead? 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. Chemical systems behave similarly: when their equilibrium is disturbed, they react to

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.

Le Châtelier's Principle: An Analogy



◀ **FIGURE 14.8 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.

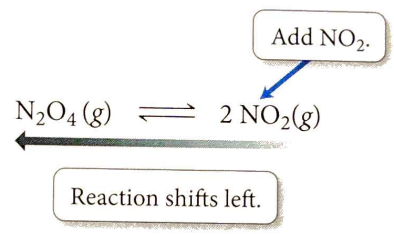
counter the disturbance. We can disturb a system in chemical equilibrium in several different ways, including changing the concentration of a reactant or product, changing the volume or pressure, and changing the temperature. We consider each of these separately.

The Effect of a Concentration Change on Equilibrium

Consider the following reaction in chemical equilibrium:

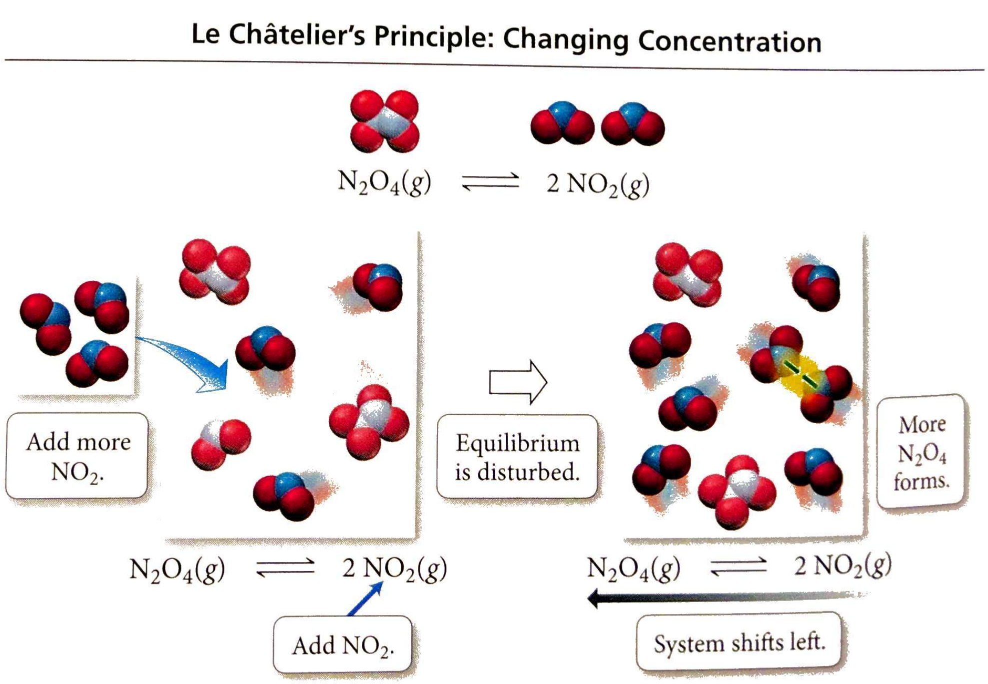
$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$$

Suppose we disturb the equilibrium by adding NO_2 to the equilibrium mixture (Figure 14.9 ▼). 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 14.10a ▶.



