

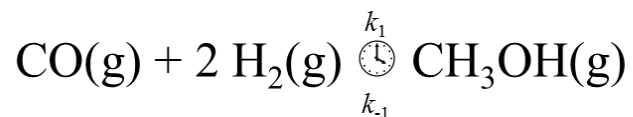
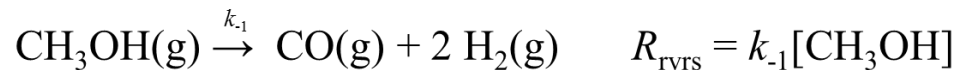
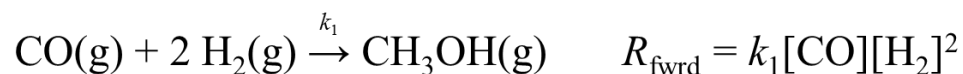
# Principles of Chemical Equilibrium



## The Concept of Equilibrium and the Equilibrium Constant

Few chemical reactions proceed in only one direction. Most are reversible, at least to some extent. At the start of a reversible process, the reaction proceeds toward the formation of products. As soon as some product molecules are formed, the reverse process begins to take place and reactant molecules are formed from product molecules.

*Chemical equilibrium is achieved when the rates of the forward and reverse reactions are equal and the concentrations of the reactants and products remain constant.*



$$R_{\text{fwrd}} = R_{\text{rvrs}}$$

Chemical equilibrium is a dynamic process.

Note that chemical equilibrium involves different substances as reactants and products. Equilibrium between two phases of the same substance is called ***physical equilibrium because the changes that occur are physical processes.***

***The vaporization*** of water in a closed container at a given temperature is an example of physical equilibrium. In this instance, the number of H<sub>2</sub>O molecules leaving and the number returning to the liquid phase are equal:

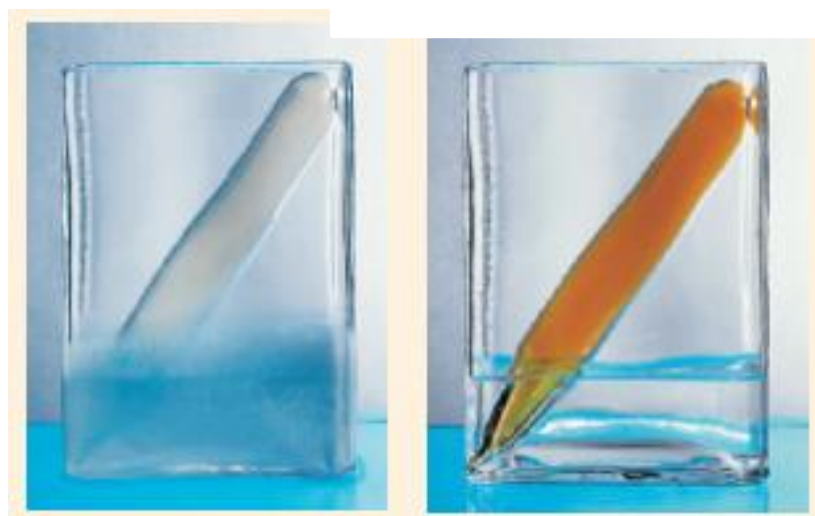


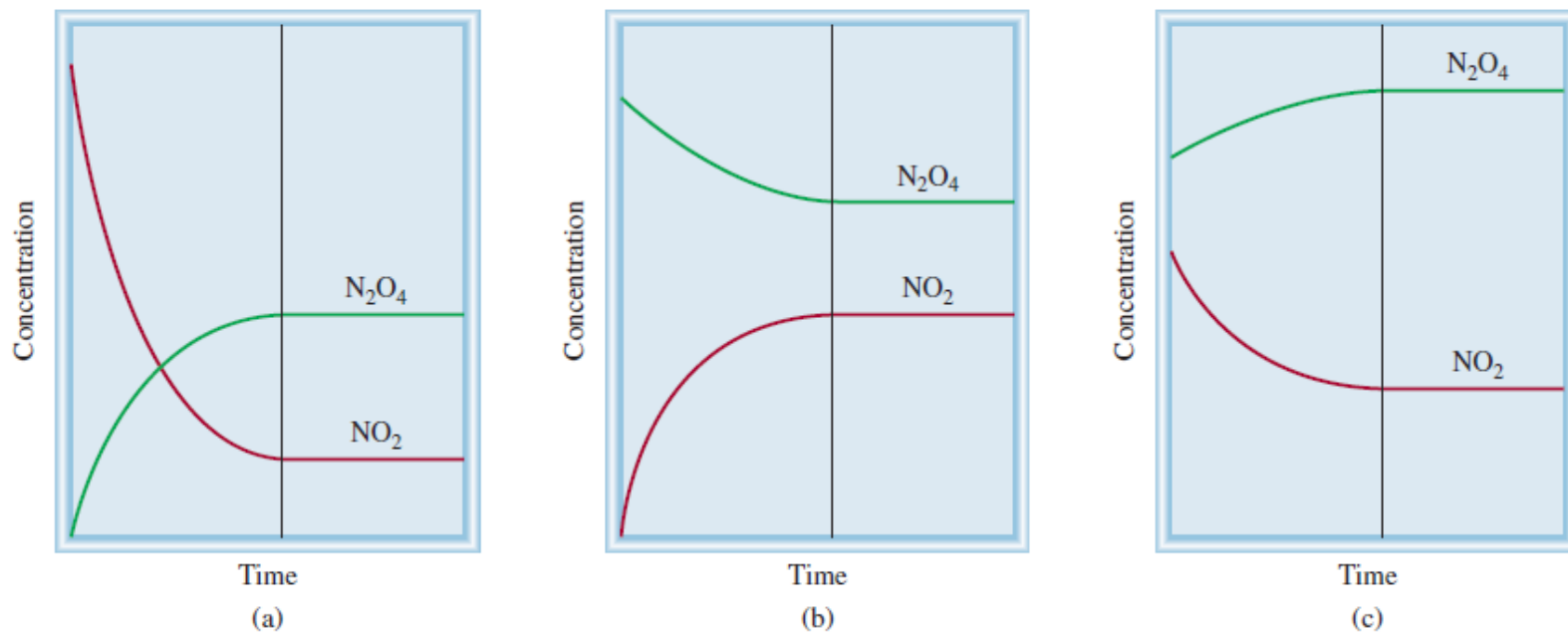
Liquid water in equilibrium with its vapor in a closed system at room temperature.

The study of physical equilibrium yields useful information, such as the equilibrium vapor pressure (see Section 11.8). However, chemists are particularly interested in chemical equilibrium processes, such as the reversible reaction involving nitrogen dioxide ( $\text{NO}_2$ ) and dinitrogen tetroxide ( $\text{N}_2\text{O}_4$ ) (Figure 14.1). The progress of the reaction



can be monitored easily because  $\text{N}_2\text{O}_4$  is a colorless gas, whereas  $\text{NO}_2$  has a dark brown color that makes it sometimes visible in polluted air. Suppose that  $\text{N}_2\text{O}_4$  is injected into an evacuated flask. Some brown color appears immediately, indicating the formation of  $\text{NO}_2$  molecules. The color intensifies as the dissociation of  $\text{N}_2\text{O}_4$  continues until eventually equilibrium is reached. Beyond that point, no further change in color is evident because the concentrations of both  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  remain constant. We can also bring about an equilibrium state by starting with pure  $\text{NO}_2$ . As some of the  $\text{NO}_2$  molecules combine to form  $\text{N}_2\text{O}_4$ , the color fades. Yet another way to create an equilibrium state is to start with a mixture of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  and monitor the system until the color stops changing.





**Figure 14.2** Change in the concentrations of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  with time, in three situations. (a) Initially only  $\text{NO}_2$  is present. (b) Initially only  $\text{N}_2\text{O}_4$  is present. (c) Initially a mixture of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  is present. In each case, equilibrium is established to the right of the vertical line.

Table 14.1 shows some experimental data for the reaction just described at 25°C. The gas concentrations are expressed in molarity, which can be calculated from the number of moles of gases present initially and at equilibrium and the volume of the flask in liters. Note that the equilibrium concentrations of NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub> vary, depending on the starting concentrations. We can look for relationships between [NO<sub>2</sub>] and [N<sub>2</sub>O<sub>4</sub>] present at equilibrium by comparing the ratio of their concentrations. The simplest ratio, that is, [NO<sub>2</sub>]/[N<sub>2</sub>O<sub>4</sub>], gives scattered values. But if we examine other possible mathematical relationships, we find that the ratio [NO<sub>2</sub>]<sup>2</sup>/[N<sub>2</sub>O<sub>4</sub>] at equilibrium gives a nearly constant value that averages 4.63·10<sup>-3</sup>, regardless of the initial concentrations present:

$$K = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = 4.63 \times 10^{-3} \quad (14.1)$$

