13 Chemical Equilibrium

Contents

In doing stoichiometry calculations we assumed that reactions proceed to completion, that is, until one of the reactants runs out. Many reactions do proceed essentially to completion. For such reactions it can be assumed that the reactants are quantitatively converted to products and that the amount of limiting reactant that remains is negligible. On the other hand, there are many chemical reactions that stop far short of completion. An example is the dimerization of nitrogen dioxide:

$$NO_2(g) + NO_2(g) \longrightarrow N_2O_4(g)$$

The reactant, NO_2, is a dark brown gas, and the product, N_2O_4, is a colorless gas. When NO_2 is placed in an evacuated, sealed glass vessel at 25°C, the initial dark brown color decreases in intensity as it is converted to colorless N_2O_4. However, even over a long period of time, the contents of the reaction vessel do not become colorless. Instead, the intensity of the brown color eventually becomes constant, which means that the concentration of NO_2 is no longer changing. This is illustrated on the molecular level in Fig. 13.1. This observation is a clear indication that the reaction has stopped short of completion. In fact, the system has reached **chemical equilibrium,** *the state where the concentrations of all reactants and products remain constant with time.*

Any chemical reactions carried out in a closed vessel will reach equilibrium. For some reactions the equilibrium position so favors the products that the reaction appears to have gone to completion. We say that the equilibrium position for such reactions lies *far to the right* (in the direction of the products). For example, when gaseous hydrogen and oxygen are mixed in stoichiometric quantities and react to form water vapor, the reaction proceeds essentially to completion. The amounts of the reactants that remain when the system reaches equilibrium are so tiny as to be negligible. By contrast, some reactions occur only to a slight extent. For example, when solid CaO is placed in a closed vessel at 25°C, the decomposition to solid Ca and gaseous O_2 is virtually undetectable. In cases like this, the equilibrium position is said to lie *far to the left* (in the direction of the reactants).

In this chapter we will discuss how and why a chemical system comes to equilibrium and the characteristics of equilibrium. In particular, we will discuss how to calculate the concentrations of the reactants and products present for a given system at equilibrium.

13.1 The Equilibrium Condition

Since no changes occur in the concentrations of reactants or products in a reaction system at equilibrium, it may appear that everything has stopped. However, this is not the case. On the molecular level, there is frantic activity. Equilibrium is not static but is a highly *dynamic* situation. The concept of chemical equilibrium is analogous to the flow of cars across a bridge connecting two island cities. Suppose the traffic flow on the bridge

Equilibrium is a dynamic situation.

The effect of temperature on the endothermic, aqueous equilibrium:

$$\underset{\text{Pink}}{Co(H_2O)_6^{2+}} + 4Cl^- \rightleftharpoons \underset{\text{Blue}}{CoCl_4^{2-}} + 6H_2O$$

The violet solution in the center is at 25°C and contains significant quantities of both pink $Co(H_2O)_6^{2+}$ *and blue* $CoCl_4^{2-}$*. When the solution is cooled, it turns pink because the equilibrium is shifted to the left. Heating the solution favors the blue* $CoCl_4^{2-}$ *ions.*

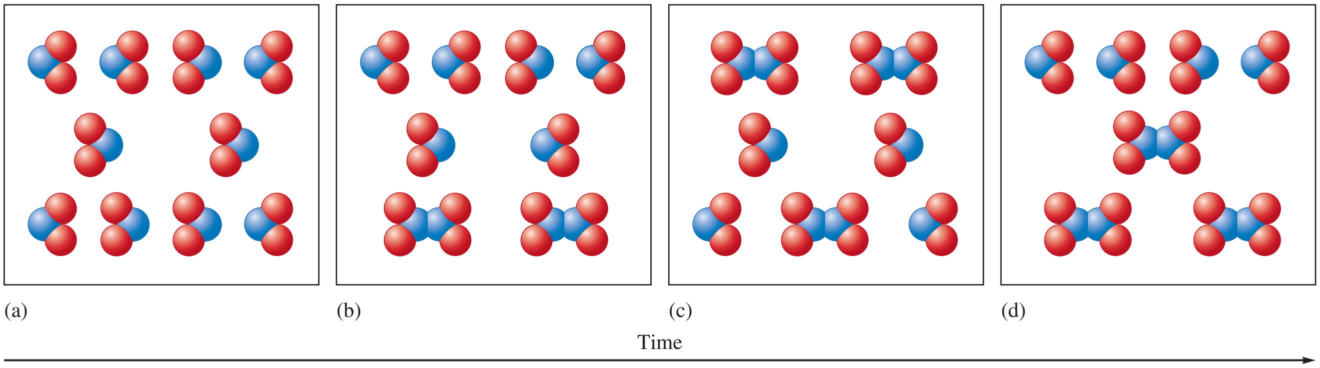


FIGURE 13.1
A molecular representation of the reaction $2NO_2(g) \longrightarrow N_2O_4(g)$ over time in a closed vessel. Note that the numbers of NO_2 and N_2O_4 in the container become constant (c and d) after sufficient time has passed.

is the same in both directions. It is obvious that there is motion, since one can see the cars traveling back and forth across the bridge, but the number of cars in each city is not changing because equal numbers of cars are entering and leaving. The result is no *net* change in the car population.

To see how this concept applies to chemical reactions, consider the reaction between steam and carbon monoxide in a closed vessel at a high temperature where the reaction takes place rapidly:

$$H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$$

Assume that the same number of moles of gaseous CO and gaseous H_2O are placed in a closed vessel and allowed to react. The plots of the concentrations of reactants and products versus time are shown in Fig. 13.2. Note that since CO and H_2O were originally present in equal molar quantities, and since they react in a 1:1 ratio, the concentrations of the two gases are always equal. Also, since H_2 and CO_2 are formed in equal amounts, they are always present in the same concentrations.

Figure 13.2 is a profile of the progress of the reaction. When CO and H_2O are mixed, they immediately begin to react to form H_2 and CO_2. This leads to a decrease in the concentrations of the reactants, but the concentrations of the products, which were initially at zero, are increasing. Beyond a certain time, indicated by the dashed line in Fig. 13.2, the concentrations of reactants and products no longer change—equilibrium has been reached. Unless the system is somehow disturbed, no further changes in concentrations will occur. Note that although the equilibrium position lies far to the right, the concentrations of reactants never go to zero; the reactants will always be present in small but constant concentrations. This is shown on the microscopic level in Fig. 13.3.

What would happen to the gaseous equilibrium mixture of reactants and products represented in Fig. 13.3, parts (c) and (d), if we injected some $H_2O(g)$ into the box? To answer this question, we need to be sure we understand the equilibrium condition: The

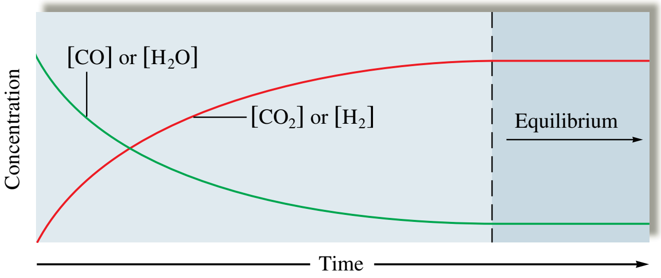


FIGURE 13.2
The changes in concentrations with time for the reaction $H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$ when equimolar quantities of $H_2O(g)$ and $CO(g)$ are mixed.

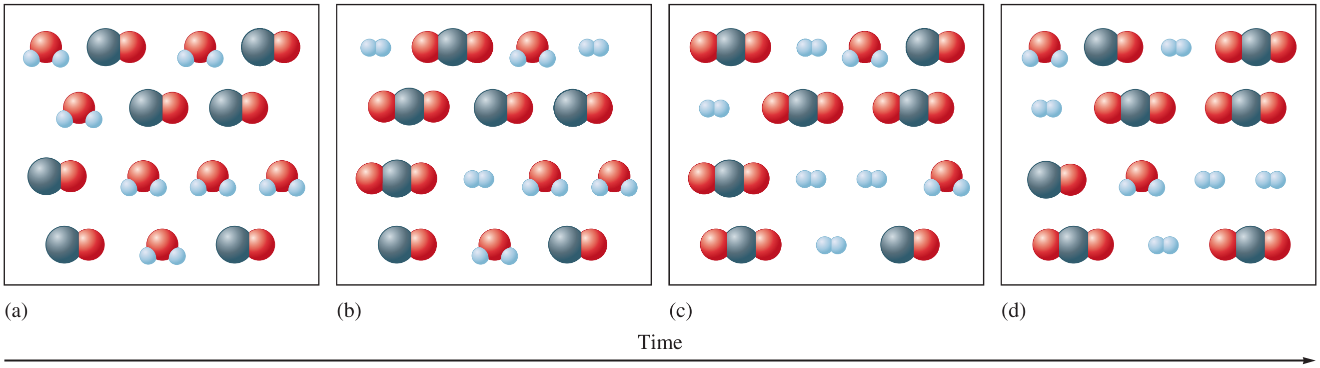


FIGURE 13.3
(a) H_2O and CO are mixed in equal numbers and begin to react (b) to form CO_2 and H_2. After time has passed, equilibrium is reached (c) and the numbers of reactant and product molecules then remain constant over time (d).

concentrations of reactants and products remain constant at equilibrium because the forward and reverse reaction rates are equal. If we inject some H_2O molecules, what will happen to the forward reaction: $H_2O + CO \rightarrow H_2 + CO_2$? It will speed up because more H_2O molecules means more collisions between H_2O and CO molecules. This in turn will form more products and will cause the reverse reaction $H_2O + CO \leftarrow H_2 + CO_2$ to speed up. Thus the system will change until the forward and reverse reaction rates again become equal. Will this new equilibrium position contain more or fewer product molecules than are shown in Fig. 13.3(c) and (d)? Think about this carefully. If you are not sure of the answer now, keep reading. We will consider this type of situation in more detail later in this chapter.

Why does equilibrium occur? We saw in Chapter 12 that molecules react by colliding with one another, and the more collisions, the faster the reaction. This is why reaction rates depend on concentrations. In this case the concentrations of H_2O and CO are lowered by the forward reaction:

$$H_2O + CO \longrightarrow H_2 + CO_2$$

As the concentrations of the reactants decrease, the forward reaction slows down (Fig. 13.4). As in the bridge traffic analogy, there is also a reverse direction:

$$H_2O + CO \longleftarrow H_2 + CO_2$$

A double arrow ($\rightleftharpoons$) is used to show that a reaction can occur in either direction.

Initially in this experiment no H_2 and CO_2 were present, and this reverse reaction could not occur. However, as the forward reaction proceeds, the concentrations of H_2 and CO_2 build up, and the rate of the reverse reaction increases (Fig. 13.4) as the forward reaction slows down. Eventually, the concentrations reach levels where the rate of the forward reaction equals the rate of the reverse reaction. The system has reached equilibrium.

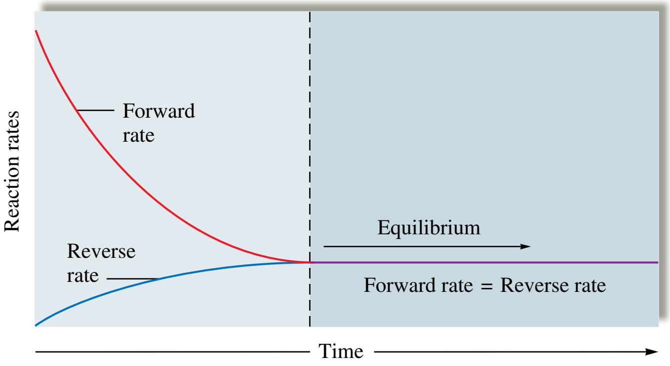


FIGURE 13.4
The changes with time in the rates of forward and reverse reactions for $H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$ when equimolar quantities of $H_2O(g)$ and $CO(g)$ are mixed. The rates do not change in the same way with time because the forward reaction has a much larger rate constant than the reverse reaction.

The relationship between equilibrium and thermodynamics is explored in Section 16.8.

The equilibrium position of a reaction—left, right, or somewhere in between—is determined by many factors: the initial concentrations, the relative energies of the reactants and products, and the relative degree of "organization" of the reactants and products. Energy and organization come into play because nature tries to achieve minimum energy and maximum disorder, as we will show in detail in Chapter 16. For now, we will simply view the equilibrium phenomenon in terms of the rates of opposing reactions.

The Characteristics of Chemical Equilibrium

To explore the important characteristics of chemical equilibrium, we will consider the synthesis of ammonia from elemental nitrogen and hydrogen:

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

The United States produces about 20 million tons of ammonia annually.

This process is of great commercial value because ammonia is an important fertilizer for the growth of corn and other crops. Ironically, this beneficial process was discovered in Germany just before World War I in a search for ways to produce nitrogen-based explosives. In the course of this work, German chemist Fritz Haber (1868–1934) pioneered the large-scale production of ammonia.

Molecules with strong bonds produce large activation energies and tend to react slowly at 25°C.

When gaseous nitrogen, hydrogen, and ammonia are mixed in a closed vessel at 25°C, no apparent change in the concentrations occurs over time, regardless of the original amounts of the gases. Why? There are two possible reasons why the concentrations of the reactants and products of a given chemical reaction remain unchanged when mixed.

1. The system is at chemical equilibrium.
2. The forward and reverse reactions are so slow that the system moves toward equilibrium at a rate that cannot be detected.

The second reason applies to the nitrogen, hydrogen, and ammonia mixture at 25°C. As we saw in Chapters 8 and 9, the N_2 molecule has a very strong triple bond (941 kJ/mol) and thus is very unreactive. Also, the H_2 molecule has an unusually strong single bond (432 kJ/mol). Therefore, mixtures of N_2, H_2, and NH_3 at 25°C can exist with no apparent change over long periods of time, unless a catalyst is introduced to speed up the forward and reverse reactions. Under appropriate conditions, the system does reach equilibrium, as shown in Fig. 13.5. Note that because of the reaction stoichiometry, H_2 disappears three times as fast as N_2 does and NH_3 forms twice as fast as N_2 disappears.

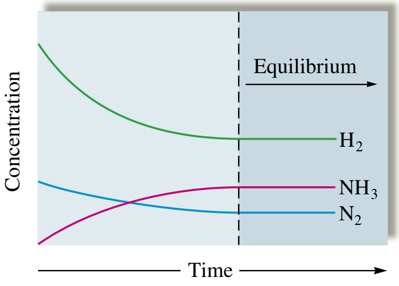


FIGURE 13.5
A concentration profile for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ when only $N_2(g)$ and $H_2(g)$ are mixed initially.

