Pearson

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

Key Concept Video **Le Châtelier's Principle**

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.

> Le Châtelier is pronounced "Le-sha-te-lyay."

The Effect of a Concentration Change on Equilibrium

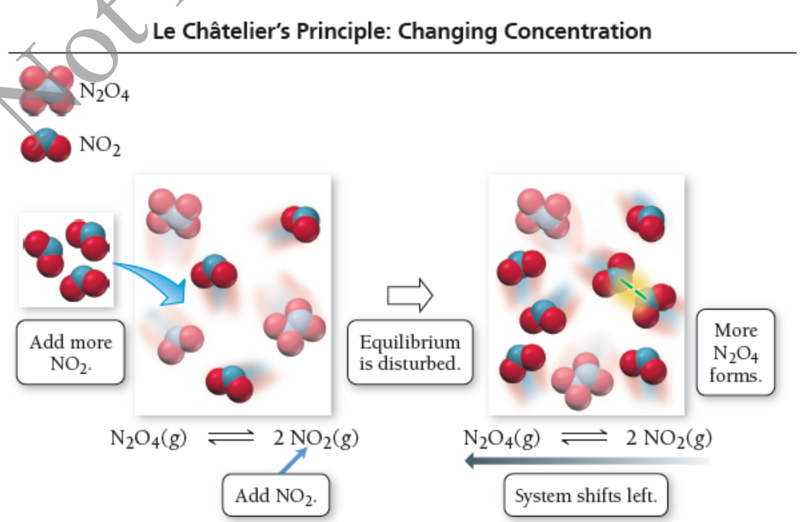
Consider the following reaction in chemical equilibrium:

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

Suppose we disturb the equilibrium by adding NO_2 to the equilibrium mixture (Figure 15.7).

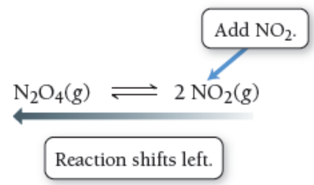
Figure 15.7 **Le Châtelier's Principle: The Effect of a Concentration Change**

Adding NO_2 causes the reaction to shift left, consuming some of the added NO_2 and forming more NO_2O_4.



Not for Distribution

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 15.8(a).



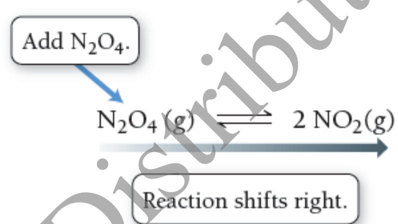
The reaction shifts to the left because the value of *Q* increases when we add a product to the reaction mixture. For example, suppose we double the concentration of NO_2.

- Before doubling the concentration of NO_2: $Q_1 = K = \frac{[NO_2]^2}{[N_2O_4]}$
- Immediately after doubling the concentration of NO_2:

$$Q_2 = \frac{(2[NO_2])^2}{[N_2O_4]} = 4 \times \frac{[NO_2]^2}{[N_2O_4]} = 4 \times Q_1 > K.$$

- Since $Q > K$, the reaction shifts to left to reestablish equilibrium.

What happens, however, 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 15.8(b).



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The reaction shifts to the right in this case because the value of *Q* changes. For example, suppose we double the concentration of N_2O_4:

- Before doubling the concentration of N_2O_4: $Q_1 = K = \frac{[NO_2]^2}{[N_2O_4]}$
- Immediately after doubling the concentration of N_2O_4:

$$Q_2 = \frac{[NO_2]^2}{2[N_2O_4]} = \frac{1}{2} \times \frac{[NO_2]^2}{[N_2O_4]} = \frac{1}{2} \times Q_1 < K.$$