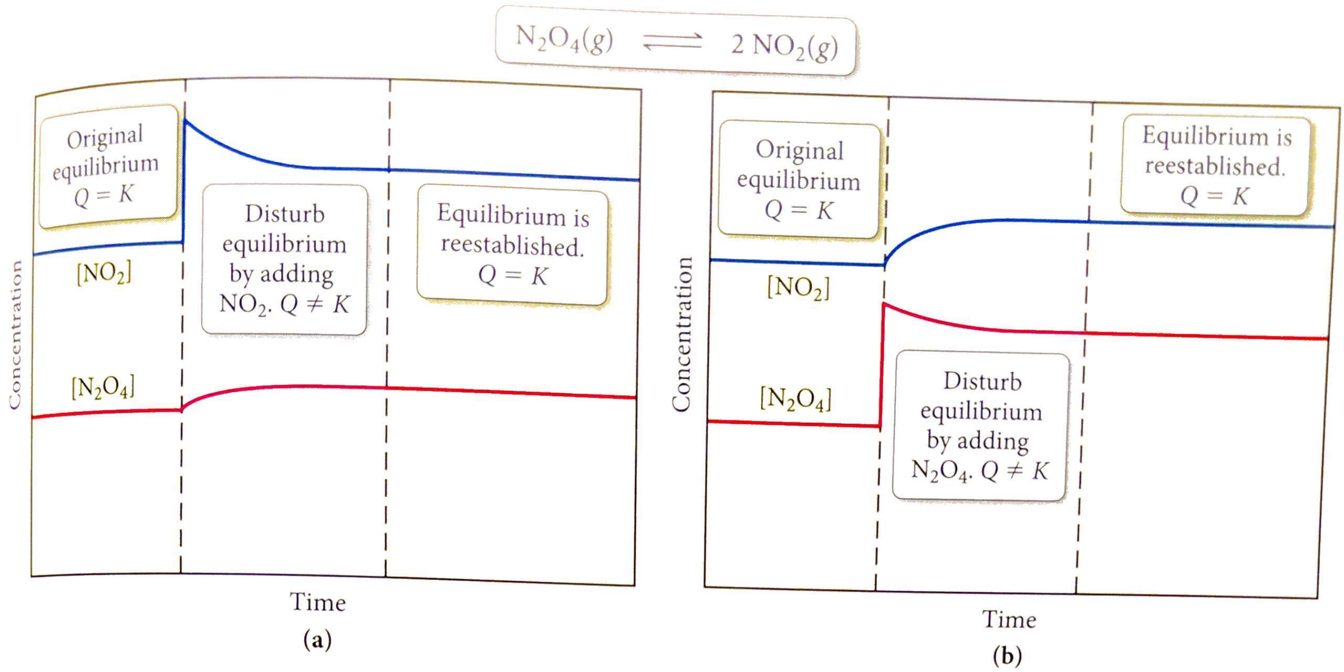
The reaction shifts to the left because the value of Q changes as follows:

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



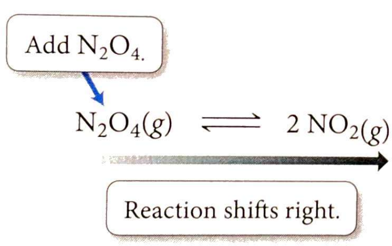
▲ **FIGURE 14.9 Le Châtelier's Principle: The Effect of a Concentration Change** Adding NO_2 causes the reaction to shift left, consuming some of the added NO_2 and forming more N_2O_4.

Le Châtelier's Principle: Graphical Representation



▲ **FIGURE 14.10 Le Châtelier's Principle: Changing Concentration** The graph shows the concentrations of NO_2 and N_2O_4 for the reaction $N_2O_4(g) \longrightarrow 2\ NO_2(g)$ 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).

On the other hand, 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 14.10b ▲.



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 right to reestablish equilibrium.

In both of these cases, 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).

EXAMPLE 14.14 The Effect of a Concentration Change on Equilibrium

Consider the following reaction at equilibrium:

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

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 14.5, solids are not included in the equilibrium expression.)

FOR PRACTICE 14.14

Consider the following reaction in chemical equilibrium:

$$2\ BrNO(g) \rightleftharpoons 2\ NO(g) + Br_2(g)$$

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 5 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:

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

What happens if we push down on the piston, lowering the volume and raising the pressure (Figure 14.11 ▸)? 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 14.11b)? 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 every 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.*

