15.3: The Equilibrium Constant (K)

Key Concept Video The Equilibrium Constant

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? The concentrations, as we can see by reexamining Figure 15.2, 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:

$$aA + bB \rightleftharpoons cC + dD$$

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. We define the **equilibrium constant (K)** for the reaction 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.

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

Law of Mass Action

$$K = \frac{\overbrace{[C]^c[D]^d}^{\text{Products}}}{\underbrace{[A]^a[B]^b}_{\text{Reactants}}}$$

In this notation, [A] represents the molar concentration of A. 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 known as the **law of mass action**.

Why is *this* particular ratio of concentrations at equilibrium—and not some other ratio—defined as the equilibrium constant? Because this particular ratio always equals the same number at equilibrium (at constant temperature), regardless of the initial concentrations of the reactants and products. For example, Table 15.1 shows several different equilibrium concentrations of H_2, I_2, and HI, each from a different set of initial concentrations. Notice that the ratio defined by the law of mass action is always the same, regardless of the initial concentrations. Whether we start with only reactants or only products, the reaction reaches equilibrium at concentrations in 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—result in the same constant, K (at constant temperature).

Table 15.1 **Initial and Equilibrium Concentrations for the Reaction $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$ at 445 °C**

Initial Concentrations	Equilibrium Concentrations	Equilibrium Constant as Defined by the Law of Mass Action

$[H_2]$	$[I_2]$	$[HI]$	$[H_2]$	$[I_2]$	$[HI]$	$K = \frac{[HI]^2}{[H_2][I_2]}$
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	$\frac{(0.934)^2}{(0.033)(0.53)} = 50$

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:

$$2\,N_2O_5(g) \rightleftharpoons 4\,NO_2(g) + O_2(g)$$

The equilibrium constant is $[NO_2]$ raised to the fourth power multiplied by $[O_2]$ raised to the first power divided by $[N_2O_5]$ raised to the second power:

$$K = \frac{[NO_2]^4[O_2]}{[N_2O_5]^2}$$

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

Example 15.1 Expressing Equilibrium Constants for Chemical Equations

Express the equilibrium constant for the chemical equation:

$$CH_3OH(g) \rightleftharpoons CO(g) + 2\,H_2(g)$$

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.

$$K = \frac{[CO][H_2]^2}{[CH_3OH]}$$

FOR PRACTICE 15.1 Express the equilibrium constant for the combustion of propane as shown by the balanced chemical equation:

$$C_3H_8(g) + 5\,O_2(g) \rightleftharpoons 3\,CO_2(g) + 4\,H_2O(g)$$

Interactive Worked Example 15.1 Expressing Equilibrium Constants for Chemical Equations

The Significance of the Equilibrium Constant

We 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:

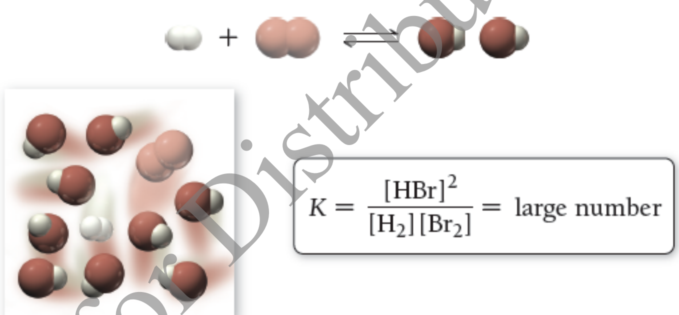
$$H_2(g) + Br_2(g) \rightleftharpoons 2\,HBr(g) \qquad K = 1.9 \times 10^{19} (\text{at } 25°C)$$

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 15.3). 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.

Figure 15.3 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.

$$H_2(g) + Br_2(g) \rightleftharpoons 2\,HBr(g)$$



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:

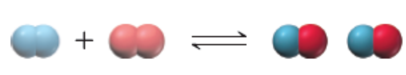
$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g) \qquad K = 4.1 \times 10^{-31} (\text{at } 25°C)$$

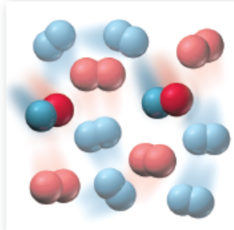
The equilibrium constant is very small, indicating that the equilibrium point for the reaction lies far to the left—high concentrations of reactants, low concentrations of products (Figure 15.4). This is fortunate because N_2 and O_2 are the main components of air. If this equilibrium constant were large, much of the N_2 and O_2 in air would react to form NO, a toxic gas.