**TABLE 14.1** The NO<sub>2</sub>-N<sub>2</sub>O<sub>4</sub> System at 25°C

Initial Concentrations (M)		Equilibrium Concentrations (M)		Ratio of Concentrations at Equilibrium	
[NO <sub>2</sub> ]	[N <sub>2</sub> O <sub>4</sub> ]	[NO <sub>2</sub> ]	[N <sub>2</sub> O <sub>4</sub> ]	$\frac{[\text{NO}_2]}{[\text{N}_2\text{O}_4]}$	$\frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$
0.000	0.670	0.0547	0.643	0.0851	4.65 × 10 <sup>-3</sup>
0.0500	0.446	0.0457	0.448	0.102	4.66 × 10 <sup>-3</sup>
0.0300	0.500	0.0475	0.491	0.0967	4.60 × 10 <sup>-3</sup>
0.0400	0.600	0.0523	0.594	0.0880	4.60 × 10 <sup>-3</sup>
0.200	0.000	0.0204	0.0898	0.227	4.63 × 10 <sup>-3</sup>

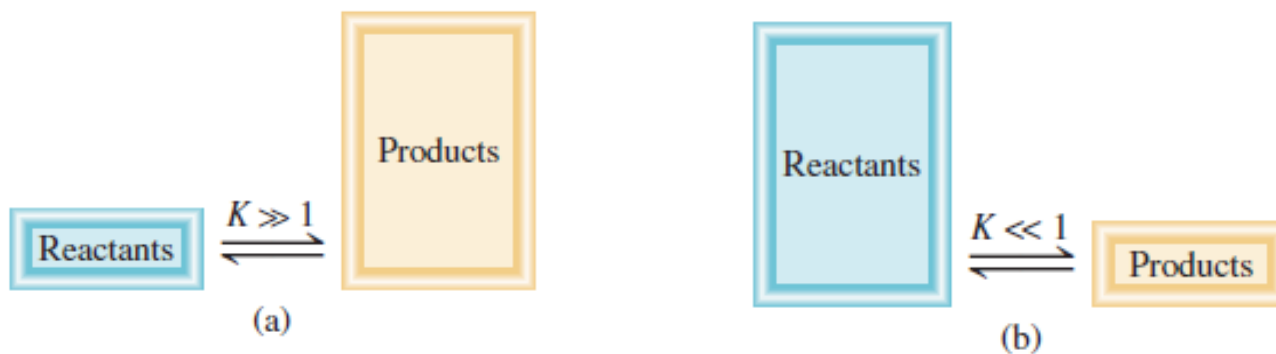
We can generalize this phenomenon with the following reaction at equilibrium:



where  $a$ ,  $b$ ,  $c$ , and  $d$  are the stoichiometric coefficients for the reacting species A, B, C, and D. For the reaction at a particular temperature

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \quad (14.2)$$

The equilibrium constant, then, is defined by a *quotient*, the numerator of which is obtained by multiplying together the equilibrium concentrations of the *products*, each raised to a power equal to its stoichiometric coefficient in the balanced equation. Applying the same procedure to the equilibrium concentrations of *reactants* gives the denominator. The magnitude of the equilibrium constant tells us whether an equilibrium reaction favors the products or reactants. If  $K$  is much greater than 1 (that is,  $K \gg 1$ ), the equilibrium will lie to the right and favors the products. Conversely, if the equilibrium constant is much smaller than 1 (that is,  $K \ll 1$ ), the equilibrium will lie to the left and favor the reactants (Figure 14.3). In this context, any number greater than 10 is considered to be much greater than 1, and any number less than 0.1 is much less than 1.



**Figure 14.3** (a) At equilibrium, there are more products than reactants, and the equilibrium is said to lie to the right. (b) In the opposite situation, when there are more reactants than products, the equilibrium is said to lie to the left.



## Writing Equilibrium Constant Expressions

The concept of equilibrium constants is extremely important in chemistry. As you will soon see, equilibrium constants are the key to solving a wide variety of stoichiometry problems involving equilibrium systems.

To use equilibrium constants, we must express them in terms of the reactant and product concentrations. Our only guide is the law of mass action [Equation (14.2)], which is the general formula for finding equilibrium concentrations. However, because the concentrations of the reactants and products can be expressed in different units and because the reacting species are not always in the same phase, there may be more than one way to express the equilibrium constant for the *same reaction*.