13.2 The Equilibrium Constant

Science is fundamentally empirical—it is based on experiment. The development of the equilibrium concept is typical. From their observations of many chemical reactions, two Norwegian chemists, Cato Maximilian Guldberg (1836–1902) and Peter Waage (1833–1900), proposed in 1864 the **law of mass action** as a general description of the equilibrium condition. Guldberg and Waage postulated that for a reaction of the type

The law of mass action is based on experimental observation.

$$jA + kB \rightleftharpoons lC + mD$$

where A, B, C, and D represent chemical species and j, k, l, and m are their coefficients in the balanced equation, the law of mass action is represented by the following **equilibrium expression:**

$$K = \frac{[C]^l[D]^m}{[A]^j[B]^k}$$

The square brackets indicate the concentrations of the chemical species *at equilibrium,* and K is a constant called the **equilibrium constant.**

Sample Exercise 13.1

Writing Equilibrium Expressions

Write the equilibrium expression for the following reaction:

$$4NH_3(g) + 7O_2(g) \rightleftharpoons 4NO_2(g) + 6H_2O(g)$$

Solution

Applying the law of mass action gives

Coefficient of NO_2

Coefficient of H_2O

$$K = \frac{[NO_2]^4[H_2O]^6}{[NH_3]^4[O_2]^7}$$

Coefficient of O_2

Coefficient of NH_3

The square brackets indicate concentration in units of mol/L.

See Exercise 13.17.

The value of the equilibrium constant at a given temperature can be calculated if we know the equilibrium concentrations of the reaction components, as illustrated in Sample Exercise 13.2.

It is very important to note at this point that the equilibrium constants are customarily given without units. The reason for this is beyond the scope of this text, but it involves corrections for the nonideal behavior of the substances taking part in the reaction. When these corrections are made, the units cancel out and the corrected K has no units. Thus we will not use units for K in this text.

Sample Exercise 13.2

Calculating the Values of *K*

The following equilibrium concentrations were observed for the Haber process at 127°C:

$$[NH_3] = 3.1 \times 10^{-2}\ \text{mol/L}$$
$$[N_2] = 8.5 \times 10^{-1}\ \text{mol/L}$$
$$[H_2] = 3.1 \times 10^{-3}\ \text{mol/L}$$

a. Calculate the value of K at 127°C for this reaction.

b. Calculate the value of the equilibrium constant at 127°C for the reaction

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

c. Calculate the value of the equilibrium constant at 127°C for the reaction given by the equation

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

Solution

a. The balanced equation for the Haber process is

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

Thus

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(3.1 \times 10^{-2})^2}{(8.5 \times 10^{-1})(3.1 \times 10^{-3})^3}$$
$$= 3.8 \times 10^4$$

Note that K is written without units.

b. This reaction is written in the reverse order from the equation given in part a. This leads to the equilibrium expression

$$K' = \frac{[N_2][H_2]^3}{[NH_3]^2}$$

which is the reciprocal of the expression used in part a. Therefore,

$$K' = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{1}{K} = \frac{1}{3.8 \times 10^4} = 2.6 \times 10^{-5}$$

c. We use the law of mass action:

$$K'' = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}}$$

If we compare this expression to that obtained in part a, we see that since

$$\frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}} = \left(\frac{[NH_3]^2}{[N_2][H_2]^3}\right)^{1/2}$$
$$K'' = K^{1/2}$$

Thus

$$K'' = K^{1/2} = (3.8 \times 10^4)^{1/2} = 1.9 \times 10^2$$

See Exercises 13.19 and 13.21 through 13.24.

We can draw some important conclusions from the results of Sample Exercise 13.2. For a reaction of the form

$$j\mathrm{A} + k\mathrm{B} \rightleftharpoons l\mathrm{C} + m\mathrm{D}$$

the equilibrium expression is

$$K = \frac{[\mathrm{C}]^l[\mathrm{D}]^m}{[\mathrm{A}]^j[\mathrm{B}]^k}$$

If this reaction is reversed, then the new equilibrium expression is

$$K' = \frac{[\mathrm{A}]^j[\mathrm{B}]^k}{[\mathrm{C}]^l[\mathrm{D}]^m} = \frac{1}{K}$$

If the original reaction is multiplied by some factor n to give

$$nj\mathrm{A} + nk\mathrm{B} \rightleftharpoons nl\mathrm{C} + nm\mathrm{D}$$

the equilibrium expression becomes

$$K'' = \frac{[\mathrm{C}]^{nl}[\mathrm{D}]^{nm}}{[\mathrm{A}]^{nj}[\mathrm{B}]^{nk}} = K^n$$

We Can Summarize These Conclusions About the Equilibrium Expression as Follows:

- The equilibrium expression for a reaction is the reciprocal of that for the reaction written in reverse.
- When the balanced equation for a reaction is multiplied by a factor n, the equilibrium expression for the new reaction is the original expression raised to the nth power. Thus $K_{\text{new}} = (K_{\text{original}})^n$.
- K values are customarily written without units.

The law of mass action applies to solution and gaseous equilibria.

The law of mass action is widely applicable. It correctly describes the equilibrium behavior of an amazing variety of chemical systems in solution and in the gas phase. Although, as we will see later, corrections must be applied in certain cases, such as for concentrated aqueous solutions and for gases at high pressures, the law of mass action provides a remarkably accurate description of all types of chemical equilibria.

A cross section showing how anhydrous ammonia is injected into the soil to act as a fertilizer.

Consider again the ammonia synthesis reaction. The equilibrium constant K always has the same value at a given temperature. At 500°C the value of K is 6.0×10^{-2}. Whenever N_2, H_2, and NH_3 are mixed together at this temperature, the system will always come to an equilibrium position such that

$$\frac{[NH_3]^2}{[N_2][H_2]^3} = 6.0 \times 10^{-2}$$

This expression has the same value at 500°C, *regardless of the amounts of the gases that are mixed together initially.*

Although the special ratio of products to reactants defined by the equilibrium expression is constant for a given reaction system at a given temperature, the *equilibrium concentrations will not always be the same.* Table 13.1 gives three sets of data for the synthesis of ammonia, showing that even though the individual sets of equilibrium concentrations are quite different for the different situations, the *equilibrium constant, which depends on the ratio of the concentrations, remains the same* (within experimental error). Note that subscript zeros indicate initial concentrations.

For a reaction at a given temperature, there are many equilibrium positions but only one value for K.

Each *set of equilibrium concentrations* is called an **equilibrium position.** It is essential to distinguish between the equilibrium constant and the equilibrium positions for a given reaction system. There is only *one* equilibrium constant for a particular system at a particular temperature, but there are an *infinite* number of equilibrium positions. The specific equilibrium position adopted by a system depends on the initial concentrations, but the equilibrium constant does not.

Sample Exercise 13.3

Equilibrium Positions

The following results were collected for two experiments involving the reaction at 600°C between gaseous sulfur dioxide and oxygen to form gaseous sulfur trioxide:

Experiment 1		**Experiment 2**	
Initial	***Equilibrium***	***Initial***	***Equilibrium***
$[SO_2]_0 = 2.00\ M$	$[SO_2] = 1.50\ M$	$[SO_2]_0 = 0.500\ M$	$[SO_2] = 0.590\ M$
$[O_2]_0 = 1.50\ M$	$[O_2] = 1.25\ M$	$[O_2]_0 = 0$	$[O_2] = 0.0450\ M$
$[SO_3]_0 = 3.00\ M$	$[SO_3] = 3.50\ M$	$[SO_3]_0 = 0.350\ M$	$[SO_3] = 0.260\ M$

Show that the equilibrium constant is the same in both cases.

Solution

The balanced equation for the reaction is

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

From the law of mass action,

$$K = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

TABLE 13.1 Results of Three Experiments for the Reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Experiment	Initial Concentrations	Equilibrium Concentrations	$K = \frac{[NH_3]^2}{[N_2][H_2]^3}$
I	$[N_2]_0 = 1.000\ M$ $[H_2]_0 = 1.000\ M$ $[NH_3]_0 = 0$	$[N_2] = 0.921\ M$ $[H_2] = 0.763\ M$ $[NH_3] = 0.157\ M$	$K = 6.02 \times 10^{-2}$
II	$[N_2]_0 = 0$ $[H_2]_0 = 0$ $[NH_3]_0 = 1.000\ M$	$[N_2] = 0.399\ M$ $[H_2] = 1.197\ M$ $[NH_3] = 0.203\ M$	$K = 6.02 \times 10^{-2}$
III	$[N_2]_0 = 2.00\ M$ $[H_2]_0 = 1.00\ M$ $[NH_3]_0 = 3.00\ M$	$[N_2] = 2.59\ M$ $[H_2] = 2.77\ M$ $[NH_3] = 1.82\ M$	$K = 6.02 \times 10^{-2}$

For Experiment 1,

$$K_1 = \frac{(3.50)^2}{(1.50)^2(1.25)} = 4.36$$

For Experiment 2,

$$K_2 = \frac{(0.260)^2}{(0.590)^2(0.0450)} = 4.32$$

The value of K is constant, within experimental error.

See Exercise 13.24.

13.3 Equilibrium Expressions Involving Pressures

So far we have been describing equilibria involving gases in terms of concentrations. Equilibria involving gases also can be described in terms of pressures. The relationship between the pressure and the concentration of a gas can be seen from the ideal gas equation:

The ideal gas equation was discussed in Section 5.3.

$$PV = nRT \qquad \text{or} \qquad P = \left(\frac{n}{V}\right)RT = CRT$$

where C equals n/V, or the number of moles n of gas per unit volume V. Thus C represents the *molar concentration of the gas.*

For the ammonia synthesis reaction, the equilibrium expression can be written in terms of concentrations, that is,

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{C_{NH_3}{}^2}{(C_{N_2})(C_{H_2}{}^3)} = K_c$$

or in terms of the *equilibrium partial pressures of the gases,* that is,

$$K_p = \frac{P_{NH_3}{}^2}{(P_{N_2})(P_{H_2}{}^3)}$$

K involves concentrations; K_p involves pressures. In some books, the symbol K_c is used instead of K.

Both the symbols K and K_c are used commonly for an equilibrium constant in terms of concentrations. We will always use K in this book. The symbol K_p represents an equilibrium constant in terms of partial pressures.

Sample Exercise 13.4 Calculating Values of K_p

The reaction for the formation of nitrosyl chloride

$$2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$$

was studied at 25°C. The pressures at equilibrium were found to be

$$\begin{aligned} P_{NOCl} &= 1.2 \text{ atm} \\ P_{NO} &= 5.0 \times 10^{-2} \text{ atm} \\ P_{Cl_2} &= 3.0 \times 10^{-1} \text{ atm} \end{aligned}$$

Calculate the value of K_p for this reaction at 25°C.

Solution

For this reaction,

$$\begin{aligned} K_p &= \frac{P_{NOCl}{}^2}{(P_{NO_2})^2(P_{Cl_2})} = \frac{(1.2)^2}{(5.0 \times 10^{-2})^2(3.0 \times 10^{-1})} \\ &= 1.9 \times 10^3 \end{aligned}$$

See Exercises 13.25 and 13.26.

$$P = CRT \quad \text{or} \quad C = \frac{P}{RT}$$

The relationship between K and K_p for a particular reaction follows from the fact that for an ideal gas, $C = P/RT$. For example, for the ammonia synthesis reaction,

$$\begin{aligned} K &= \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{C_{NH_3}{}^2}{(C_{N_2})(C_{H_2}{}^3)} \\ &= \frac{\left(\frac{P_{NH_3}}{RT}\right)^2}{\left(\frac{P_{N_2}}{RT}\right)\left(\frac{P_{H_2}}{RT}\right)^3} = \frac{P_{NH_3}{}^2}{(P_{N_2})(P_{H_2}{}^3)} \times \frac{\left(\frac{1}{RT}\right)^2}{\left(\frac{1}{RT}\right)^4} \\ &= \frac{P_{NH_3}{}^2}{(P_{N_2})(P_{H_2}{}^3)}(RT)^2 \\ &= K_p(RT)^2 \end{aligned}$$

However, for the synthesis of hydrogen fluoride from its elements,

$$H_2(g) + F_2(g) \rightleftharpoons 2HF(g)$$

the relationship between K and K_p is given by

$$\begin{aligned} K &= \frac{[HF]^2}{[H_2][F_2]} = \frac{C_{HF}{}^2}{(C_{H_2})(C_{F_2})} \\ &= \frac{\left(\frac{P_{HF}}{RT}\right)^2}{\left(\frac{P_{H_2}}{RT}\right)\left(\frac{P_{F_2}}{RT}\right)} = \frac{P_{HF}{}^2}{(P_{H_2})(P_{F_2})} \\ &= K_p \end{aligned}$$

Thus, for this reaction, K is equal to K_p. This equality occurs because the sum of the coefficients on either side of the balanced equation is identical, so the terms in RT cancel out. In the equilibrium expression for the ammonia synthesis reaction, the sum of the powers in the numerator is different from that in the denominator, and K does not equal K_p.

For the general reaction

$$jA + kB \rightleftharpoons lC + mD$$

the relationship between K and K_p is

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

where Δn is the sum of the coefficients of the *gaseous* products minus the sum of the coefficients of the *gaseous* reactants. This equation is quite easy to derive from the definitions of K and K_p and the relationship between pressure and concentration. For the preceding general reaction,

$$\begin{aligned} K_p &= \frac{(P_C{}^l)(P_D{}^m)}{(P_A{}^j)(P_B{}^k)} = \frac{(C_C \times RT)^l(C_D \times RT)^m}{(C_A \times RT)^j(C_B \times RT)^k} \\ &= \frac{(C_C{}^l)(C_D{}^m)}{(C_A{}^j)(C_B{}^k)} \times \frac{(RT)^{l+m}}{(RT)^{j+k}} = K(RT)^{(l+m)-(j+k)} \\ &= K(RT)^{\Delta n} \end{aligned}$$

Δn always involves products minus reactants.

where $\Delta n = (l + m) - (j + k)$, the difference in the sums of the coefficients for the gaseous products and reactants.

Sample Exercise 13.5 Calculating K from K_p

Using the value of K_p obtained in Sample Exercise 13.4, calculate the value of K at 25°C for the reaction

$$2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$$

Solution

From the value of K_p, we can calculate K using

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

where $T = 25 + 273 = 298$ K and

$$\Delta n = \underset{\substack{\nearrow \\ \text{Sum of} \\ \text{product} \\ \text{coefficients}}}{2} - \underset{\substack{\nwarrow \\ \text{Sum of} \\ \text{reactant} \\ \text{coefficients}}}{(2 + 1)} = -1$$

Thus

$$K_p = K(RT)^{\overset{\substack{\Delta n \\ \downarrow}}{-1}} = \frac{K}{RT}$$

and

$$\begin{aligned} K &= K_p(RT) \\ &= (1.9 \times 10^3)(0.08206)(298) \\ &= 4.6 \times 10^4 \end{aligned}$$

See Exercises 13.27 and 13.28.

13.4 Heterogeneous Equilibria

So far we have discussed equilibria only for systems in the gas phase, where all reactants and products are gases. These are **homogeneous equilibria.** However, many equilibria involve more than one phase and are called **heterogeneous equilibria.** For example, the thermal decomposition of calcium carbonate in the commercial preparation of lime occurs by a reaction involving both solid and gas phases:

Lime is among the top five chemicals manufactured in the United States in terms of the amount produced.

$$CaCO_3(s) \rightleftharpoons \underset{\substack{\uparrow \\ \text{Lime}}}{CaO(s)} + CO_2(g)$$

Straightforward application of the law of mass action leads to the equilibrium expression

The concentrations of pure liquids and solids are constant.

$$K' = \frac{[CO_2][CaO]}{[CaCO_3]}$$

However, experimental results show that the *position of a heterogeneous equilibrium does not depend on the amounts of pure solids or liquids present* (see Fig. 13.6). The fundamental reason for this behavior is that the concentrations of pure solids and liquids cannot change. Thus the equilibrium expression for the decomposition of solid calcium carbonate might be represented as

$$K' = \frac{[CO_2]C_1}{C_2}$$

where C_1 and C_2 are constants representing the concentrations of the solids CaO and $CaCO_3$, respectively. This expression can be rearranged to give

$$\frac{C_2K'}{C_1} = K = [CO_2]$$

The Seven Sisters chalk cliffs in East Sussex, England. The chalk is made up of compressed calcium carbonate skeletons of microscopic algae from the late Cretaceous Period.