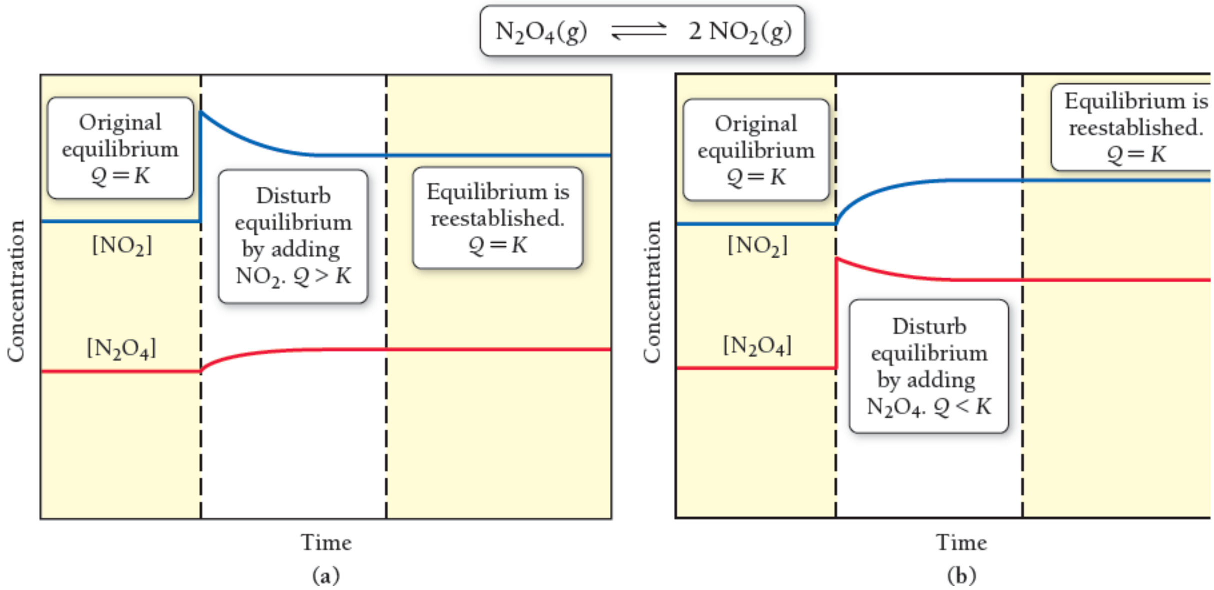
- Since $Q_1 < K$, the reaction shifts to the right to reestablish equilibrium.

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.

Figure 15.8 Le Châtelier's Principle: Changing Concentration

These two graphs each show the concentrations of NO_2 and N_2O_4 for the reaction $N_2O_4(g) \rightarrow 2\ NO_2(g)$ 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).

Le Châtelier's Principle: Graphical Representation



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).

Not for Distribution

Example 15.14 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 CO_2 to the reaction mixture? What is the effect of adding $CaCO_3$?

SOLUTION Adding 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 $CaCO_3$ has no effect on the position of the equilibrium. (Note that, as we saw in Section 15.5, solids are not included in the equilibrium expression.)

FOR PRACTICE 15.14 Consider the following reaction in chemical equilibrium:

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

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

Interactive Worked Example 15.14 **The Effect of a Concentration Change on Equilibrium**

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

How does a system in chemical equilibrium respond to a volume change? Recall from Chapter 10 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.

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

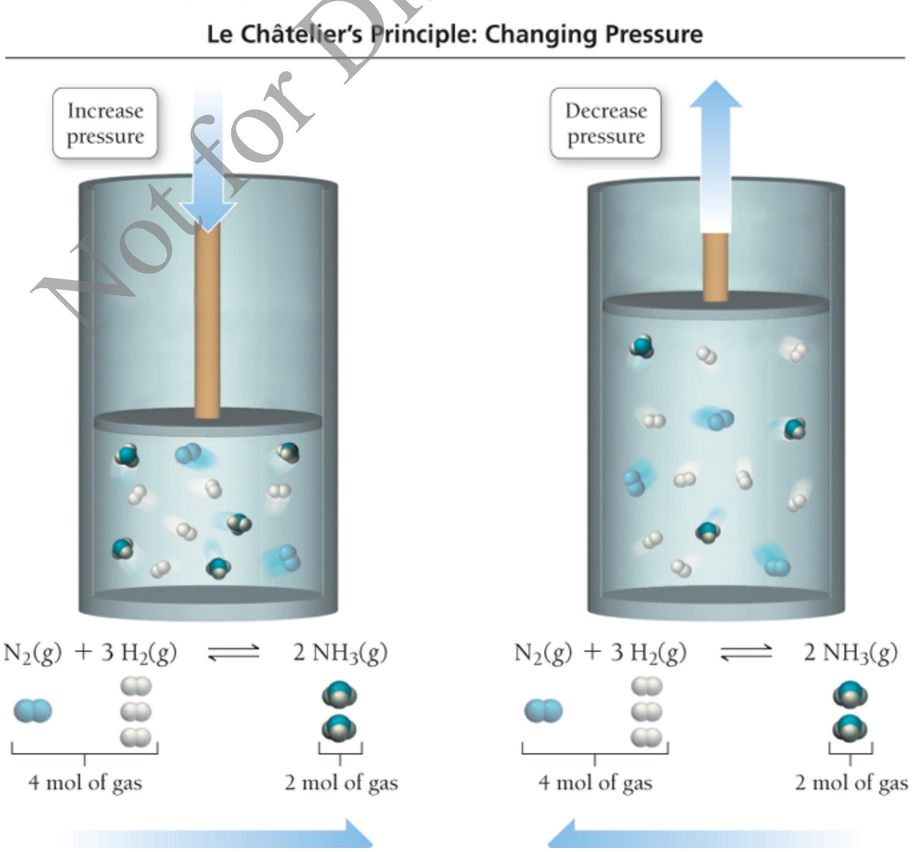
For example, consider the following reaction at equilibrium in a cylinder equipped with a moveable piston:

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

What happens if we push down on the piston, lowering the volume and raising the pressure (Figure 15.9)? 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.