## Homogeneous Equilibria

The term **homogeneous equilibrium** applies to reactions in which all reacting species are in the same phase. An example of homogeneous gas-phase equilibrium is the dissociation of  $\text{N}_2\text{O}_4$ . The equilibrium constant, as given in Equation (14.1), is



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

Note that the subscript in  $K_c$  indicates that the concentrations of the reacting species are expressed in molarity or moles per liter. The concentrations of reactants and products in gaseous reactions can also be expressed in terms of their partial pressures.

we see that at constant temperature, the pressure  $P$  of a gas is directly related to the concentration in mol/L of the gas; that is,  $P=(n/V)RT$ . Thus, for the equilibrium process



we can write

$$K_P = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} \quad (14.3)$$

where  $P_{\text{NO}_2}$  and  $P_{\text{N}_2\text{O}_4}$  are the equilibrium partial pressures (in atm) of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$ , respectively. The subscript in  $K_P$  tells us that equilibrium concentrations are expressed in terms of pressure.

In general,  $K_c$  is not equal to  $K_p$ , because the partial pressures of reactants and products are not equal to their concentrations expressed in moles per liter. A simple relationship between  $K_p$  and  $K_c$  can be derived as follows. Let us consider the following equilibrium in the gas phase:



where  $a$  and  $b$  are stoichiometric coefficients. The equilibrium constant  $K_c$  is given by

$$K_c = \frac{[B]^b}{[A]^a}$$

and the expression for  $K_p$  is

$$K_p = \frac{P_B^b}{P_A^a}$$

where  $P_A$  and  $P_B$  are the partial pressures of A and B. Assuming ideal gas behavior,

$$P_A V = n_A RT$$
$$P_A = \frac{n_A RT}{V}$$

where  $V$  is the volume of the container in liters. Also

$$P_B V = n_B RT$$
$$P_B = \frac{n_B RT}{V}$$

Substituting these relations into the expression for  $K_p$ , we obtain

$$K_p = \frac{\left(\frac{n_B RT}{V}\right)^b}{\left(\frac{n_A RT}{V}\right)^a} = \frac{\left(\frac{n_B}{V}\right)^b}{\left(\frac{n_A}{V}\right)^a} (RT)^{b-a}$$

Now both  $n_A/V$  and  $n_B/V$  have units of mol/L and can be replaced by [A] and [B], so that

$$K_p = \frac{[B]^b}{[A]^a} (RT)^{\Delta n}$$
$$= K_c (RT)^{\Delta n} \quad (14.4)$$

where

$$\Delta n = b - a$$

= moles of gaseous products – moles of gaseous reactants

Because pressures are usually expressed in atm, the gas constant  $R$  is given by 0.0821 L · atm/K · mol, and we can write the relationship between  $K_p$  and  $K_c$  as

$$K_p = K_c (0.0821T)^{\Delta n} \quad (14.5)$$

## Heterogeneous Equilibria

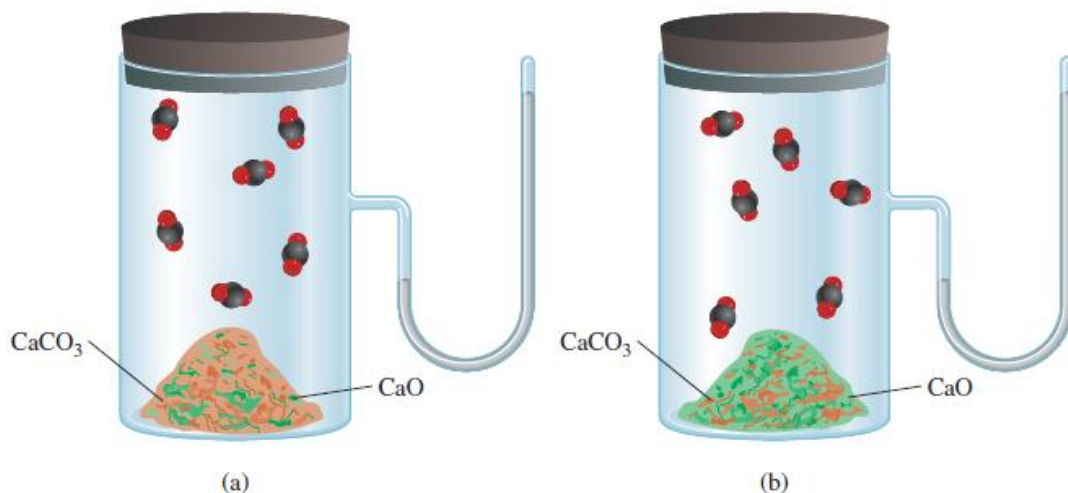
As you might expect, a **heterogeneous equilibrium results from a reversible reaction** involving reactants and products that are in different phases. For example, when calcium carbonate is heated in a closed vessel, the following equilibrium is attained:



The two solids and one gas constitute three separate phases. At equilibrium, we might write the equilibrium constant as

$$K'_c = \frac{[\text{CaO}][\text{CO}_2]}{[\text{CaCO}_3]}$$

The “concentration” of a solid, like its density, is an intensive property and does not depend on how much of the substance is present.



**Figure 14.4** In (a) and (b) the equilibrium pressure of CO<sub>2</sub> is the same at the same temperature, despite the presence of different amounts of CaCO<sub>3</sub> and CaO.

For this reason, the terms [CaCO<sub>3</sub>] and [CaO] are themselves constants and can be combined with the equilibrium constant. We can simplify Equation (14.6) by writing

$$\frac{[\text{CaCO}_3]}{[\text{CaO}]} K'_c = K_c = [\text{CO}_2] \quad (14.7)$$

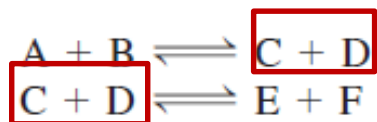
Alternatively, we can express the equilibrium constant as

$$K_P = P_{\text{CO}_2} \quad (14.8)$$

The equilibrium constant in this case is numerically equal to the pressure of  $\text{CO}_2$  gas, an easily measurable quantity.



The reactions we have considered so far are all relatively simple. A more complicated situation is one in which the product molecules in one equilibrium system are involved in a second equilibrium process:

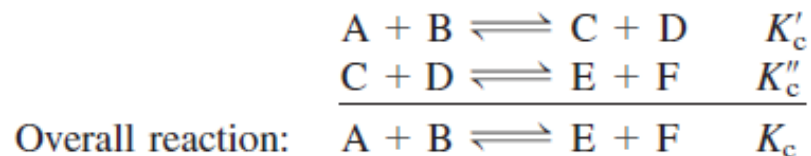


The products formed in the first reaction, C and D, react further to form products E and F. At equilibrium we can write two separate equilibrium constants:

$$K_c' = \frac{[C][D]}{[A][B]}$$

$$K_c'' = \frac{[E][F]}{[C][D]}$$

The overall reaction is given by the sum of the two reactions



and the equilibrium constant  $K_c$  for the overall reaction is

$$K_c = \frac{[E][F]}{[A][B]}$$

We obtain the same expression if we take the product of the expressions for  $K'_c$  and  $K''_c$ :

$$K'_c K''_c = \frac{[C][D]}{[A][B]} \times \frac{[E][F]}{[C][D]} = \frac{[E][F]}{[A][B]}$$

Therefore,

$$K_c = K'_c K''_c \quad (14.9)$$

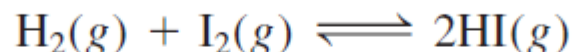
## Relationship of K to the Balanced Chemical Equation

The equilibrium constant expression and the value of  $K$  both depend on how we write the equation for a reaction. Here are some general rules to keep in mind.

- When we *reverse* an equation, we *invert* the value of  $K$ .
- When we *multiply* the coefficients in a balanced equation by a common factor we raise the equilibrium constant to the *corresponding power*
- When we *divide* the coefficients in a balanced equation by a common factor we take the *corresponding root* of the equilibrium constant (square root, cube root, )

## Predicting the Direction of a Reaction

The equilibrium constant  $K_c$  for the formation of hydrogen iodide from molecular hydrogen and molecular iodine in the gas phase



is 54.3 at 430°C. Suppose that in a certain experiment we place 0.243 mole of  $\text{H}_2$ , 0.146 mole of  $\text{I}_2$ , and 1.98 moles of  $\text{HI}$  all in a 1.00-L container at 430°C. Will there be a net reaction to form more  $\text{H}_2$  and  $\text{I}_2$  or more  $\text{HI}$ ? Inserting the starting concentrations in the equilibrium constant expression, we write