We can generalize from this result as follows: If pure solids or pure liquids are involved in a chemical reaction, their concentrations *are not included in the equilibrium expression* for the reaction. This simplification occurs *only* with pure solids or liquids, not with solutions or gases, since in these last two cases the concentrations can vary.

For example, in the decomposition of liquid water to gaseous hydrogen and oxygen,

$$2H_2O(l) \rightleftharpoons 2H_2(g) + O_2(g)$$

where

$$K = [H_2]^2[O_2] \quad \text{and} \quad K_p = (P_{H_2}{}^2)(P_{O_2})$$

water is not included in either equilibrium expression because it is a pure liquid. However, if the reaction were carried out under conditions where the water is a gas rather than a liquid, that is,

$$2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$$

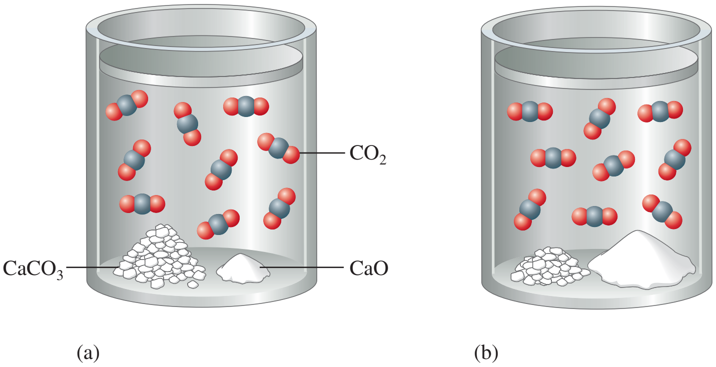


FIGURE 13.6
The position of the equilibrium $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ does not depend on the amounts of $CaCO_3(s)$ and $CaO(s)$ present.

then

$$K = \frac{[H_2]^2[O_2]}{[H_2O]^2} \quad \text{and} \quad K_p = \frac{(P_{H_2}{}^2)(P_{O_2})}{P_{H_2O}{}^2}$$

because the concentration or pressure of water vapor can change.

Sample Exercise 13.6 Equilibrium Expressions for Heterogeneous Equilibria

Write the expressions for K and K_p for the following processes:

a. Solid phosphorus pentachloride decomposes to liquid phosphorus trichloride and chlorine gas.
b. Deep blue solid copper(II) sulfate pentahydrate is heated to drive off water vapor to form white solid copper(II) sulfate.

Solution

a. The reaction is

$$PCl_5(s) \rightleftharpoons PCl_3(l) + Cl_2(g)$$

The equilibrium expressions are

$$K = [Cl_2] \qquad \text{and} \qquad K_p = P_{Cl_2}$$

In this case neither the pure solid PCl_5 nor the pure liquid PCl_3 is included in the equilibrium expressions.

b. The reaction is

$$CuSO_4 \cdot 5H_2O(s) \rightleftharpoons CuSO_4(s) + 5H_2O(g)$$

The equilibrium expressions are

$$K = [H_2O]^5 \qquad \text{and} \qquad K_p = (P_{H_2O})^5$$

The solids are not included.

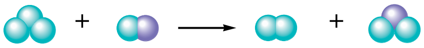
See Exercise 13.29.

Hydrated copper(II) sulfate on the left. Water applied to anhydrous copper(II) sulfate, on the right, forms the hydrated compound.

13.5 Applications of the Equilibrium Constant

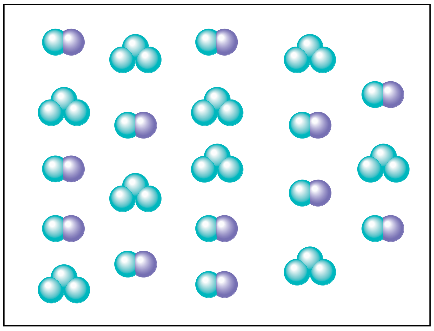
Knowing the equilibrium constant for a reaction allows us to predict several important features of the reaction: the tendency of the reaction to occur (but not the speed of the reaction), whether a given set of concentrations represents an equilibrium condition, and the equilibrium position that will be achieved from a given set of initial concentrations.

To introduce some of these ideas, we will first consider the reaction



where 🔵 and 🟣 represent two different types of atoms. Assume that this reaction has an equilibrium constant equal to 16.

In a given experiment, the two types of molecules are mixed together in the following amounts:



After the system reacts and comes to equilibrium, what will the system look like? We know that at equilibrium the ratio

$$\frac{(N_{\text{🔵🔵}})(N_{\text{🟣🔵🔵}})}{(N_{\text{🔵🔵🔵}})(N_{\text{🔵🟣}})} = 16$$

must be satisfied, where each N represents the number of molecules of each type. We originally have 9 🔵🔵🔵 molecules and 12 🔵🟣 molecules. As a place to start, let's just assume that 5 🔵🔵🔵 molecules disappear for the system to reach equilibrium. Since equal numbers of the 🔵🔵🔵 and 🔵🟣 molecules react, this means that 5 🔵🟣 molecules also will disappear. This also means that 5 🔵🔵 molecules and 5 🟣🔵🔵 molecules will be formed. We can summarize as follows:

Initial Conditions	***New Conditions***
9 🔵🔵🔵 molecules	9 − 5 = 4 🔵🔵🔵 molecules
12 🔵🟣 molecules	12 − 5 = 7 🔵🟣 molecules
0 🟣🔵🔵 molecules	0 + 5 = 5 🟣🔵🔵 molecules
0 🔵🔵 molecules	0 + 5 = 5 🔵🔵 molecules

Do the new conditions represent equilibrium for this reaction system? We can find out by taking the ratio of the numbers of molecules:

$$\frac{(N_{\text{🔵🔵}})(N_{\text{🟣🔵🔵}})}{(N_{\text{🔵🔵🔵}})(N_{\text{🔵🟣}})} = \frac{(5)(5)}{(4)(7)} = 0.9$$

Thus this is not an equilibrium position because the ratio is not 16, as required for equilibrium. In which direction must the system move to achieve equilibrium? Since the observed ratio is smaller than 16, we must increase the numerator and decrease the denominator: The system needs to move to the right (toward more products) to achieve equilibrium. That is, more than 5 of the original reactant molecules must disappear to reach equilibrium for this system. How can we find the correct number? Since we do not know the number of molecules that need to disappear to reach equilibrium, let's call this number *x*. Now we can set up a table similar to the one we used earlier:

Initial Conditions		***Equilibrium Conditions***
9  molecules	x  disappear	$9-x$  molecules
12  molecules	x  disappear	$12-x$  molecules
0  molecules	x  form	x  molecules
0  molecules	x  form	x  molecules

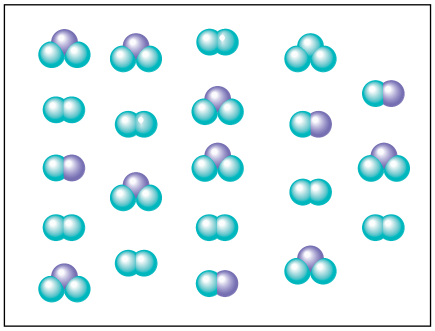
For the system to be at equilibrium, we know that the following ratio must be satisfied:

(N )(N ) / (N )(N ) $= 16 = \frac{(x)(x)}{(9-x)(12-x)}$

The easiest way to solve for *x* here is by trial and error. From our previous discussion we know that *x* is greater than 5. Also, we know that it must be less than 9 because we have only 9  molecules to start. We can't use all of them or we will have a zero in the denominator, which causes the ratio to be infinitely large. By trial and error, we find that $x = 8$ because

$$\frac{(x)(x)}{(9-x)(12-x)} = \frac{(8)(8)}{(9-8)(12-8)} = \frac{64}{4} = 16$$

The equilibrium mixture can be pictured as follows:



Note that it constains 8  molecules, 8  molecules, 1  molecule, and 4  molecules as required.

This pictorial example should help you understand the fundamental ideas of equilibrium. Now we will proceed to a more systematic quantitative treatment of chemical equilibrium.

The Extent of a Reaction

The inherent tendency for a reaction to occur is indicated by the magnitude of the equilibrium constant. A value of *K* much larger than 1 means that at equilibrium the reaction system will consist of mostly products—the equilibrium lies to the right. Another way of saying this is that reactions with very large equilibrium constants go essentially to completion. On the other hand, a very small value of K means that the system at equilibrium will consist of mostly reactants—the equilibrium position is far to the left. The given reaction does not occur to any significant extent.

It is important to understand that *the size of K and the time required to reach equilibrium are not directly related.* The time required to achieve equilibrium depends on the reaction rate, which is determined by the size of the activation energy. The size of K is determined by thermodynamic factors such as the difference in energy between products and reactants. This difference is represented in Fig. 13.7 and will be discussed in detail in Chapter 16.

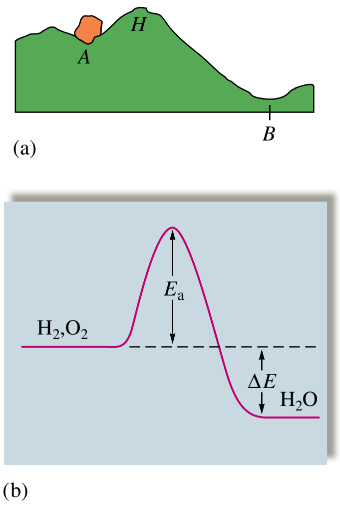


FIGURE 13.7
(a) A physical analogy illustrating the difference between thermodynamic and kinetic stabilities. The boulder is thermodynamically more stable (lower potential energy) in position *B* than in position *A* but cannot get over the hump *H*. (b) The reactants H_2 and O_2 have a strong tendency to form H_2O. That is, H_2O has lower energy than H_2 and O_2. However, the large activation energy E_a prevents the reaction at 25°C. In other words, the magnitude of K for the reaction depends on ΔE, but the reaction rate depends on E_a.

Reaction Quotient

When the reactants and products of a given chemical reaction are mixed, it is useful to know whether the mixture is at equilibrium or, if not, the direction in which the system must shift to reach equilibrium. If the concentration of one of the reactants or products is zero, the system will shift in the direction that produces the missing component. However, if all the initial concentrations are nonzero, it is more difficult to determine the direction of the move toward equilibrium. To determine the shift in such cases, we use the **reaction quotient, Q.** The reaction quotient is obtained by applying the law of mass action using *initial concentrations* instead of equilibrium concentrations. For example, for the synthesis of ammonia

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

the expression for the reaction quotient is

$$Q = \frac{[NH_3]_0^{\,2}}{[N_2]_0[H_2]_0^{\,3}}$$

where the subscript zeros indicate initial concentrations.

To determine in which direction a system will shift to reach equilibrium, we compare the values of Q and K. There are three possible cases:

1. *Q is equal to K.* The system is at equilibrium; no shift will occur.
2. *Q is greater than K.* In this case, the ratio of initial concentrations of products to initial concentrations of reactants is too large. To reach equilibrium, a net change of products to reactants must occur. The system *shifts to the left,* consuming products and forming reactants, until equilibrium is achieved.
3. *Q is less than K.* In this case, the ratio of initial concentrations of products to initial concentrations of reactants is too small. The *system must shift to the right,* consuming reactants and forming products, to attain equilibrium.

Sample Exercise 13.7

Using the Reaction Quotient

For the synthesis of ammonia at 500°C, the equilibrium constant is 6.0×10^{-2}. Predict the direction in which the system will shift to reach equilibrium in each of the following cases:

a. $[NH_3]_0 = 1.0 \times 10^{-3}\,M$; $[N_2]_0 = 1.0 \times 10^{-5}\,M$; $[H_2]_0 = 2.0 \times 10^{-3}\,M$
b. $[NH_3]_0 = 2.00 \times 10^{-4}\,M$; $[N_2]_0 = 1.50 \times 10^{-5}\,M$; $[H_2]_0 = 3.54 \times 10^{-1}\,M$
c. $[NH_3]_0 = 1.0 \times 10^{-4}\,M$; $[N_2]_0 = 5.0\,M$; $[H_2]_0 = 1.0 \times 10^{-2}\,M$

Solution

a. First we calculate the value of Q:

$$Q = \frac{[NH_3]_0^{\,2}}{[N_2]_0[H_2]_0^{\,3}} = \frac{(1.0 \times 10^{-3})^2}{(1.0 \times 10^{-5})(2.0 \times 10^{-3})^3}$$
$$= 1.3 \times 10^7$$

Since $K = 6.0 \times 10^{-2}$, Q is much greater than K. To attain equilibrium, the concentrations of the products must be decreased and the concentrations of the reactants increased. The system will shift to the left:

$$N_2 + 3H_2 \longleftarrow 2NH_3$$

b. We calculate the value of Q:

$$Q = \frac{[NH_3]_0^{\,2}}{[N_2]_0[H_2]_0^{\,3}} = \frac{(2.00 \times 10^{-4})^2}{(1.50 \times 10^{-5})(3.54 \times 10^{-1})^3}$$
$$= 6.01 \times 10^{-2}$$

In this case $Q = K$, so the system is at equilibrium. No shift will occur.

c. The value of Q is

$$Q = \frac{[NH_3]_0^{\,2}}{[N_2]_0[H_2]_0^{\,3}} = \frac{(1.0 \times 10^{-4})^2}{(5.0)(1.0 \times 10^{-2})^3}$$
$$= 2.0 \times 10^{-3}$$

Here Q is less than K, so the system will shift to the right to attain equilibrium by increasing the concentration of the product and decreasing the reactant concentrations:

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

See Exercises 13.33 through 13.36.

Calculating Equilibrium Pressures and Concentrations

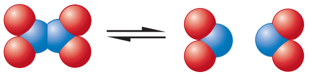
A typical equilibrium problem involves finding the equilibrium concentrations (or pressures) of reactants and products, given the value of the equilibrium constant and the initial concentrations (or pressures). However, since such problems sometimes become complicated mathematically, we will develop useful strategies for solving them by considering cases for which we know one or more of the equilibrium concentrations (or pressures).

Sample Exercise 13.8

Calculating Equilibrium Pressures I

Dinitrogen tetroxide in its liquid state was used as one of the fuels on the lunar lander for the NASA Apollo missions. In the gas phase it decomposes to gaseous nitrogen dioxide:

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



Consider an experiment in which gaseous N_2O_4 was placed in a flask and allowed to reach equilibrium at a temperature where $K_p = 0.133$. At equilibrium, the pressure of N_2O_4 was found to be 2.71 atm. Calculate the equilibrium pressure of $NO_2(g)$.