Figure 15.4 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.

$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$$





$$K = \frac{[NO]^2}{[N_2][O_2]} = \text{small number}$$

> Direct comparison of equilibrium constants is valid only when the stoichiometry of the corresponding reactions is the same.

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.

Conceptual Connection 15.1 **Equilibrium Constants**

Relationships between the Equilibrium Constant and the Chemical Equation

If a chemical equation is modified in some way, the equilibrium constant for the equation changes because of the modification. The three modifications we list and discuss here are common.

1. **If we reverse the equation, we invert the equilibrium constant.** For example, consider this equilibrium equation:

   $$A + 2\,B \rightleftharpoons 3\,C$$

   The expression for the equilibrium constant of this reaction is:

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

   If we reverse the equation:

   $$3\,C \rightleftharpoons A + 2\,B$$

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

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

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

   $$A + 2\,B \rightleftharpoons 3\,C \qquad K = \frac{[C]^3}{[A][B]^2}$$

   If we multiply the equation by n, we get:

   $$n\,A + 2n\,B \rightleftharpoons 3n\,C$$

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

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

3. **If we add two or more individual chemical equations to obtain an overall equation, we 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:

$$\mathrm{A} \rightleftharpoons 2\,\mathrm{B} \qquad K_1 = \frac{[\mathrm{B}]^2}{[\mathrm{A}]}$$

$$2\,\mathrm{B} \rightleftharpoons 3\,\mathrm{C} \qquad K_2 = \frac{[\mathrm{C}]^3}{[\mathrm{B}]^2}$$

The two equations sum as follows:

$$\begin{array}{r} \mathrm{A} \rightleftharpoons 2\,\mathrm{B} \\ 2\,\mathrm{B} \rightleftharpoons 3\,\mathrm{C} \\ \hline \mathrm{A} \rightleftharpoons 3\,\mathrm{C} \end{array}$$

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

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

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

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

Conceptual Connection 15.2 **The Equilibrium Constant and the Chemical Equation**

Example 15.2 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:

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \qquad K = 5.6 \times 10^5$$

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

$$NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \qquad K' = ?$$

SOLUTION You want to manipulate the given reaction and value of K to obtain the desired reaction and value of K. Note 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.

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \qquad K = 5.6 \times 10^5$$

$$2\,NH_3(g) \rightleftharpoons N_2(g) + 3\,H_2(g) \qquad K_{\text{reverse}} = \frac{1}{5.6 \times 10^5}$$

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

$$NH_3(g) \rightleftharpoons \tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g)$$

$$K' = K_{\text{reverse}}^{1/2} = \left(\frac{1}{5.6 \times 10^5}\right)^{1/2}$$

Calculate the value of K'.

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

FOR PRACTICE 15.2 Consider the following chemical equation and equilibrium constant at 25 °C:

$$2\,COF_2(g) \rightleftharpoons CO_2(g) + CF_4(g) \qquad K = 2.2 \times 10^6$$

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

$$2\,CO_2(g) + 2\,CF_4(g) \rightleftharpoons 4\,COF_2(g) \qquad K' = ?$$

FOR MORE PRACTICE 15.2 Predict the equilibrium constant for the first reaction given the equilibrium constants for the second and third reactions:

$$\begin{array}{lcll} CO_2(g) + 3\,H_2(g) & \rightleftharpoons & CH_3OH(g) + H_2O(g) & K_1 = ? \\ CO(g) + H_2O(g) & \rightleftharpoons & CO_2(g) + H_2(g) & K_2 = 1.0 \times 10^5 \\ CO(g) + 2\,H_2(g) & \rightleftharpoons & CH_3OH(g) & K_3 = 1.4 \times 10^7 \end{array}$$