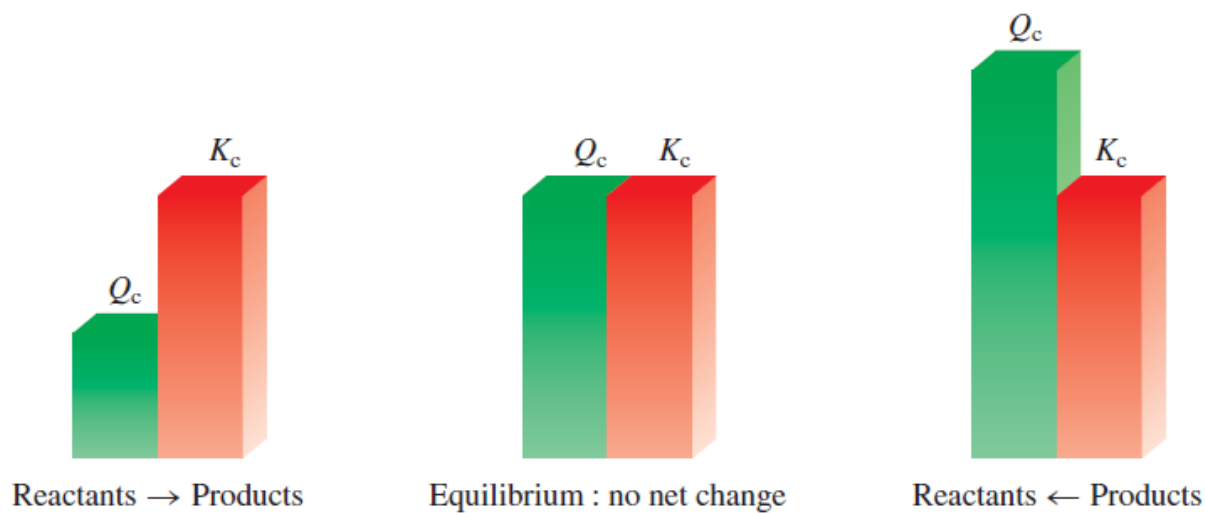
$$\frac{[\text{HI}]_0^2}{[\text{H}_2]_0[\text{I}_2]_0} = \frac{(1.98)^2}{(0.243)(0.146)} = 111$$

where the subscript 0 indicates initial concentrations (before equilibrium is reached). Because the quotient  $[\text{HI}]_0^2/[\text{H}_2]_0[\text{I}_2]_0$  is greater than  $K_c$ , this system is not at equilibrium.

For reactions that have not reached equilibrium, such as the formation of HI considered above, we obtain the *reaction quotient* ( $Q_c$ ), instead of the equilibrium constant *by substituting the initial concentrations into the equilibrium constant expression*. To determine the direction in which the net reaction will proceed to achieve equilibrium, we compare the values of  $Q_c$  and  $K_c$ . The three possible cases are as follows:

- $Q_c < K_c$      The ratio of initial concentrations of products to reactants is too small. To reach equilibrium, reactants must be converted to products. The system proceeds from left to right (consuming reactants, forming products) to reach equilibrium.
- $Q_c = K_c$      The initial concentrations are equilibrium concentrations. The system is at equilibrium.
- $Q_c > K_c$      The ratio of initial concentrations of products to reactants is too large. To reach equilibrium, products must be converted to reactants. The system proceeds from right to left (consuming products, forming reactants) to reach equilibrium.

Condition	Direction of Net Chemical Change
$Q < K$	To the right ( $\longrightarrow$ )
$Q > K$	To the left ( $\longleftarrow$ )
$Q = K$	Equilibrium; no net change ( $\rightleftharpoons$ )



**Figure 14.5** The direction of a reversible reaction to reach equilibrium depends on the relative magnitudes of  $Q_c$  and  $K_c$ . Note that  $K_c$  is a constant at a given temperature, but  $Q_c$  varies according to the relative amounts of reactants and products present.

## Calculating Equilibrium Concentrations

If we know the equilibrium constant for a particular reaction, we can calculate the concentrations in the equilibrium mixture from the initial concentrations. Commonly, only the initial reactant concentrations are given. Let us consider the following system involving two organic compounds, *cis*-stilbene and *trans*-stilbene, in a nonpolar hydrocarbon solvent (Figure 14.6):



The equilibrium constant ( $K_c$ ) for this system is 24.0 at 200°C. Suppose that initially only *cis*-stilbene is present at a concentration of 0.850 mol/L. How do we calculate the concentrations of *cis*- and *trans*-stilbene at equilibrium? From the