Apollo II lunar landing module at Tranquility Base, 1969.

Solution

We know that the equilibrium pressures of the gases NO_2 and N_2O_4 must satisfy the relationship

$$K_p = \frac{P_{NO_2}{}^2}{P_{N_2O_4}} = 0.133$$

Since we know $P_{N_2O_4}$, we can simply solve for P_{NO_2}:

$$P_{NO_2}{}^2 = K_p(P_{N_2O_4}) = (0.133)(2.71) = 0.360$$

Therefore,

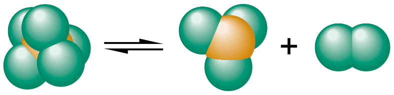
$$P_{NO_2} = \sqrt{0.360} = 0.600$$

See Exercises 13.37 and 13.38.

Sample Exercise 13.9 Calculating Equilibrium Pressures II

At a certain temperature a 1.00-L flask initially contained 0.298 mol $PCl_3(g)$ and 8.70×10^{-3} mol $PCl_5(g)$. After the system had reached equilibrium, 2.00×10^{-3} mol $Cl_2(g)$ was found in the flask. Gaseous PCl_5 decomposes according to the reaction

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$



Calculate the equilibrium concentrations of all species and the value of *K*.

Solution

The equilibrium expression for this reaction is

$$K = \frac{[Cl_2][PCl_3]}{[PCl_5]}$$

To find the value of *K*, we must calculate the equilibrium concentrations of all species and then substitute these quantities into the equilibrium expression. The best method for finding the equilibrium concentrations is to begin with the initial concentrations, which we will define as the concentrations before any shift toward equilibrium has occurred. We will then modify these initial concentrations appropriately to find the equilibrium concentrations.

The initial concentrations are

$$[Cl_2]_0 = 0$$

$$[PCl_3]_0 = \frac{0.298 \text{ mol}}{1.00 \text{ L}} = 0.298\ M$$

$$[PCl_5]_0 = \frac{8.70 \times 10^{-3} \text{ mol}}{1.00 \text{ L}} = 8.70 \times 10^{-3}\ M$$

Next we find the change required to reach equilibrium. Since no Cl_2 was initially present but $2.00 \times 10^{-3}\ M$ Cl_2 is present at equilibrium, 2.00×10^{-3} mol PCl_5 must have decomposed to form 2.00×10^{-3} mol Cl_2 and 2.00×10^{-3} mol PCl_3. In other words, to reach equilibrium, the reaction shifted to the right:

$$\begin{array}{ccccc} PCl_5(g) & \longrightarrow & PCl_3(g) & + & Cl_2(g) \\ 2.00 \times 10^{-3}\text{ mol} & \longrightarrow & 2.00 \times 10^{-3}\text{ mol} & + & 2.00 \times 10^{-3}\text{ mol} \\ \uparrow & & \nwarrow & & \nearrow \\ \text{Net amount of PCl}_5 & & \multicolumn{3}{c}{\text{Net amounts of}} \\ \text{decomposed} & & \multicolumn{3}{c}{\text{products formed}} \end{array}$$

Now we apply this change to the initial concentrations to obtain the equilibrium concentrations:

$$[Cl_2] = \underset{\nwarrow [Cl_2]_0}{0} + \frac{2.00 \times 10^{-3}\text{ mol}}{1.00\text{ L}} = 2.00 \times 10^{-3}\ M$$

$$[PCl_3] = \underset{\nwarrow [PCl_3]_0}{0.298\ M} + \frac{2.00 \times 10^{-3}\text{ mol}}{1.00\text{ L}} = 0.300\ M$$

$$[PCl_5] = \underset{\nwarrow [PCl_5]_0}{8.70 \times 10^{-3}\ M} - \frac{2.00 \times 10^{-3}\text{ mol}}{1.00\text{ L}} = 6.70 \times 10^{-3}\ M$$

These equilibrium concentrations can now be used to find K:

$$K = \frac{[Cl_2][PCl_3]}{[PCl_5]} = \frac{(2.00 \times 10^{-3})(0.300)}{6.70 \times 10^{-3}}$$
$$= 8.96 \times 10^{-2}$$

See Exercises 13.39 through 13.42.

Sometimes we are not given any of the equilibrium concentrations (or pressures), only the initial values. Then we must use the stoichiometry of the reaction to express concentrations (or pressures) at equilibrium in terms of the initial values. This is illustrated in Sample Exercise 13.10.

Sample Exercise 13.10 Calculating Equilibrium Concentrations I

Carbon monoxide reacts with steam to produce carbon dioxide and hydrogen. At 700 K the equilibrium constant is 5.10. Calculate the equilibrium concentrations of all species if 1.000 mol of each component is mixed in a 1.000-L flask.

Solution

The balanced equation for the reaction is

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

and

$$K = \frac{[CO_2][H_2]}{[CO][H_2O]} = 5.10$$

Next we calculate the initial concentrations:

$$[CO]_0 = [H_2O]_0 = [CO_2]_0 = [H_2]_0 = \frac{1.000\text{ mol}}{1.000\text{ L}} = 1.000\ M$$

Is the system at equilibrium, and if not, which way will it shift to reach the equilibrium position? These questions can be answered by calculating Q:

$$Q = \frac{[CO_2]_0[H_2]_0}{[CO]_0[H_2O]_0} = \frac{(1.000 \text{ mol/L})(1.000 \text{ mol/L})}{(1.000 \text{ mol/L})(1.000 \text{ mol/L})} = 1.000$$

Since Q is less than K, the system is not at equilibrium initially but must shift to the right.

What are the equilibrium concentrations? As before, we start with the initial concentrations and modify them to obtain the equilibrium concentrations. We must ask this question: How much will the system shift to the right to attain the equilibrium condition? In Sample Exercise 13.9 the change needed for the system to reach equilibrium was given. However, in this case we do not have this information.

Since the required change in concentrations is unknown at this point, we will define it in terms of x. Let's assume that x mol/L CO must react for the system to reach equilibrium. This means that the initial concentration of CO will decrease by x mol/L:

$$\underset{\substack{\uparrow \\ \text{Equilibrium}}}{[CO]} = \underset{\substack{\uparrow \\ \text{Initial}}}{[CO]_0} - \underset{\substack{\uparrow \\ \text{Change}}}{x}$$

Since each CO molecule reacts with one H_2O molecule, the concentration of water vapor also must decrease by x mol/L:

$$[H_2O] = [H_2O]_0 - x$$

As the reactant concentrations decrease, the product concentrations increase. Since all the coefficients are 1 in the balanced reaction, 1 mol CO reacting with 1 mol H_2O will produce 1 mol CO_2 and 1 mol H_2. Or in the present case, to reach equilibrium, x mol/L CO will react with x mol/L H_2O to give an additional x mol/L CO_2 and x mol/L H_2:

$$x\text{CO} + x\text{H}_2\text{O} \longrightarrow x\text{CO}_2 + x\text{H}_2$$

Thus the initial concentrations of CO_2 and H_2 will increase by x mol/L:

$$[CO_2] = [CO_2]_0 + x$$
$$[H_2] = [H_2]_0 + x$$

Now we have all the equilibrium concentrations defined in terms of the initial concentrations and the change x:

Initial Concentration (mol/L)	Change (mol/L)	Equilibrium Concentration (mol/L)
$[CO]_0 = 1.000$	$-x$	$1.000 - x$
$[H_2O]_0 = 1.000$	$-x$	$1.000 - x$
$[CO_2]_0 = 1.000$	$+x$	$1.000 + x$
$[H_2]_0 = 1.000$	$+x$	$1.000 + x$

Note that the sign of x is determined by the direction of the shift. In this example, the system shifts to the right, so the product concentrations increase and the reactant concentrations decrease. Also note that because the coefficients in the balanced equation are all 1, the magnitude of the change is the same for all species.

Now since we know that the equilibrium concentrations must satisfy the equilibrium expression, we can find the value of x by substituting these concentrations into the expression

$$K = 5.10 = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(1.000 + x)(1.000 + x)}{(1.000 - x)(1.000 - x)} = \frac{(1.000 + x)^2}{(1.000 - x)^2}$$

Since the right side of the equation is a perfect square, the solution of the problem can be simplified by taking the square root of both sides:

$$\sqrt{5.10} = 2.26 = \frac{1.000 + x}{1.000 - x}$$

Multiplying and collecting terms gives

$$x = 0.387 \text{ mol/L}$$

Thus the system shifts to the right, consuming 0.387 mol/L CO and 0.387 mol/L H_2O and forming 0.387 mol/L CO_2 and 0.387 mol/L H_2.

Now the equilibrium concentrations can be calculated:

$$[CO] = [H_2O] = 1.000 - x = 1.000 - 0.387 = 0.613\ M$$
$$[CO_2] = [H_2] = 1.000 + x = 1.000 + 0.387 = 1.387\ M$$

Reality Check: These values can be checked by substituting them back into the equilibrium expression to make sure they give the correct value for K:

$$K = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(1.387)^2}{(0.613)^2} = 5.12$$

This result is the same as the given value of K (5.10) within round-off error, so the answer must be correct.

See Exercise 13.45.

Sample Exercise 13.11

Calculating Equilibrium Concentrations II

Assume that the reaction for the formation of gaseous hydrogen fluoride from hydrogen and fluorine has an equilibrium constant of 1.15×10^2 at a certain temperature. In a particular experiment, 3.000 mol of each component was added to a 1.500-L flask. Calculate the equilibrium concentrations of all species.

Solution

The balanced equation for the reaction is

$$H_2(g) + F_2(g) \rightleftharpoons 2HF(g)$$

The equilibrium expression is

$$K = 1.15 \times 10^2 = \frac{[HF]^2}{[H_2][F_2]}$$

We first calculate the initial concentrations:

$$[HF]_0 = [H_2]_0 = [F_2]_0 = \frac{3.000 \text{ mol}}{1.500 \text{ L}} = 2.000\ M$$

Then we find the value of Q:

$$Q = \frac{[HF]_0^2}{[H_2]_0[F_2]_0} = \frac{(2.000)^2}{(2.000)(2.000)} = 1.000$$

Since Q is much less than K, the system must shift to the right to reach equilibrium.

What change in the concentrations is necessary? Since this is presently unknown, we will define the change needed in terms of x. Let x equal the number of moles per liter of H_2 consumed to reach equilibrium. The stoichiometry of the reaction shows that x mol/L F_2 also will be consumed and $2x$ mol/L HF will be formed:

$$\begin{array}{ccccc} H_2(g) & + & F_2(g) & \longrightarrow & 2HF(g) \\ x\text{ mol/L} & + & x\text{ mol/L} & \longrightarrow & 2x\text{ mol/L} \end{array}$$

Now the equilibrium concentrations can be expressed in terms of x:

Initial Concentration (mol/L)	Change (mol/L)	Equilibrium Concentration (mol/L)
$[H_2]_0 = 2.000$	$-x$	$[H_2] = 2.000 - x$
$[F_2]_0 = 2.000$	$-x$	$[F_2] = 2.000 - x$
$[HF]_0 = 2.000$	$+2x$	$[HF] = 2.000 + 2x$

These concentrations can be represented in a shorthand table as follows:

We often refer to this form as an **ICE** table (indicated by the first letters of Initial, Change, and Equilibrium).

	$H_2(g)$	+	$F_2(g)$	$\rightleftharpoons$	$2HF(g)$
Initial:	2.000		2.000		2.000
Change:	$-x$		$-x$		$+2x$
Equilibrium:	$2.000 - x$		$2.000 - x$		$2.000 + 2x$

To solve for x, we substitute the equilibrium concentrations into the equilibrium expression:

$$K = 1.15 \times 10^2 = \frac{[HF]^2}{[H_2][F_2]} = \frac{(2.000 + 2x)^2}{(2.000 - x)^2}$$

The right side of this equation is a perfect square, so taking the square root of both sides gives

$$\sqrt{1.15 \times 10^2} = \frac{2.000 + 2x}{2.000 - x}$$

which yields $x = 1.528$. The equilibrium concentrations can now be calculated:

$$[H_2] = [F_2] = 2.000\ M - x = 0.472\ M$$
$$[HF] = 2.000\ M + 2x = 5.056\ M$$

Reality Check: Checking these values by substituting them into the equilibrium expression gives

$$\frac{[HF]^2}{[H_2][F_2]} = \frac{(5.056)^2}{(0.472)^2} = 1.15 \times 10^2$$

which agrees with the given value of K.

See Exercise 13.46.

13.6 Solving Equilibrium Problems

We have already considered most of the strategies needed to solve equilibrium problems. The typical procedure for analyzing a chemical equilibrium problem can be summarized as follows:

Procedure for Solving Equilibrium Problems

➥ 1 **Write the balanced equation for the reaction.**

➥ 2 **Write the equilibrium expression using the law of mass action.**

➥ 3 **List the initial concentrations.**

➥ 4 **Calculate *Q*, and determine the direction of the shift to equilibrium.**

➥ 5 **Define the change needed to reach equilibrium, and define the equilibrium concentrations by applying the change to the initial concentrations.**

➥ 6 **Substitute the equilibrium concentrations into the equilibrium expression, and solve for the unknown.**

➥ 7 **Check your calculated equilibrium concentrations by making sure they give the correct value of *K*.**

So far we have been careful to choose systems in which we can solve for the unknown by taking the square root of both sides of the equation. However, this type of system is not really very common, and we must now consider a more typical problem. Suppose for a synthesis of hydrogen fluoride from hydrogen and fluorine, 3.000 mol H_2 and 6.000 mol F_2 are mixed in a 3.000-L flask. Assume that the equilibrium constant for the synthesis reaction at this temperature is 1.15×10^2. We calculate the equilibrium concentration of each component as follows:

➥ 1 We begin, as usual, by writing the balanced equation for the reaction:

$$H_2(g) + F_2(g) \rightleftharpoons 2HF(g)$$

➥ 2 The equilibrium expression is

$$K = 1.15 \times 10^2 = \frac{[HF]^2}{[H_2][F_2]}$$

➥ 3 The initial concentrations are

$$[H_2]_0 = \frac{3.000 \text{ mol}}{3.000 \text{ L}} = 1.000\ M$$

$$[F_2]_0 = \frac{6.000 \text{ mol}}{3.000 \text{ L}} = 2.000\ M$$

$$[HF]_0 = 0$$

➥ 4 There is no need to calculate Q because no HF is present initially, and we know that the system must shift to the right to reach equilibrium.

➥ 5 If we let x represent the number of moles per liter of H_2 consumed to reach equilibrium, we can represent the equilibrium concentrations as follows:

	$H_2(g)$	+	$F_2(g)$	$\rightleftharpoons$	$2HF(g)$
Initial:	1.000		2.000		0
Change:	$-x$		$-x$		$+2x$
Equilibrium:	$1.000 - x$		$2.000 - x$		$2x$

➥ **6** Substituting the equilibrium concentrations into the equilibrium expression gives

$$K = 1.15 \times 10^2 = \frac{[HF]^2}{[H_2][F_2]} = \frac{(2x)^2}{(1.000 - x)(2.000 - x)}$$

Since the right side of this equation is not a perfect square, we cannot take the square root of both sides, but must use some other procedure.