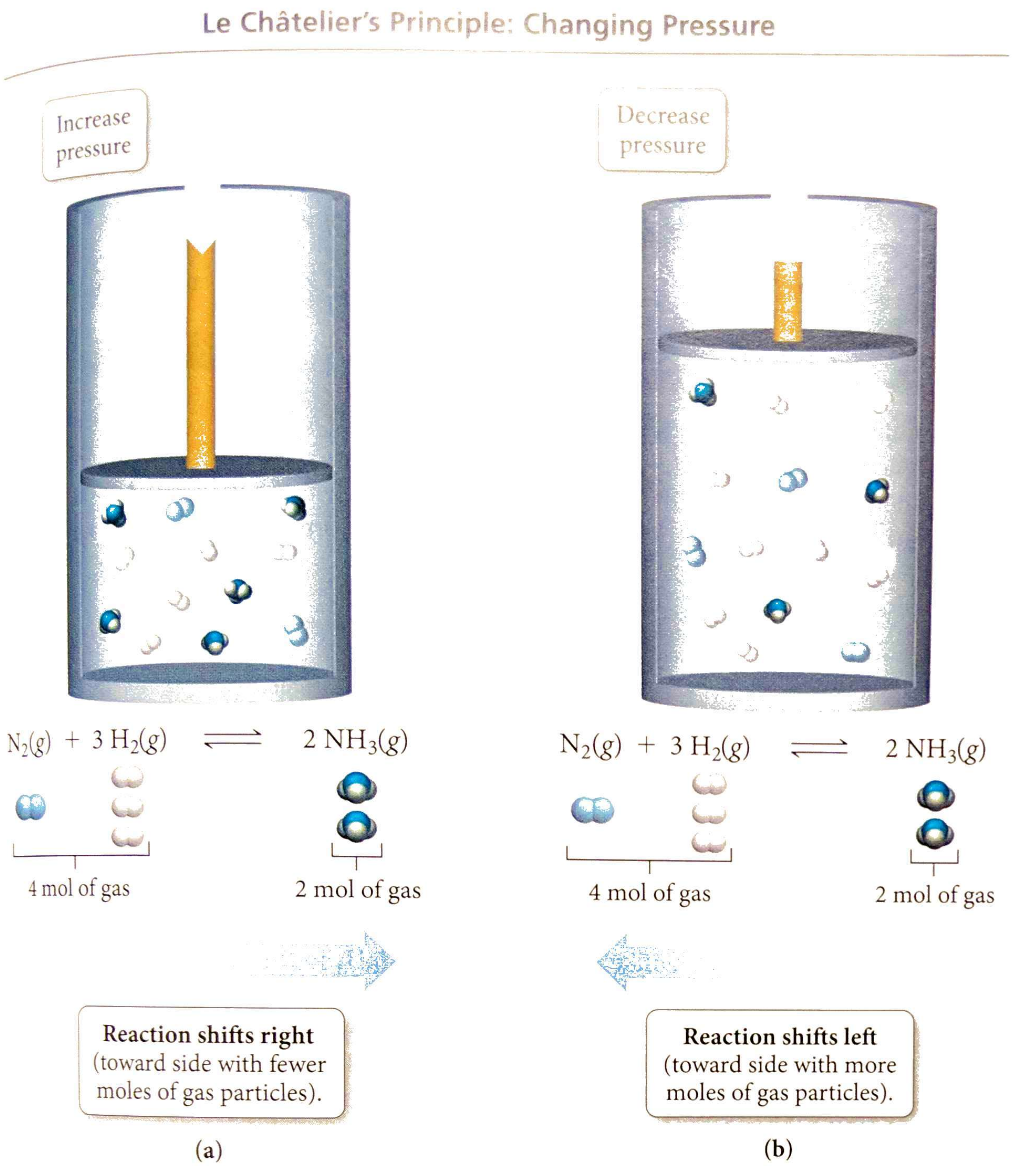


FIGURE 14.11 Le Châtelier's Principle: The Effect of a Pressure Change (a) Decreasing the volume increases the pressure, causing the reaction to shift to the right (fewer moles of gas, lower pressure). (b) Increasing the volume reduces the pressure, causing the reaction to shift to the left (more moles of gas, higher pressure).

- 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.