	<i>cis</i> -stilbene	$\rightleftharpoons$	<i>trans</i> -stilbene
Initial ( $M$ ):	0.850		0
Change ( $M$ ):	$-x$		$+x$
Equilibrium ( $M$ ):	$(0.850 - x)$		$x$

A positive (+) change represents an increase and a negative (–) change a decrease in concentration at equilibrium. Next, we set up the equilibrium constant expression

$$K_c = \frac{[\textit{trans}\text{-stilbene}]}{[\textit{cis}\text{-stilbene}]}$$
$$24.0 = \frac{x}{0.850 - x}$$
$$x = 0.816 M$$

Having solved for  $x$ , we calculate the equilibrium concentrations of *cis*-stilbene and *trans*-stilbene as follows:

$$[\textit{cis}\text{-stilbene}] = (0.850 - 0.816) M = 0.034 M$$
$$[\textit{trans}\text{-stilbene}] = 0.816 M$$



## Factors That Affect Chemical Equilibrium

Chemical equilibrium represents a balance between forward and reverse reactions. In most cases, this balance is quite delicate. Changes in experimental conditions may disturb the balance and shift the equilibrium position so that more or less of the desired product is formed.

When we say that an equilibrium position shifts to the right, for example, we mean that the net reaction is now from left to right. Variables that can be controlled experimentally are concentration, pressure, volume, and temperature.

## Le Châtelier's Principle

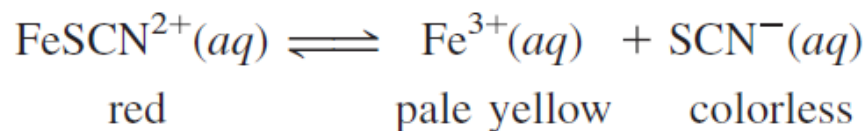
There is a general rule that helps us to predict the direction in which an equilibrium reaction will move when a change in concentration, pressure, volume, or temperature occurs.

The rule, known as **Le Châtelier's† principle**, states that if an external stress is applied to a system at equilibrium, the system adjusts in such a way that the stress is partially offset as the system reaches a new equilibrium position.

The word “stress” here means a change in concentration, pressure, volume, or temperature that removes the system from the equilibrium state. We will use Le Châtelier's principle to assess the effects of such changes.

## Changes in Concentration

Iron(III) thiocyanate [ $\text{Fe}(\text{SCN})_3$ ] dissolves readily in water to give a red solution. The red color is due to the presence of hydrated  $\text{FeSCN}^{2+}$  ion. The equilibrium between undissociated  $\text{FeSCN}^{2+}$  and the  $\text{Fe}^{3+}$  and  $\text{SCN}^-$  ions is given by



What happens if we add some sodium thiocyanate ( $\text{NaSCN}$ ) to this solution? In this case, the stress applied to the equilibrium system is an increase in the concentration of  $\text{SCN}^-$  (from the dissociation of  $\text{NaSCN}$ ). To offset this stress, some  $\text{Fe}^{3+}$  ions react with the added  $\text{SCN}^-$  ions, and the equilibrium shifts from right to left:

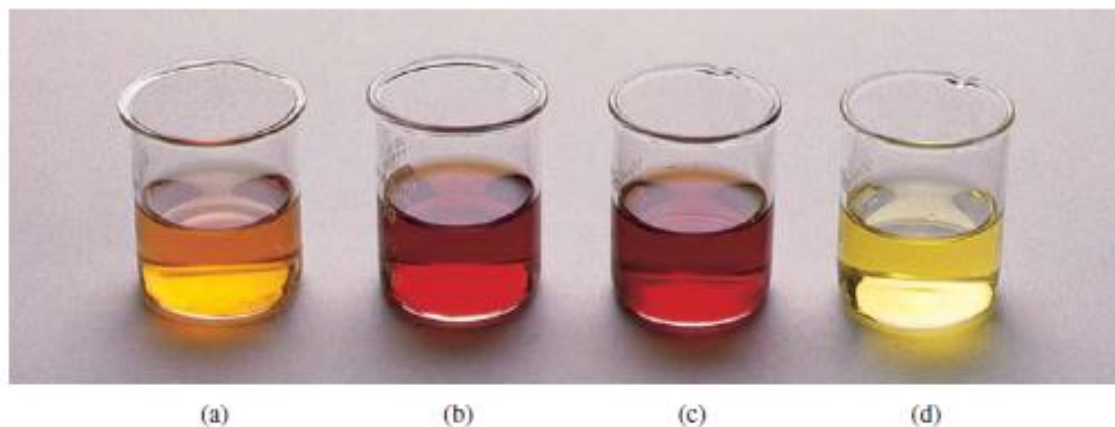


Consequently, the red color of the solution deepens (Figure 14.7). Similarly, if we added iron(III) nitrate [ $\text{Fe}(\text{NO}_3)_3$ ] to the original solution, the red color would also deepen because the additional  $\text{Fe}^{3+}$  ions [from  $\text{Fe}(\text{NO}_3)_3$ ] would shift the equilibrium from right to left.