First, do the indicated multiplication:

$$(1.000 - x)(2.000 - x)(1.15 \times 10^2) = (2x)^2$$

or

$$(1.15 \times 10^2)x^2 - 3.000(1.15 \times 10^2)x + 2.000(1.15 \times 10^2) = 4x^2$$

and collect terms

$$(1.11 \times 10^2)x^2 - (3.45 \times 10^2)x + 2.30 \times 10^2 = 0$$

This is a quadratic equation of the general form

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

Use of the quadratic formula is explained in Appendix 1.4.

where the roots can be obtained from the quadratic formula:

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

In this example, $a = 1.11 \times 10^2$, $b = -3.45 \times 10^2$, and $c = 2.30 \times 10^2$. Substituting these values into the quadratic formula gives two values for x:

$$x = 2.14 \text{ mol/L} \quad \text{and} \quad x = 0.968 \text{ mol/L}$$

Both these results cannot be valid (since a *given* set of initial concentrations leads to only *one* equilibrium position). How can we choose between them? Since the expression for the equilibrium concentration of H_2 is

$$[H_2] = 1.000\,M - x$$

the value of x cannot be 2.14 mol/L (because subtracting 2.14 M from 1.000 M gives a negative concentration of H_2, which is physically impossible). Thus the correct value for x is 0.968 mol/L, and the equilibrium concentrations are as follows:

$$[H_2] = 1.000\,M - 0.968\,M = 3.2 \times 10^{-2}\,M$$
$$[F_2] = 2.000\,M - 0.968\,M = 1.032\,M$$
$$[HF] = 2(0.968\,M) = 1.936\,M$$

Reality Check:

➥ **7** We can check these concentrations by substituting them into the equilibrium expression:

$$\frac{[HF]^2}{[H_2][F_2]} = \frac{(1.936)^2}{(3.2 \times 10^{-2})(1.032)} = 1.13 \times 10^2$$

This value is in close agreement with the given value for K (1.15×10^2), so the calculated equilibrium concentrations are correct.

This procedure is further illustrated for a problem involving pressures in Sample Exercise 13.12.

Sample Exercise 13.12

Calculating Equilibrium Pressures

Assume that gaseous hydrogen iodide is synthesized from hydrogen gas and iodine vapor at a temperature where the equilibrium constant is 1.00×10^2. Suppose HI at 5.000×10^{-1} atm, H_2 at 1.000×10^{-2} atm, and I_2 at 5.000×10^{-3} atm are mixed in a 5.000-L flask. Calculate the equilibrium pressures of all species.

Solution

The balanced equation for this process is

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

and the equilibrium expression in terms of pressure is

$$K_p = \frac{P_{HI}{}^2}{(P_{H_2})(P_{I_2})} = 1.00 \times 10^2$$

The given initial pressures are

$$P_{HI}{}^0 = 5.000 \times 10^{-1} \text{ atm}$$
$$P_{H_2}{}^0 = 1.000 \times 10^{-2} \text{ atm}$$
$$P_{I_2}{}^0 = 5.000 \times 10^{-3} \text{ atm}$$

The value of Q for this system is

$$Q = \frac{(P_{HI}{}^0)^2}{(P_{H_2}{}^0)(P_{I_2}{}^0)} = \frac{(5.000 \times 10^{-1} \text{ atm})^2}{(1.000 \times 10^{-2} \text{ atm})(5.000 \times 10^{-3} \text{ atm})} = 5.000 \times 10^3$$

Since Q is greater than K, the system will shift to the left to reach equilibrium.

So far we have used moles or concentrations in stoichiometric calculations. However, it is equally valid to use pressures for a gas-phase system at constant temperature and volume because in this case pressure is directly proportional to the number of moles:

$$P = n\left(\frac{RT}{V}\right) \longleftarrow \text{Constant if constant } T \text{ and } V$$

Thus we can represent the change needed to achieve equilibrium in terms of pressures.

Let x be the change in pressure (in atm) of H_2 as the system shifts left toward equilibrium. This leads to the following equilibrium pressures:

	$H_2(g)$	+	$I_2(g)$	$\rightleftharpoons$	$2HI(g)$
Initial:	1.000×10^{-2}		5.000×10^{-3}		5.000×10^{-1}
Change:	$+x$		$+x$		$-2x$
Equilibrium:	$1.000 \times 10^{-2} + x$		$5.000 \times 10^{-3} + x$		$5.000 \times 10^{-1} - 2x$

Substitution into the equilibrium expression gives

$$K_p = \frac{(P_{HI})^2}{(P_{H_2})(P_{I_2})} = \frac{(5.000 \times 10^{-1} - 2x)^2}{(1.000 \times 10^{-2} + x)(5.000 \times 10^{-3} + x)}$$

Multiplying and collecting terms yield the quadratic equation where $a = 9.60 \times 10^1$, $b = 3.5$, and $c = -2.45 \times 10^{-1}$:

$$(9.60 \times 10^1)x^2 + 3.5x - (2.45 \times 10^{-1}) = 0$$

From the quadratic formula, the correct value for x is $x = 3.55 \times 10^{-2}$ atm. The equilibrium pressures can now be calculated from the expressions involving x:

$$P_{HI} = 5.000 \times 10^{-1} \text{ atm} - 2(3.55 \times 10^{-2}) \text{ atm} = 4.29 \times 10^{-1} \text{ atm}$$
$$P_{H_2} = 1.000 \times 10^{-2} \text{ atm} + 3.55 \times 10^{-2} \text{ atm} = 4.55 \times 10^{-2} \text{ atm}$$
$$P_{I_2} = 5.000 \times 10^{-3} \text{ atm} + 3.55 \times 10^{-2} \text{ atm} = 4.05 \times 10^{-2} \text{ atm}$$

Reality Check:

$$\frac{P_{\mathrm{HI}}{}^2}{P_{\mathrm{H_2}} \cdot P_{\mathrm{I_2}}} = \frac{(4.29 \times 10^{-1})^2}{(4.55 \times 10^{-2})(4.05 \times 10^{-2})} = 99.9$$

This agrees with the given value of K (1.00×10^2), so the calculated equilibrium concentrations are correct.

See Exercises 13.47 through 13.50.

Treating Systems That Have Small Equilibrium Constants

We have seen that fairly complicated calculations are often necessary to solve equilibrium problems. However, under certain conditions, simplifications are possible that greatly reduce the mathematical difficulties. For example, gaseous NOCl decomposes to form the gases NO and Cl_2. At 35°C the equilibrium constant is 1.6×10^{-5}. In an experiment in which 1.0 mol NOCl is placed in a 2.0-L flask, what are the equilibrium concentrations?

The balanced equation is

$$2\mathrm{NOCl}(g) \rightleftharpoons 2\mathrm{NO}(g) + \mathrm{Cl_2}(g)$$

and

$$K = \frac{[\mathrm{NO}]^2[\mathrm{Cl_2}]}{[\mathrm{NOCl}]^2} = 1.6 \times 10^{-5}$$

The initial concentrations are

$$[\mathrm{NOCl}]_0 = \frac{1.0\ \mathrm{mol}}{2.0\ \mathrm{L}} = 0.50\ M \qquad [\mathrm{NO}]_0 = 0 \qquad [\mathrm{Cl_2}]_0 = 0$$

Since there are no products initially, the system will move to the right to reach equilibrium. We will define x as the change in concentration of Cl_2 needed to reach equilibrium. The changes in the concentrations of NOCl and NO can then be obtained from the balanced equation:

$$\begin{array}{ccccc} 2\mathrm{NOCl}(g) & \longrightarrow & 2\mathrm{NO}(g) & + & \mathrm{Cl_2}(g) \\ 2x & \longrightarrow & 2x & + & x \end{array}$$

The concentrations can be summarized as follows:

	$2\mathrm{NOCl}(g)$	$\rightleftharpoons$	$2\mathrm{NO}(g)$	+	$\mathrm{Cl_2}(g)$
Initial:	0.50		0		0
Change:	$-2x$		$+2x$		$+x$
Equilibrium:	$0.50 - 2x$		$2x$		x

The equilibrium concentrations must satisfy the equilibrium expression

$$K = 1.6 \times 10^{-5} = \frac{[\mathrm{NO}]^2[\mathrm{Cl_2}]}{[\mathrm{NOCl}]^2} = \frac{(2x)^2(x)}{(0.50 - 2x)^2}$$

Multiplying and collecting terms will give an equation with terms containing x^3, x^2, and x, which requires complicated methods to solve directly. However, we can avoid this situation by recognizing that since K is so small (1.6×10^{-5}), the system will not proceed far to the right to reach equilibrium. That is, *x represents a relatively small number.* The consequence of this fact is that the term $(0.50 - 2x)$ can be approximated by 0.50. That is, when x is small,

$$0.50 - 2x \approx 0.50$$

Approximations can simplify complicated math, but their validity should be checked carefully.

Making this approximation allows us to simplify the equilibrium expression:

$$1.6 \times 10^{-5} = \frac{(2x)^2(x)}{(0.50 - 2x)^2} \approx \frac{(2x)^2(x)}{(0.50)^2} = \frac{4x^3}{(0.50)^2}$$

Solving for x^3 gives

$$x^3 = \frac{(1.6 \times 10^{-5})(0.50)^2}{4} = 1.0 \times 10^{-6}$$

and $x = 1.0 \times 10^{-2}$.

How valid is this approximation? If $x = 1.0 \times 10^{-2}$, then

$$0.50 - 2x = 0.50 - 2(1.0 \times 10^{-2}) = 0.48$$

The difference between 0.50 and 0.48 is 0.02, or 4% of the initial concentration of NOCl, a relatively small discrepancy that will have little effect on the outcome. That is, since $2x$ is very small compared with 0.50, the value of x obtained in the approximate solution should be very close to the exact value. We use this approximate value of x to calculate the equilibrium concentrations:

$$[\mathrm{NOCl}] = 0.50 - 2x \approx 0.50\,M$$
$$[\mathrm{NO}] = 2x = 2(1.0 \times 10^{-2}\,M) = 2.0 \times 10^{-2}\,M$$
$$[\mathrm{Cl_2}] = x = 1.0 \times 10^{-2}\,M$$

Reality Check:

$$\frac{[\mathrm{NO}]^2[\mathrm{Cl_2}]}{[\mathrm{NOCl}]^2} = \frac{(2.0 \times 10^{-2})^2(1.0 \times 10^{-2})}{(0.50)^2} = 1.6 \times 10^{-5}$$

Since the given value of K is 1.6×10^{-5}, these calculated concentrations are correct.

This problem was much easier to solve than it appeared at first because the *small value of* K *and the resulting small shift to the right to reach equilibrium allowed simplification.*

13.7 Le Châtelier's Principle

It is important to understand the factors that control the *position* of a chemical equilibrium. For example, when a chemical is manufactured, the chemists and chemical engineers in charge of production want to choose conditions that favor the desired product as much as possible. That is, they want the equilibrium to lie far to the right. When Fritz Haber was developing the process for the synthesis of ammonia, he did extensive studies on how temperature and pressure affect the equilibrium concentration of ammonia. Some of his results are given in Table 13.2. Note that the equilibrium amount of NH_3 increases

TABLE 13.2 The Percent by Mass of NH_3 at Equilibrium in a Mixture of N_2, H_2, and NH_3 as a Function of Temperature and Total Pressure*

	Total Pressure		
Temperature (°C)	*300 atm*	*400 atm*	*500 atm*
400	48% NH_3	55% NH_3	61% NH_3
500	26% NH_3	32% NH_3	38% NH_3
600	13% NH_3	17% NH_3	21% NH_3

*Each experiment was begun with a 3:1 mixture of H_2 and N_2.

with an increase in pressure but decreases as the temperature is increased. Thus the amount of NH_3 present at equilibrium is favored by conditions of low temperature and high pressure.

However, this is not the whole story. Carrying out the process at low temperatures is not feasible because then the reaction is too slow. Even though the equilibrium tends to shift to the right as the temperature is lowered, the attainment of equilibrium would be much too slow at low temperatures to be practical. This emphasizes once again that we must study both the thermodynamics and the kinetics of a reaction before we really understand the factors that control it.

We can qualitatively predict the effects of changes in concentration, pressure, and temperature on a system at equilibrium by using **Le Châtelier's principle,** which states that *if a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction that tends to reduce that change.* Although this rule sometimes oversimplifies the situation, it works remarkably well.

Visualization: Le Châtelier's Principle

The Effect of a Change in Concentration

To see how we can predict the effect of change in concentration on a system at equilibrium, we will consider the ammonia synthesis reaction. Suppose there is an equilibrium position described by these concentrations:

$$[N_2] = 0.399\ M \qquad [H_2] = 1.197\ M \qquad [NH_3] = 0.202\ M$$

What will happen if 1.000 mol/L N_2 is suddenly injected into the system? We can answer this question by calculating the value of Q. The concentrations before the system adjusts are

$$[N_2]_0 = 0.399\ M + \underset{\substack{\uparrow\\ \text{Added } N_2}}{1.000\ M} = 1.399\ M$$

$$[H_2]_0 = 1.197\ M$$

$$[NH_3]_0 = 0.202\ M$$

Note we are labeling these as "initial concentrations" because the system is no longer at equilibrium. Then

$$Q = \frac{[NH_3]_0{}^2}{[N_2]_0[H_2]_0{}^3} = \frac{(0.202)^2}{(1.399)(1.197)^3} = 1.70 \times 10^{-2}$$

Since we are not given the value of K, we must calculate it from the first set of equilibrium concentrations:

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(0.202)^2}{(0.399)(1.197)^3} = 5.96 \times 10^{-2}$$

As expected, Q is less than K because the concentration of N_2 was increased.

The system will shift to the right to come to the new equilibrium position. Rather than do the calculations, we simply summarize the results:

Equilibrium Position I		**Equilibrium Position II**
$[N_2] = 0.399\ M$	$\xRightarrow[\text{of } N_2 \text{ added}]{1.000\text{ mol/L}}$	$[N_2] = 1.348\ M$
$[H_2] = 1.197\ M$		$[H_2] = 1.044\ M$
$[NH_3] = 0.202\ M$		$[NH_3] = 0.304\ M$

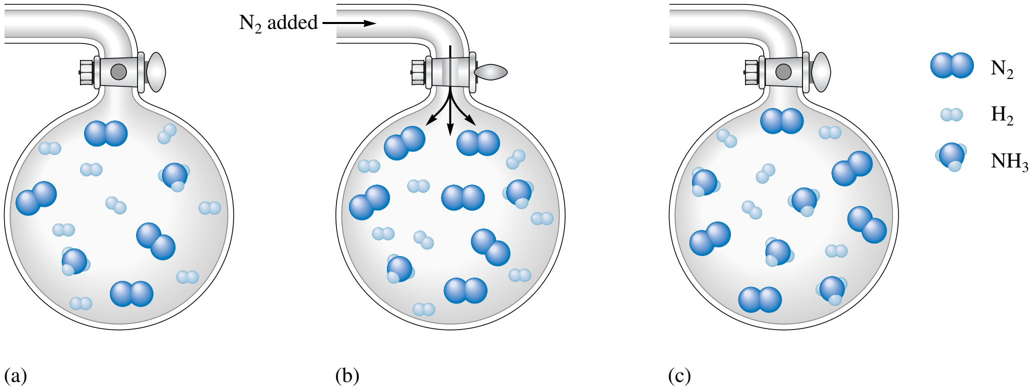


FIGURE 13.8
(a) The initial equilibrium mixture of N_2, H_2, and NH_3. (b) Addition of N_2. (c) The new equilibrium position for the system containing more N_2 (due to addition of N_2), less H_2, and more NH_3 than in (a).