EXAMPLE 14.15 The Effect of a Volume Change on Equilibrium

Consider the following reaction at chemical equilibrium:

$$2\ KClO_3(s) \rightleftharpoons 2\ KCl(s) + 3\ O_2(g)$$

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 14.15

Consider the following reaction at chemical equilibrium:

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

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

The Effect of a Temperature Change on Equilibrium

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

According to Le Châtelier's principle, if the temperature of a system at equilibrium is changed, the system will shift in a direction to counter that change. So, if the temperature is increased, the reaction will shift in the direction that tends to decrease the temperature and vice versa. Recall from Chapter 6 that an exothermic reaction (negative ΔH) emits heat:

$$\text{Exothermic reaction: } A + B \rightleftharpoons C + D + \text{heat}$$

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

$$\text{Endothermic reaction: } A + B + \text{heat} \rightleftharpoons C + D$$

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:

Add heat

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) + \text{heat}$$

Reaction shifts left.
Smaller K

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:

Remove heat

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2NH_3(g) + \text{heat}$$

Reaction shifts right.
Larger K

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:

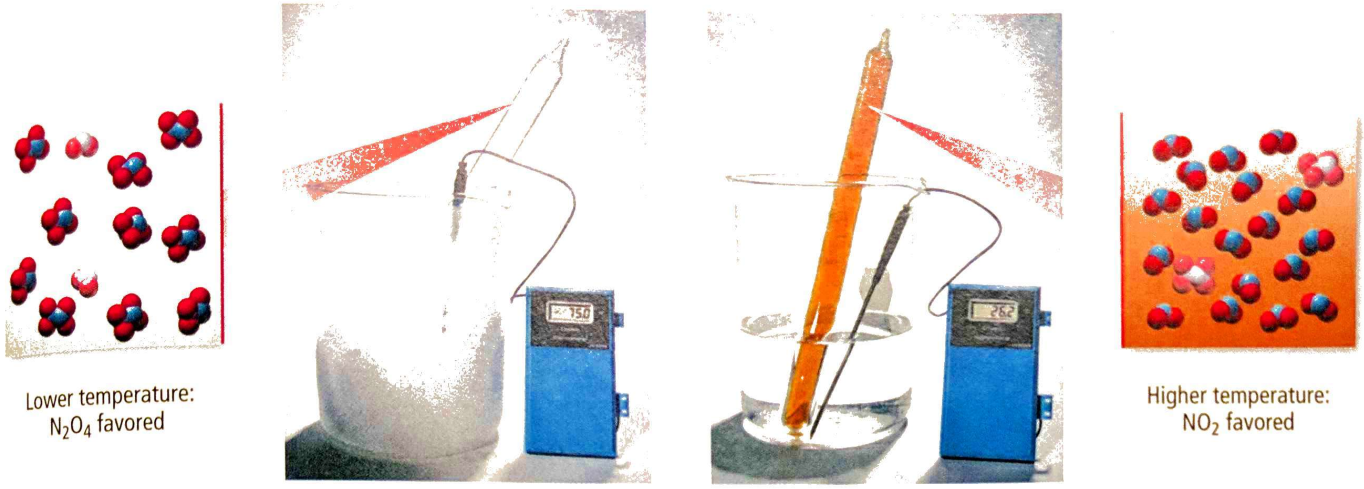
Add heat

$$\underset{\text{colorless}}{N_2O_4(g)} + \text{heat} \rightleftharpoons \underset{\text{brown}}{2\,NO_2(g)}$$

Reaction shifts right.
Larger K

Le Châtelier's Principle: Changing Temperature

$$\underset{\text{colorless}}{N_2O_4(g)} + \text{heat} \rightleftharpoons \underset{\text{brown}}{2\,NO_2(g)}$$



▲ **FIGURE 14.12** **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.

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. Since N_2O_4 is colorless and NO_2 is brown, the effects of changing the temperature of this reaction are easily seen (Figure 14.12 ▲). 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:

Remove heat ↑

$$\underset{\text{colorless}}{N_2O_4(g)} + \text{heat} \rightleftharpoons \underset{\text{brown}}{2\,NO_2(g)}$$

←

Reaction shifts left.
Smaller 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.