Now suppose we add some oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ) to the original solution. Oxalic acid ionizes in water to form the oxalate ion,  $\text{C}_2\text{O}_4^{2-}$ , which binds strongly to the  $\text{Fe}^{3+}$  ions. The formation of the stable yellow ion  $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$  removes free  $\text{Fe}^{3+}$  ions in solution. Consequently, more  $\text{FeSCN}^{2+}$  units dissociate and the equilibrium shifts from left to right:



The red solution will turn yellow due to the formation of  $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$  ions.



**Figure 14.7** Effect of concentration change on the position of equilibrium. (a) An aqueous  $\text{Fe}(\text{SCN})_3$  solution. The color of the solution is due to both the red  $\text{FeSCN}^{2+}$  and the yellow  $\text{Fe}^{3+}$  ions. (b) After the addition of some  $\text{NaSCN}$  to the solution in (a), the equilibrium shifts to the left. (c) After the addition of some  $\text{Fe}(\text{NO}_3)_3$  to the solution in (a), the equilibrium shifts to the left. (d) After the addition of some  $\text{H}_2\text{C}_2\text{O}_4$  to the solution in (a), the equilibrium shifts to the right. The yellow color is due to the  $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$  ions.

This experiment demonstrates that all reactants and products are present in the reacting system at equilibrium. Second, increasing the concentrations of the products ( $\text{Fe}^{3+}$  or  $\text{SCN}^{-}$ ) shifts the equilibrium to the left, and decreasing the concentration of the product  $\text{Fe}^{3+}$  shifts the equilibrium to the right. These results are just as predicted by Le Châtelier's principle.

## Effect of Temperature on Equilibrium

We can think of changing the temperature of an equilibrium mixture in terms of adding heat (raising the temperature) or removing heat (lowering the temperature). According to Le Châtelier's principle, adding heat favors the reaction in which heat is absorbed (*endothermic* reaction). Removing heat favors the reaction in which heat is evolved (*exothermic* reaction). Stated in terms of changing temperature,

*Raising the temperature of an equilibrium mixture shifts the equilibrium condition in the direction of the endothermic reaction. Lowering the temperature causes a shift in the direction of the exothermic reaction.*

*For endothermic reactions,  $K$  increases as temperature increases. For exothermic reactions,  $K$  decreases as temperature increases.*

## Changes in Volume and Pressure

Changes in pressure ordinarily do not affect the concentrations of reacting species in condensed phases (say, in an aqueous solution) because liquids and solids are virtually incompressible. On the other hand, concentrations of gases are greatly affected by changes in pressure.

## Effect of Changes in Pressure or Volume on Equilibrium

There are three ways to change the pressure of a constant-temperature equilibrium mixture.

**1. Add or remove a gaseous reactant or product.** The effect of these actions on the equilibrium condition is simply that caused by adding or removing a reaction component, as described previously.

**2. Add an inert gas to the constant-volume reaction mixture.** This has the effect of increasing the *total* pressure, but the partial pressures of the reacting species are all unchanged. An inert gas added to a constant-volume equilibrium mixture has no effect on the equilibrium condition.

**3. Change the pressure by changing the volume of the system.** Decreasing the volume of the system increases the pressure, and increasing the system volume decreases the pressure. Thus, the effect of this type of pressure change is simply that of a volume change.

In general, an increase in pressure (decrease in volume) favors the net reaction that decreases the total number of moles of gases (the reverse reaction, in this case), and a decrease in pressure (increase in volume) favors the net reaction that increases the total number of moles of gases (here, the forward reaction).

For reactions in which there is no change in the number of moles of gases, a pressure (or volume) change has no effect on the position of equilibrium.



## Effect of a Catalyst on Equilibrium

A catalyst is a substance that, when added to a reaction mixture, speeds up both the forward and reverse reactions. Equilibrium is achieved more rapidly, but the equilibrium amounts are unchanged by the catalyst. Consider again reaction