Note from these data that the equilibrium position does in fact shift to the right: The concentration of H_2 decreases, the concentration of NH_3 increases, and of course, since nitrogen is added, the concentration of N_2 shows an increase relative to the amount present in the original equilibrium position. (However, notice that the nitrogen showed a decrease relative to the amount present immediately after addition of the 1.000 mol N_2.)

We can understand this shift by thinking about reaction rates. When we add N_2 molecules to the system, the number of collisions between N_2 and H_2 will increase, thus increasing the rate of the forward reaction and in turn increasing the rate of formation of NH_3 molecules. More NH_3 molecules will in turn lead to a higher rate for the reverse reaction. Eventually, the forward and reverse reaction rates will again become equal, and the system will reach its new equilibrium position.

We can predict this shift qualitatively by using Le Châtelier's principle. Since the change imposed is the addition of nitrogen, Le Châtelier's principle predicts that the system will shift in a direction that consumes nitrogen. This reduces the effect of the addition. Thus Le Châtelier's principle correctly predicts that adding nitrogen will cause the equilibrium to shift to the right (see Fig. 13.8).

If ammonia had been added instead of nitrogen, the system would have shifted to the left to consume ammonia. So another way of stating Le Châtelier's principle is to say that *if a component (reactant or product) is added to a reaction system at equilibrium (at constant T and P or constant T and V), the equilibrium position will shift in the direction that lowers the concentration of that component. If a component is removed, the opposite effect occurs.*

The system shifts in the direction that compensates for the imposed change.

Sample Exercise 13.13 Using Le Châtelier's Principle I

Arsenic can be extracted from its ores by first reacting the ore with oxygen (called *roasting*) to form solid As_4O_6, which is then reduced using carbon:

$$As_4O_6(s) + 6C(s) \rightleftharpoons As_4(g) + 6CO(g)$$

Predict the direction of the shift of the equilibrium position in response to each of the following changes in conditions.

a. Addition of carbon monoxide
b. Addition or removal of carbon or tetraarsenic hexoxide (As_4O_6)
c. Removal of gaseous arsenic (As_4)

Solution

a. Le Châtelier's principle predicts that the shift will be away from the substance whose concentration is increased. The equilibrium position will shift to the left when carbon monoxide is added.

b. Since the amount of a pure solid has no effect on the equilibrium position, changing the amount of carbon or tetraarsenic hexoxide will have no effect.

c. If gaseous arsenic is removed, the equilibrium position will shift to the right to form more products. In industrial processes, the desired product is often continuously removed from the reaction system to increase the yield.

See Exercise 13.57.

The Effect of a Change in Pressure

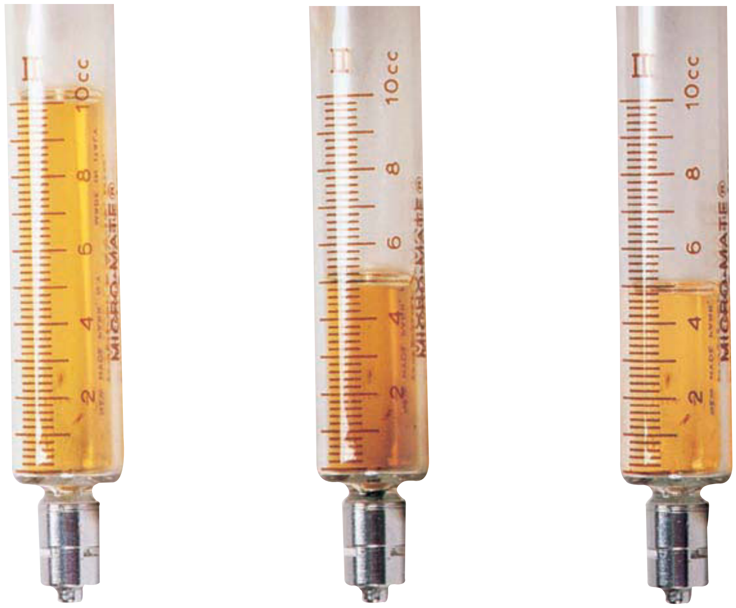
Visualization: Equilibrium Decomposition of N_2O_4

Basically, there are three ways to change the pressure of a reaction system involving gaseous components:

1. Add or remove a gaseous reactant or product.
2. Add an inert gas (one not involved in the reaction).
3. Change the volume of the container.

We have already considered the addition or removal of a reactant or product. When an inert gas is added, there is no effect on the equilibrium position. *The addition of an inert gas increases the total pressure but has no effect on the concentrations or partial pressures of the reactants or products.* That is, in this case the added molecules do not participate in the reaction in any way and thus cannot affect the equilibrium in any way. Thus the system remains at the original equilibrium position.

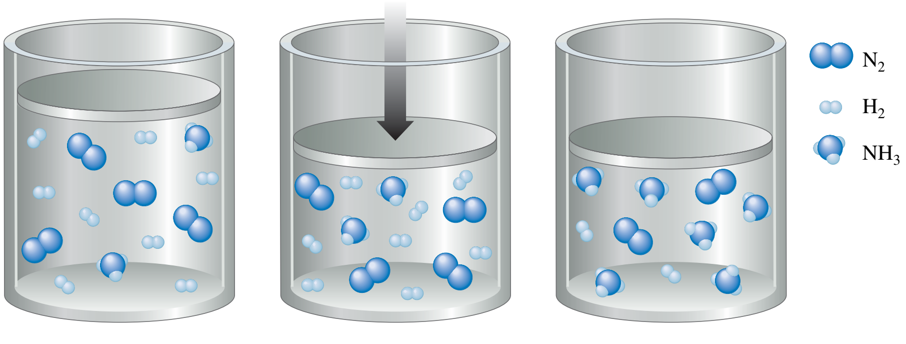
When the volume of the container is changed, the concentrations (and thus the partial pressures) of both reactants and products are changed. We could calculate Q and predict the direction of the shift. However, for systems involving gaseous components, there is an easier way: We focus on the volume. The central idea is that *when the volume of the*


(a) (b) (c)

(a) Brown $NO_2(g)$ and colorless $N_2O_4(g)$ in equilibrium in a syringe. (b) The volume is suddenly decreased, giving a greater concentration of both N_2O_4 and NO_2 (indicated by the darker brown color). (c) A few seconds after the sudden volume decrease, the color is much lighter brown as the equilibrium shifts the brown $NO_2(g)$ to colorless $N_2O_4(g)$ as predicted by Le Châtelier's principle, since in the equilibrium

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

the product side has the smaller number of molecules.



(a) (b) (c)

FIGURE 13.9
(a) A mixture of $NH_3(g)$, $N_2(g)$, and $H_2(g)$ at equilibrium. (b) The volume is suddenly decreased. (c) The new equilibrium position for the system containing more NH_3 and less N_2 and H_2. The reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ shifts to the right (toward the side with fewer molecules) when the container volume is decreased.

container holding a gaseous system is reduced, the system responds by reducing its own volume. This is done by decreasing the total number of gaseous molecules in the system.

To see that this is true, we can rearrange the ideal gas law to give

$$V = \left(\frac{RT}{P}\right)n$$

or at constant T and P,

$$V \propto n$$

That is, at constant temperature and pressure, the volume of a gas is directly proportional to the number of moles of gas present.

Suppose we have a mixture of the gases nitrogen, hydrogen, and ammonia at equilibrium (Fig. 13.9). If we suddenly reduce the volume, what will happen to the equilibrium position? The reaction system can reduce its volume by reducing the number of molecules present. This means that the reaction

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

will shift to the right, since in this direction four molecules (one of nitrogen and three of hydrogen) react to produce two molecules (of ammonia), thus *reducing the total number of gaseous molecules present.* The new equilibrium position will be farther to the right than the original one. That is, the equilibrium position will shift toward the side of the reaction involving the smaller number of gaseous molecules in the balanced equation.

The opposite is also true. When the container volume is increased, the system will shift so as to increase its volume. An increase in volume in the ammonia synthesis system will produce a shift to the left to increase the total number of gaseous molecules present.

Sample Exercise 13.14

Using Le Châtelier's Principle II

Predict the shift in equilibrium position that will occur for each of the following processes when the volume is reduced.

a. The preparation of liquid phosphorus trichloride by the reaction

$$P_4(s) + 6Cl_2(g) \rightleftharpoons 4PCl_3(l)$$

b. The preparation of gaseous phosphorus pentachloride according to the equation

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

c. The reaction of phosphorus trichloride with ammonia:

$$PCl_3(g) + 3NH_3(g) \rightleftharpoons P(NH_2)_3(g) + 3HCl(g)$$

Solution

a. Since P_4 and PCl_3 are a pure solid and a pure liquid, respectively, we need to consider only the effect of the change in volume on Cl_2. The volume is decreased, so the position of the equilibrium will shift to the right, since the reactant side contains six gaseous molecules and the product side has none.

b. Decreasing the volume will shift the given reaction to the right, since the product side contains only one gaseous molecule while the reactant side has two.

c. Both sides of the balanced reaction equation have four gaseous molecules. A change in volume will have no effect on the equilibrium position. There is no shift in this case.

See Exercise 13.58.

The Effect of a Change in Temperature

It is important to realize that although the changes we have just discussed may alter the equilibrium *position,* they do not alter the equilibrium *constant.* For example, the addition of a reactant shifts the equilibrium position to the right but has no effect on the value of the equilibrium constant; the new equilibrium concentrations satisfy the original equilibrium constant.

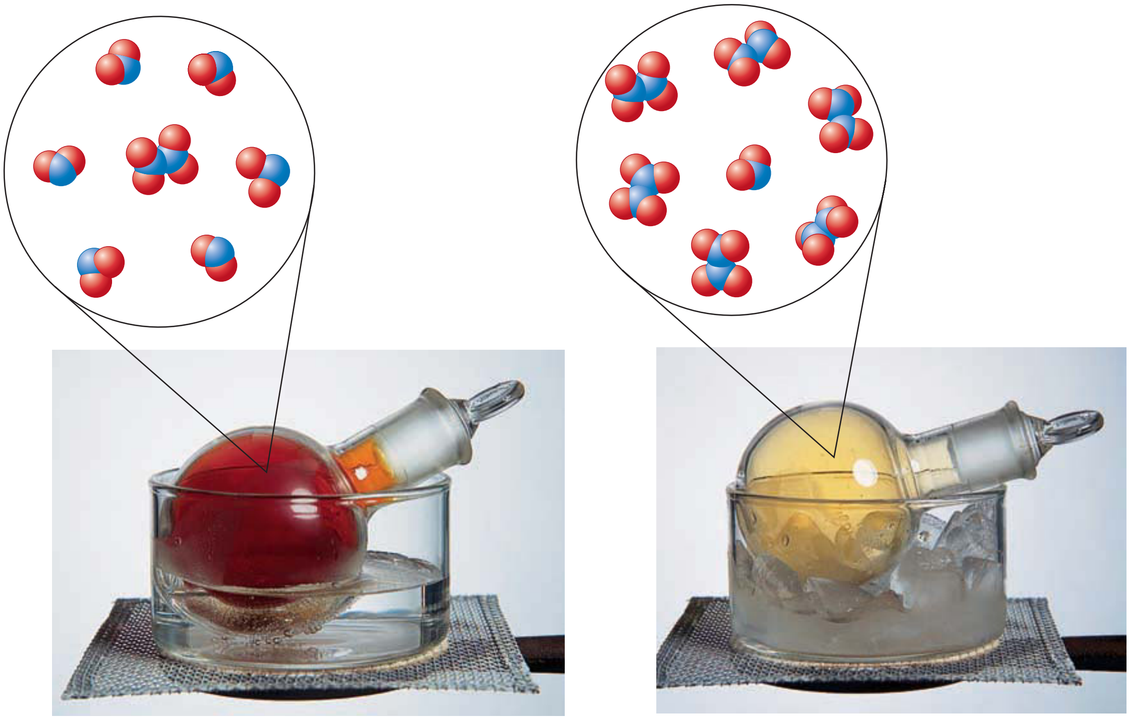
The effect of temperature on equilibrium is different, however, because *the value of K changes with temperature.* We can use Le Châtelier's principle to predict the direction of the change.

The synthesis of ammonia from nitrogen and hydrogen is exothermic. We can represent this by treating energy as a product:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 92 \text{ kJ}$$

Of course, energy is not a chemical product of this reaction, but thinking of it in this way makes it easy to apply Le Châtelier's principle.

If energy is added to this system at equilibrium by heating it, Le Châtelier's principle predicts that the shift will be in the direction that consumes energy, that is, to the left. Note that this shift decreases the concentration of NH_3 and increases the concentrations of N_2



Shifting the $N_2O_4(g) \rightarrow 2NO_2(g)$ equilibrium by changing the temperature. (a) At 100°C the flask is definitely reddish brown due to a large amount of NO_2 present. (b) At 0°C the equilibrium is shifted toward colorless $N_2O_4(g)$.

and H_2, thus *decreasing the value of K*. The experimentally observed change in K with temperature for this reaction is indicated in Table 13.3. The value of K decreases with increased temperature, as predicted.

On the other hand, for an endothermic reaction, such as the decomposition of calcium carbonate,

$$556\text{ kJ} + CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

an increase in temperature will cause the equilibrium to shift to the right and the value of K to increase.

In summary, to use Le Châtelier's principle to describe the effect of a temperature change on a system at equilibrium, treat energy as a reactant (in an endothermic process) or as a product (in an exothermic process), and predict the direction of the shift in the same way as when an actual reactant or product is added or removed. Although Le Châtelier's principle cannot predict the size of the change in K, it does correctly predict the direction of the change.

TABLE 13.3 Observed Value of *K* for the Ammonia Synthesis Reaction as a Function of Temperature*

Temperature (K)	*K*
500	90
600	3
700	0.3
800	0.04

*For this exothermic reaction, the value of K decreases as the temperature increases, as predicted by Le Châtelier's principle.

Sample Exercise 13.15

Using Le Châtelier's Principle III

For each of the following reactions, predict how the value of K changes as the temperature is increased.

a. $N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \qquad \Delta H° = 181\text{ kJ}$
b. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H° = -198\text{ kJ}$

Solution

a. This is an endothermic reaction, as indicated by the positive value for $\Delta H°$. Energy can be viewed as a reactant, and K increases (the equilibrium shifts to the right) as the temperature is increased.

b. This is an exothermic reaction (energy can be regarded as a product). As the temperature is increased, the value of K decreases (the equilibrium shifts to the left).

See Exercises 13.63 and 13.64.