Figure 15.9 **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).



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A change in volume, like a change in concentration, generally changes the value of Q (with some exceptions, which we discuss later in this section of the chapter). For example, suppose we decrease the volume of a nitrogen, hydrogen, and ammonia equilibrium mixture to $\frac{1}{2}$ of its original volume. We observe the following:

- Before halving the volume: $Q_1 = K = \dfrac{[NH_3]^2}{[N_2][H_2]^3} = \dfrac{\left(\frac{n_{NH_3}}{V}\right)^2}{\left(\frac{n_{N_2}}{V}\right)\left(\frac{n_{H_2}}{V}\right)^3}$
- Immediately after halving the volume:

$$Q_2 = \frac{\left(\frac{n_{NH_3}}{\frac{1}{2}V}\right)^2}{\left(\frac{n_{N_2}}{\frac{1}{2}V}\right)\left(\frac{n_{H_2}}{\frac{1}{2}V}\right)^3} = \frac{4\left(\frac{n_{NH_3}}{V}\right)^2}{2\left(\frac{n_{N_2}}{V}\right)8\left(\frac{n_{H_2}}{V}\right)^3} = \frac{1}{4} \times \frac{\left(\frac{n_{NH_3}}{V}\right)^2}{\left(\frac{n_{N_2}}{V}\right)\left(\frac{n_{H_2}}{V}\right)^3} = \frac{1}{4} \times Q_1 < K.$$

- Since $Q < K$, the reaction shifts to the right—toward the direction of fewer gas moles—to reestablish equilibrium.

> We can express the concentration of any substance as the number of moles of the substance divided by the volume: $[A] = n_a/V$.

Not for Distribution

Consider the same reaction mixture at equilibrium again. What happens if, this time, we pull *up* on the piston, *increasing* the volume (Figure 15.9b)? 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. Like a decrease in volume, an increase in volume changes Q.

For example, suppose we increase the volume of a nitrogen, hydrogen, and ammonia equilibrium mixture to twice its original volume:

- Before doubling the volume: $Q_1 = K = \dfrac{[NH_3]^2}{[N_2][H_2]^3} = \dfrac{\left(\frac{n_{NH_3}}{V}\right)^2}{\left(\frac{n_{N_2}}{V}\right)\left(\frac{n_{H_2}}{V}\right)^3}$
- Immediately after doubling the volume:

$$Q_2 = \frac{\left(\frac{n_{NH_3}}{2V}\right)^2}{\left(\frac{n_{N_2}}{2V}\right)\left(\frac{n_{H_2}}{2V}\right)^3} = \frac{\frac{1}{4}\left(\frac{n_{NH_3}}{V}\right)^2}{\frac{1}{2}\left(\frac{n_{N_2}}{V}\right)\frac{1}{8}\left(\frac{n_{H_2}}{V}\right)^3} = 4 \times \frac{\left(\frac{n_{NH_3}}{V}\right)^2}{\left(\frac{n_{N_2}}{V}\right)\left(\frac{n_{H_2}}{V}\right)^3} = 4 \times Q_1 < K.$$

- Since $Q > K$, the reaction shifts to the left to reestablish equilibrium.

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 volume of the reaction mixture does not change and so Q does not change. Consequently, there is no effect, and the reaction does not shift in either direction. Similarly, if a reaction has equal moles of gas particles on both sides of the reaction, the effects of a volume change on Q cancel each other out and there is no effect on the reaction (the reaction does not shift in either direction).

Example 15.15 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 mol 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 15.15 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?