We have seen how Le Châtelier's principle can be used to predict the effect of several types of changes on a system at equilibrium. To summarize these ideas, Table 13.4 shows how various changes affect the equilibrium position of the endothermic reaction

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad \Delta H° = 58\text{ kJ}$$

TABLE 13.4 Shifts in the Equilibrium Position for the Reaction 58 kJ + $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

Change	Shift
Addition of $N_2O_4(g)$	Right
Addition of $NO_2(g)$	Left
Removal of $N_2O_4(g)$	Left
Removal of $NO_2(g)$	Right
Addition of He(g)	None
Decrease container volume	Left
Increase container volume	Right
Increase temperature	Right
Decrease temperature	Left

Key Terms

chemical equilibrium

Section 13.2
law of mass action
equilibrium expression
equilibrium constant
equilibrium position

Section 13.4
homogeneous equilibria
heterogeneous equilibria

Section 13.5
reaction quotient, Q

Section 13.7
Le Châtelier's principle

For Review

Chemical equilibrium

- When a reaction takes place in a closed system, it reaches a condition where the concentrations of the reactants and products remain constant over time
- Dynamic state: reactants and products are interconverted continually
  - Forward rate = reverse rate
- The law of mass action: for the reaction

$$jA + kB \rightleftharpoons mC + nD$$

$$K = \frac{[C]^m[D]^n}{[A]^j[B]^k} = \text{equilibrium constant}$$

  - A pure liquid or solid is never included in the equilibrium expression
  - For a gas-phase reaction the reactants and products can be described in terms of their partial pressures and the equilibrium constant is called K_p:

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

  where Δn is the sum of the coefficients of the gaseous products minus the sum of the coefficients of the gaseous reactants

Equilibrium position

- A set of reactant and product concentrations that satisfies the equilibrium constant expression
  - There is one value of K for a given system at a given temperature
  - There are an infinite number of equilibrium positions at a given temperature depending on the initial concentrations
- A small value of K means the equilibrium lies to the left; a large value of K means the equilibrium lies to the right
  - The size of K has no relationship to the speed at which equilibrium is achieved
- Q, the reaction quotient, applies the law of mass action to initial concentrations rather than equilibrium concentrations
  - If $Q > K$, the system will shift to the left to achieve equilibrium
  - If $Q < K$, the system will shift to the right to achieve equilibrium
- Finding the concentrations that characterize a given equilibrium position:

  1. Start with the given initial concentrations (pressures)
  2. Define the change needed to reach equilibrium
  3. Apply the change to the initial concentrations (pressures) and solve for the equilibrium concentrations (pressures)

Le Châtelier's principle

- Enables qualitative prediction of the effects of changes in concentration, pressure, and temperature on a system at equilibrium
- If a change in conditions is imposed on a system at equilibrium, the system will shift in a direction that compensates for the imposed change
  - In other words, when a stress is placed on a system at equilibrium, the system shifts in the direction that relieves the stress

REVIEW QUESTIONS

1. Characterize a system at chemical equilibrium with respect to each of the following.
   a. the rates of the forward and reverse reactions
   b. the overall composition of the reaction mixture
   For a general reaction $3A(g) + B(g) \longrightarrow 2C(g)$, if one starts an experiment with only reactants present, show what the plot of concentrations of A, B, and C versus time would look like. Also sketch the plot illustrating the rate of the forward reaction and rate of the reverse reaction versus time.
2. What is the law of mass action? Is it true that the value of K depends on the amounts of reactants and products mixed together initially? Explain. Is it true that reactions with large equilibrium constant values are very fast? Explain. There is only one value of the equilibrium constant for a particular system at a particular temperature, but there is an infinite number of equilibrium positions. Explain.
3. Consider the following reactions at some temperature:

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g) \qquad K = 1.6 \times 10^{-5}$$
$$2NO(g) \rightleftharpoons N_2(g) + O_2(g) \qquad K = 1 \times 10^{31}$$

For each reaction, assume some quantities of the reactants were placed in separate containers and allowed to come to equilibrium. Describe the relative amounts of reactants and products that would be present at equilibrium. At equilibrium, which is faster, the forward or reverse reaction in each case?

4. What is the difference between K and K_p? When does $K = K_p$ for a reaction? When does $K \neq K_p$ for a reaction? If the coefficients in a reaction equation are tripled, how is the new value of K related to the initial value of K? If a reaction is reversed, how is the value of K_p for the reversed reaction related to the value of K_p for the initial reaction?
5. What are homogeneous equilibria? Heterogeneous equilibria? What is the difference in writing K expressions for homogeneous versus heterogeneous reactions? Summarize which species are included in the K expression and which species are not included.
6. Distinguish between the terms *equilibrium constant* and *reaction quotient.* When $Q = K$, what does this say about a reaction? When $Q < K$, what does this say about a reaction? When $Q > K$, what does this say about a reaction?
7. Summarize the steps for solving equilibrium problems (see the beginning of Section 13.6). In general, when solving an equilibrium problem, you should always set up an ICE table. What is an ICE table?
8. A common type of reaction we will study is that having a very small K value ($K \ll 1$). Solving for equilibrium concentrations in an equilibrium problem usually requires many mathematical operations to be performed. However, the math involved when solving equilibrium problems for reactions having small K values ($K \ll 1$) is simplified. What assumption is made when solving the equilibrium concentrations for reactions with small K values? Whenever assumptions are made, they must be checked for validity. In general, the "5% rule" is used to check the validity of assuming x (or $2x$, $3x$, and so on) is very small compared to some number. When x (or $2x$, $3x$, and so on) is less than 5% of the number the assumption was made against, then the assumption is said to be valid. If the 5% rule fails, what do you do to solve for the equilibrium concentrations?
9. What is Le Châtelier's principle? Consider the reaction $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$. If this reaction is at equilibrium, what happens when the following changes occur?
   a. $NOCl(g)$ is added.
   b. $NO(g)$ is added.
   c. $NOCl(g)$ is removed.
   d. $Cl_2(g)$ is removed.
   e. The container volume is decreased.

   For each of these changes, what happens to the value of K for the reaction as equilibrium is reached again? Give an example of a reaction for which the addition or removal of one of the reactants or products has no effect on the equilibrium position.

   In general, how will the equilibrium position of a gas-phase reaction be affected if the volume of the reaction vessel changes? Are there reactions that will not have their equilibria shifted by a change in volume? Explain. Why does changing the pressure in a rigid container by adding an inert gas not shift the equilibrium position for a gas-phase reaction?
10. The only "stress" (change) that also changes the value of K is a change in temperature. For an exothermic reaction, how does the equilibrium position change as temperature increases, and what happens to the value of K? Answer the same questions for an endothermic reaction. If the value of K increases with a decrease in temperature, is the reaction exothermic or endothermic? Explain.

Active Learning Questions

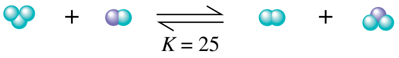
These questions are designed to be used by groups of students in class. The questions allow students to explore their understanding of concepts through discussion and peer teaching. The real value of these questions is the learning that occurs while students talk to each other about chemical concepts.

1. Consider an equilibrium mixture of four chemicals (A, B, C, and D, all gases) reacting in a closed flask according to the equation:

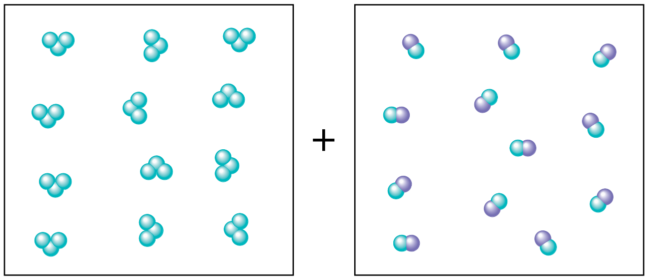
$$A + B \rightleftharpoons C + D$$

   a. You add more A to the flask. How does the concentration of each chemical compare to its original concentration after equilibrium is reestablished? Justify your answer.
   b. You have the original setup at equilibrium, and add more D to the flask. How does the concentration of each chemical compare to its original concentration after equilibrium is reestablished? Justify your answer.

2. The boxes shown below represent a set of initial conditions for the reaction:



Draw a quantitative molecular picture that shows what this system looks like after the reactants are mixed in one of the boxes and the system reaches equilibrium. Support your answer with calculations.



3. For the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, consider two possibilities: (a) you mix 0.5 mol of each reactant, allow the system to come to equilibrium, and then add another mole of H_2 and allow the system to reach equilibrium again, or (b) you mix 1.5 mol H_2 and 0.5 mol I_2 and allow the system to reach equilibrium. Will the final equilibrium mixture be different for the two procedures? Explain.

4. Given the reaction $A(g) + B(g) \rightleftharpoons C(g) + D(g)$, consider the following situations:
   i. You have 1.3 *M* A and 0.8 *M* B initially.
   ii. You have 1.3 *M* A, 0.8 *M* B, and 0.2 *M* C initially.
   iii. You have 2.0 *M* A and 0.8 *M* B initially.

   Order the preceding situations in terms of increasing equilibrium concentration of D. Explain your order. Then give the order in terms of increasing equilibrium concentration of B and explain.

5. Consider the reaction $A(g) + 2B(g) \rightleftharpoons C(g) + D(g)$ in a 1.0-L rigid flask. Answer the following questions for each situation (a–d):
   i. Estimate a range (as small as possible) for the requested substance. For example, [A] could be between 95 *M* and 100 *M*.
   ii. Explain how you decided on the limits for the estimated range.
   iii. Indicate what other information would enable you to narrow your estimated range.
   iv. Compare the estimated concentrations for a through d, and explain any differences.

   a. If at equilibrium [A] = 1 *M*, and then 1 mol C is added, estimate the value for [A] once equilibrium is reestablished.
   b. If at equilibrium [B] = 1 *M*, and then 1 mol C is added, estimate the value for [B] once equilibrium is reestablished.
   c. If at equilibrium [C] = 1 *M*, and then 1 mol C is added, estimate the value for [C] once equilibrium is reestablished.
   d. If at equilibrium [D] = 1 *M*, and then 1 mol C is added, estimate the value for [D] once equilibrium is reestablished.

6. Consider the reaction $A(g) + B(g) \rightleftharpoons C(g) + D(g)$. A friend asks the following: "I know we have been told that if a mixture of A, B, C, and D is at equilibrium and more of A is added, more C and D will form. But how can more C and D form if we do not add more B?" What do you tell your friend?

7. Consider the following statements: "Consider the reaction $A(g) + B(g) \rightleftharpoons C(g)$, for which at equilibrium [A] = 2 *M*, [B] = 1 *M*, and [C] = 4 *M*. To a 1-L container of the system at equilibrium you add 3 moles of B. A possible equilibrium condition is [A] = 1 *M*, [B] = 3 *M*, and [C] = 6 *M* because in both cases $K = 2$." Indicate everything that is correct in these statements and everything that is incorrect. Correct the incorrect statements, and explain.

8. Le Châtelier's principle is stated (Section 13.7) as follows: "If a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction that tends to reduce that change." The system $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is used as an example in which the addition of nitrogen gas at equilibrium results in a decrease in H_2 concentration and an increase in NH_3 concentration. In the experiment the volume is assumed to be constant. On the other hand, if N_2 is added to the reaction system in a container with a piston so that the pressure can be held constant, the amount of NH_3 actually could decrease and the concentration of H_2 would increase as equilibrium is reestablished. Explain how this can happen. Also, if you consider this same system at equilibrium, the addition of an inert gas, holding the pressure constant, *does* affect the equilibrium position. Explain why the addition of an inert gas to this system in a rigid container does not affect the equilibrium position.

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide.*

Questions

9. Consider the following reaction:

$$H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$$

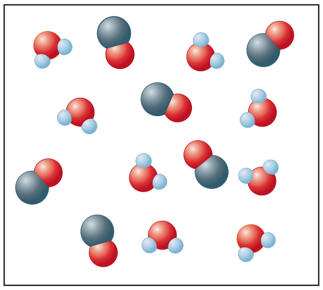
Amounts of H_2O, CO, H_2, and CO_2 are put into a flask so that the composition corresponds to an equilibrium position. If the CO placed in the flask is labeled with radioactive ^{14}C, will ^{14}C be found only in CO molecules for an indefinite period of time? Explain.

10. Consider the same reaction as in Exercise 9. In one experiment 1.0 mol $H_2O(g)$ and 1.0 mol $CO(g)$ are put into a flask and heated to 350°C. In a second experiment 1.0 mol $H_2(g)$ and 1.0 mol $CO_2(g)$ are put into another flask with the same volume as the first. This mixture is also heated to 350°C. After equilibrium is reached, will there be any difference in the composition of the mixtures in the two flasks?

11. Consider the following reaction at some temperature:

$$H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g) \qquad K = 2.0$$

Some molecules of H_2O and CO are placed in a 1.0-L container as shown below.

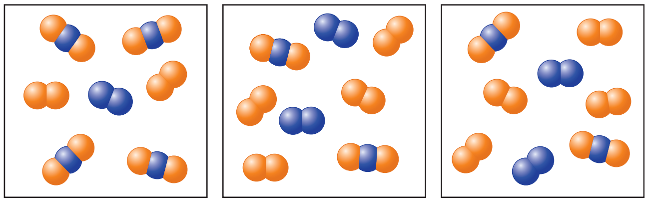


When equilibrium is reached, how many molecules of H_2O, CO, H_2 and CO_2 are present? Do this problem by trial and error—that is, if two molecules of CO react, is this equilibrium; if three molecules of CO react, is this equilibrium; and so on.

12. Consider the following generic reaction:

$$2A_2B(g) \rightleftharpoons 2A_2(g) + B_2(g)$$

Some molecules of A_2B are placed in a 1.0-L container. As time passes, several snapshots of the reaction mixture are taken as illustrated below.



Which illustration is the first to represent an equilibrium mixture? Explain. How many molecules of A_2B reacted initially?

13. Explain the difference between K, K_p, and Q.

14. Consider the following reactions.

$$H_2(g) + I_2(g) \longrightarrow 2HI(g) \quad \text{and} \quad H_2(g) + I_2(s) \longrightarrow 2HI(g)$$

List two property differences between these two reactions that relate to equilibrium.

15. For a typical equilibrium problem, the value of K and the initial reaction conditions are given for a specific reaction, and you are asked to calculate the equilibrium concentrations. Many of these calculations involve solving a quadratic or cubic equation. What can you do to avoid solving a quadratic or cubic equation and still come up with reasonable equilibrium concentrations?

16. Which of the following statements is(are) true? Correct the false statement(s).

a. When a reactant is added to a system at equilibrium at a given temperature, the reaction will shift right to reestablish equilibrium.

b. When a product is added to a system at equilibrium at a given temperature, the value of K for the reaction will increase when equilibrium is reestablished.

c. When temperature is increased for a reaction at equilibrium, the value of K for the reaction will increase.

d. When the volume of a reaction container is increased for a system at equilibrium at a given temperature, the reaction will shift left to reestablish equilibrium.

e. Addition of a catalyst (a substance that increases the speed of the reaction) has no effect on the equilibrium position.

Exercises

In this section similar exercises are paired.