Not for Distribution

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

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. However, 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 9 that an exothermic reaction (negative ΔH) emits heat:

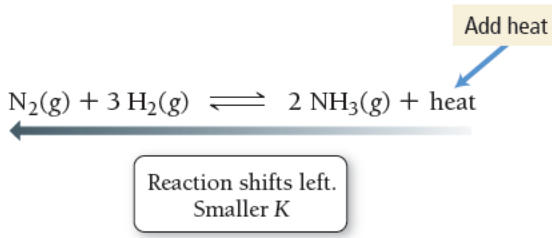
$$\text{Exothermic reaction: } A + B \rightleftharpoons C + D + \text{heat}$$

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

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

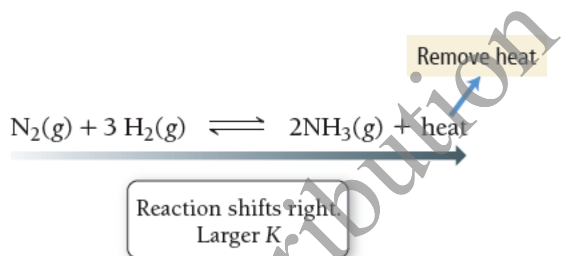
We can think of heat as a reactant in an endothermic reaction.

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:



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 fewer products and more reactants. Note that, unlike adding 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:



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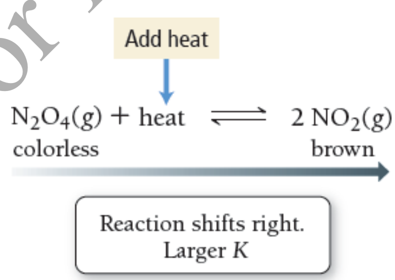
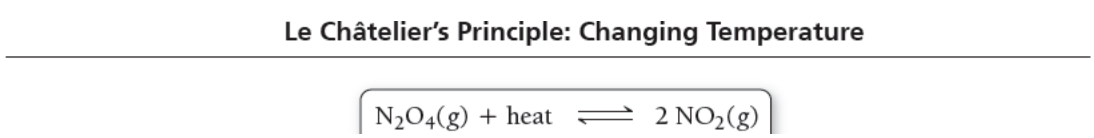
In contrast, for an *endothermic* reaction, raising the temperature (adding heat) causes the reaction to shift right to absorb the added heat. For example, the following reaction is endothermic:



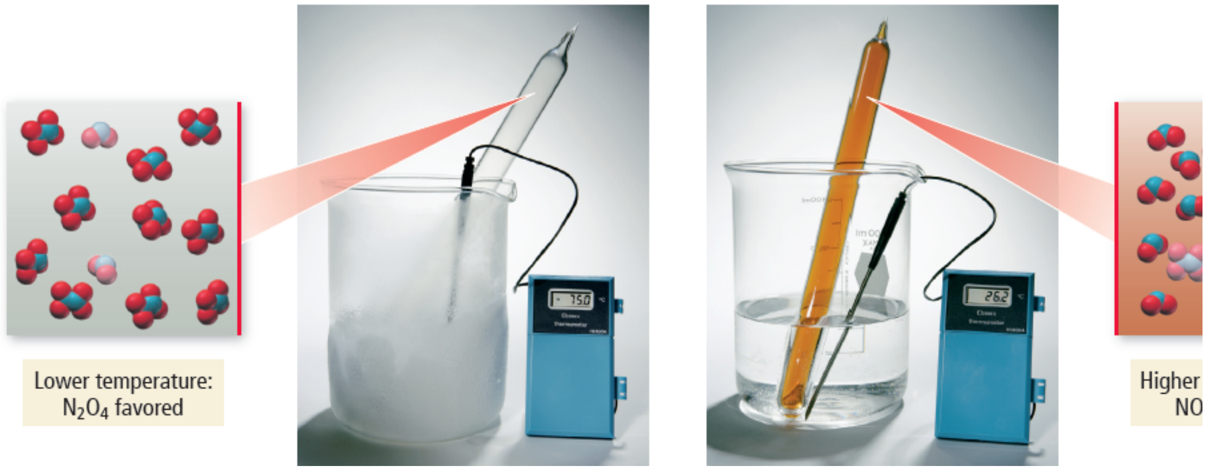
Raising the temperature of an equilibrium mixture of these two gases causes the reaction to shift right, absorbing some of the added heat and producing more products because the value of *K* has increased. Since N_2O_4 is colorless and NO_2 is brown, the effects of changing the temperature of this reaction are easily seen (Figure 15.10).

Figure 15.10 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.



colorless brown



In contrast, lowering the temperature (removing heat) of a reaction mixture of these two gases causes the reaction to shift left, releasing heat, forming fewer 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*

Not for Distribution

We can quantify the relationship between the value of the equilibrium constant and the temperature using an equation derived from thermodynamic considerations. We will cover this equation in Section 18.9.

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 15.16 The Effect of a Temperature Change on Equilibrium

The following reaction is endothermic:

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

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:

$$\text{heat} + CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

Raising the temperature is equivalent to 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 15.16 The following reaction is exothermic:

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

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

Not for Distribution

Not for Distribution

Not for Distribution