The Equilibrium Constant

17. Write the equilibrium expression (K) for each of the following gas-phase reactions.

a. $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

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

c. $SiH_4(g) + 2Cl_2(g) \rightleftharpoons SiCl_4(g) + 2H_2(g)$

d. $2PBr_3(g) + 3Cl_2(g) \rightleftharpoons 2PCl_3(g) + 3Br_2(g)$

18. Write the equilibrium expression (K_p) for each reaction in Exercise 17.

19. At a given temperature, $K = 1.3 \times 10^{-2}$ for the reaction

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

Calculate values of K for the following reactions at this temperature.

a. $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$

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

c. $NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$

d. $2N_2(g) + 6H_2(g) \rightleftharpoons 4NH_3(g)$

20. For the reaction

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

$K_p = 3.5 \times 10^4$ at 1495 K. What is the value of K_p for the following reactions at 1495 K?

a. $HBr(g) \rightleftharpoons \frac{1}{2}H_2(g) + \frac{1}{2}Br_2(g)$

b. $2HBr(g) \rightleftharpoons H_2(g) + Br_2(g)$

c. $\frac{1}{2}H_2(g) + \frac{1}{2}Br_2(g) \rightleftharpoons HBr(g)$

21. For the reaction

$$2NO(g) + 2H_2(g) \rightleftharpoons N_2(g) + 2H_2O(g)$$

it is determined that, at equilibrium at a particular temperature, the concentrations are as follows: $[NO(g)] = 8.1 \times 10^{-3}\,M$, $[H_2(g)] = 4.1 \times 10^{-5}\,M$, $[N_2(g)] = 5.3 \times 10^{-2}\,M$, and $[H_2O(g)] = 2.9 \times 10^{-3}\,M$. Calculate the value of K for the reaction at this temperature.

22. For the reaction

$$N_2(g) + 3Cl_2(g) \rightleftharpoons 2NCl_3(g)$$

an analysis of an equilibrium mixture is performed at a certain temperature. It is found that $[NCl_3(g)] = 1.9 \times 10^{-1}\,M$, $[N_2(g)] = 1.4 \times 10^{-3}\,M$, and $[Cl_2(g)] = 4.3 \times 10^{-4}\,M$. Calculate K for the reaction at this temperature.

23. At a particular temperature, a 3.0-L flask contains 2.4 mol Cl_2, 1.0 mol NOCl, and 4.5×10^{-3} mol NO. Calculate K at this temperature for the following reaction:

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

24. At a particular temperature a 2.00-L flask at equilibrium contains 2.80×10^{-4} mol N_2, 2.50×10^{-5} mol O_2, and 2.00×10^{-2} mol N_2O. Calculate K at this temperature for the reaction

$$2N_2(g) + O_2(g) \rightleftharpoons 2N_2O(g)$$

If $[N_2] = 2.00 \times 10^{-4}\,M$, $[N_2O] = 0.200\,M$, and $[O_2] = 0.00245\,M$, does this represent a system at equilibrium?

25. The following equilibrium pressures at a certain temperature were observed for the reaction

$$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$$

$$P_{NO_2} = 0.55 \text{ atm}$$
$$P_{NO} = 6.5 \times 10^{-5} \text{ atm}$$
$$P_{O_2} = 4.5 \times 10^{-5} \text{ atm}$$

Calculate the value for the equilibrium constant K_p at this temperature.

26. The following equilibrium pressures were observed at a certain temperature for the reaction

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

$$P_{NH_3} = 3.1 \times 10^{-2} \text{ atm}$$
$$P_{N_2} = 8.5 \times 10^{-1} \text{ atm}$$
$$P_{H_2} = 3.1 \times 10^{-3} \text{ atm}$$

Calculate the value for the equilibrium constant K_p at this temperature.

If $P_{N_2} = 0.525$ atm, $P_{NH_3} = 0.0167$ atm, and $P_{H_2} = 0.00761$ atm, does this represent a system at equilibrium?

27. At 327°, the equilibrium concentrations are $[CH_3OH] = 0.15\,M$, $[CO] = 0.24\,M$, and $[H_2] = 1.1\,M$ for the reaction

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

Calculate K_p at this temperature.

28. At 1100 K, $K_p = 0.25$ for the reaction

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

What is the value of K at this temperature?

29. Write expressions for K and K_p for the following reactions.

a. $2NH_3(g) + CO_2(g) \rightleftharpoons N_2CH_4O(s) + H_2O(g)$
b. $2NBr_3(s) \rightleftharpoons N_2(g) + 3Br_2(g)$
c. $2KClO_3(s) \rightleftharpoons 2KCl(s) + 3O_2(g)$
d. $CuO(s) + H_2(g) \rightleftharpoons Cu(l) + H_2O(g)$

30. For which reactions in Exercise 29 is K_p equal to K?

31. Consider the following reaction at a certain temperature:

$$4Fe(s) + 3O_2(g) \rightleftharpoons 2Fe_2O_3(s)$$

An equilibrium mixture contains 1.0 mol Fe, 1.0×10^{-3} mol O_2, and 2.0 mol Fe_2O_3 all in a 2.0-L container. Calculate the value of K for this reaction.

32. In a study of the reaction

$$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

at 1200 K it was observed that when the equilibrium partial pressure of water vapor is 15.0 torr, that total pressure at equilibrium is 36.3 torr. Calculate the value of K_p for this reaction at 1200 K. *Hint:* Apply Dalton's law of partial pressures.

Equilibrium Calculations

33. The equilibrium constant, K, is 2.4×10^3 at a certain temperature for the reaction

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

For which of the following sets of conditions is the system at equilibrium? For those that are not at equilibrium, in which direction will the system shift?

a. A 1.0-L flask contains 0.024 mol NO, 2.0 mol N_2, and 2.6 mol O_2.
b. A 2.0-L flask contains 0.032 mol NO, 0.62 mol N_2, and 4.0 mol O_2.
c. A 3.0-L flask contains 0.060 mol NO, 2.4 mol N_2, and 1.7 mol O_2.

34. The equilibrium constant, K_p, is 2.4×10^3 at a certain temperature for the reaction

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

For which of the following sets of conditions is the system at equilibrium? For those that are not at equilibrium, in which direction will the system shift?

a. $P_{NO} = 0.010$ atm, $P_{N_2} = 0.11$ atm, $P_{O_2} = 2.0$ atm
b. $P_{NO} = 0.0078$ atm, $P_{N_2} = 0.36$ atm, $P_{O_2} = 0.67$ atm
c. $P_{NO} = 0.0062$ atm, $P_{N_2} = 0.51$ atm, $P_{O_2} = 0.18$ atm

35. At 900°C, $K_p = 1.04$ for the reaction

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

At a low temperature, dry ice (solid CO_2), calcium oxide, and calcium carbonate are introduced into a 50.0-L reaction chamber. The temperature is raised to 900°C, resulting in the dry ice converting to gaseous CO_2. For the following mixtures, will the initial amount of calcium oxide increase, decrease, or remain the same as the system moves toward equilibrium at 900°C?

a. 655 g $CaCO_3$, 95.0 g CaO, $P_{CO_2} = 2.55$ atm
b. 780 g $CaCO_3$, 1.00 g CaO, $P_{CO_2} = 1.04$ atm
c. 0.14 g $CaCO_3$, 5000 g CaO, $P_{CO_2} = 1.04$ atm
d. 715 g $CaCO_3$, 813 g CaO, $P_{CO_2} = 0.211$ atm

36. Ethyl acetate is synthesized in a nonreacting solvent (not water) according to the following reaction:

$$\underset{\text{Acetic acid}}{CH_3CO_2H} + \underset{\text{Ethanol}}{C_2H_5OH} \rightleftharpoons \underset{\text{Ethyl acetate}}{CH_3CO_2C_2H_5} + H_2O \qquad K = 2.2$$

For the following mixtures (a–d), will the concentration of H_2O increase, decrease, or remain the same as equilibrium is established?

a. $[CH_3CO_2C_2H_5] = 0.22\ M$, $[H_2O] = 0.10\ M$, $[CH_3CO_2H] = 0.010\ M$, $[C_2H_5OH] = 0.010\ M$
b. $[CH_3CO_2C_2H_5] = 0.22\ M$, $[H_2O] = 0.0020\ M$, $[CH_3CO_2H] = 0.0020\ M$, $[C_2H_5OH] = 0.10\ M$
c. $[CH_3CO_2C_2H_5] = 0.88\ M$, $[H_2O] = 0.12\ M$, $[CH_3CO_2H] = 0.044\ M$, $[C_2H_5OH] = 6.0\ M$
d. $[CH_3CO_2C_2H_5] = 4.4\ M$, $[H_2O] = 4.4\ M$, $[CH_3CO_2H] = 0.88\ M$, $[C_2H_5OH] = 10.0\ M$
e. What must the concentration of water be for a mixture with $[CH_3CO_2C_2H_5] = 2.0\ M$, $[CH_3CO_2H] = 0.10\ M$, $[C_2H_5OH] = 5.0\ M$ to be at equilibrium?
f. Why is water included in the equilibrium expression for this reaction?

37. For the reaction

$$2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$$

$K = 2.4 \times 10^{-3}$ at a given temperature. At equilibrium it is found that $[H_2O(g)] = 1.1 \times 10^{-1}\ M$ and $[H_2(g)] = 1.9 \times 10^{-2}\ M$. What is the concentration of $O_2(g)$ under these conditions?

38. The reaction

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

has $K_p = 109$ at 25°C. If the equilibrium partial pressure of Br_2 is 0.0159 atm and the equilibrium partial pressure of NOBr is 0.0768 atm, calculate the partial pressure of NO at equilibrium.

39. A 1.00-L flask was filled with 2.00 mol gaseous SO_2 and 2.00 mol gaseous NO_2 and heated. After equilibrium was reached, it was found that 1.30 mol gaseous NO was present. Assume that the reaction

$$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$$

occurs under these conditions. Calculate the value of the equilibrium constant, K, for this reaction.

40. A sample of $S_8(g)$ is placed in an otherwise empty rigid container at 1325 K at an initial pressure of 1.00 atm, where it decomposes to $S_2(g)$ by the reaction

$$S_8(g) \rightleftharpoons 4S_2(g)$$

At equilibrium, the partial pressure of S_8 is 0.25 atm. Calculate K_p for this reaction at 1325 K.

41. At a particular temperature, 12.0 mol of SO_3 is placed into a 3.0-L rigid container, and the SO_3 dissociates by the reaction

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

At equilibrium, 3.0 mol of SO_2 is present. Calculate K for this reaction.

42. At a certain temperature, 4.0 mol NH_3 is introduced into a 2.0-L container, and the NH_3 partially dissociates by the reaction

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

At equilibrium, 2.0 mol NH_3 remains. What is the value of K for this reaction?

43. An initial mixture of nitrogen gas and hydrogen gas is reacted in a rigid container at a certain temperature by the reaction

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

At equilibrium, the concentrations are $[H_2] = 5.0\ M$, $[N_2] = 8.0\ M$, and $[NH_3] = 4.0\ M$. What were the concentrations of nitrogen gas and hydrogen gas that were reacted initially?

44. Nitrogen gas (N_2) reacts with hydrogen gas (H_2) to form ammonia (NH_3). At 200°C in a closed container, 1.00 atm of nitrogen gas is mixed with 2.00 atm of hydrogen gas. At equilibrium, the total pressure is 2.00 atm. Calculate the partial pressure of hydrogen gas at equilibrium.

45. At a particular temperature, $K = 3.75$ for the reaction

$$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$$

If all four gases had initial concentrations of 0.800 M, calculate the equilibrium concentrations of the gases.

46. At a particular temperature, $K = 1.00 \times 10^2$ for the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

In an experiment, 1.00 mol H_2, 1.00 mol I_2, and 1.00 mol HI are introduced into a 1.00-L container. Calculate the concentrations of all species when equilibrium is reached.

47. At 2200°C, $K_p = 0.050$ for the reaction

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

What is the partial pressure of NO in equilibrium with N_2 and O_2 that were placed in a flask at initial pressures of 0.80 and 0.20 atm, respectively?

48. At 25°C, $K = 0.090$ for the reaction

$$H_2O(g) + Cl_2O(g) \rightleftharpoons 2HOCl(g)$$

Calculate the concentrations of all species at equilibrium for each of the following cases.

a. 1.0 g H_2O and 2.0 g Cl_2O are mixed in a 1.0-L flask.
b. 1.0 mol pure HOCl is placed in a 2.0-L flask.

49. At 1100 K, $K_p = 0.25$ for the reaction

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

Calculate the equilibrium partial pressures of SO_2, O_2, and SO_3 produced from an initial mixture in which $P_{SO_2} = P_{O_2} = 0.50$ atm and $P_{SO_3} = 0$. (*Hint:* If you don't have a graphing calculator, then use the method of successive approximations to solve, as discussed in Appendix 1.4.)

50. At a particular temperature, $K_p = 0.25$ for the reaction

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

- **a.** A flask containing only N_2O_4 at an initial pressure of 4.5 atm is allowed to reach equilibrium. Calculate the equilibrium partial pressures of the gases.
- **b.** A flask containing only NO_2 at an initial pressure of 9.0 atm is allowed to reach equilibrium. Calculate the equilibrium partial pressures of the gases.
- **c.** From your answers to parts a and b, does it matter from which direction an equilibrium position is reached?

51. At 35°C, $K = 1.6 \times 10^{-5}$ for the reaction

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

Calculate the concentrations of all species at equilibrium for each of the following original mixtures.

- **a.** 2.0 mol pure NOCl in a 2.0-L flask
- **b.** 1.0 mol NOCl and 1.0 mol NO in a 1.0-L flask
- **c.** 2.0 mol NOCl and 1.0 mol Cl_2 in a 1.0-L flask

52. At a particular temperature, $K = 4.0 \times 10^{-7}$ for the reaction

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

In an experiment, 1.0 mol N_2O_4 is placed in a 10.0-L vessel. Calculate the concentrations of N_2O_4 and NO_2 when this reaction reaches equilibrium.

53. At a particular temperature, $K = 2.0 \times 10^{-6}$ for the reaction

$$2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$$

If 2.0 mol CO_2 is initially placed into a 5.0-L vessel, calculate the equilibrium concentrations of all species.

54. Lexan is a plastic used to make compact discs, eyeglass lenses, and bullet-proof glass. One of the compounds used to make Lexan is phosgene ($COCl_2$), an extremely poisonous gas. Phosgene decomposes by the reaction

$$COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$$

for which $K_p = 6.8 \times 10^{-9}$ at 100°C. If pure phosgene at an initial pressure of 1.0 atm decomposes, calculate the equilibrium pressures of all species.

55. At 25°C, $K_p = 2.9 \times 10^{-3}$ for the reaction

$$NH_4OCONH_2(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$$

In an experiment carried out at 25°C, a certain amount of NH_4OCONH_2 is placed in an evacuated rigid container and allowed to come to equilibrium. Calculate the total pressure in the container at equilibrium.

56. A sample of solid ammonium chloride was placed in an evacuated container and then heated so that it decomposed to ammonia gas and hydrogen chloride gas. After heating, the total pressure in the container was found to be 4.4 atm. Calculate K_p at this temperature for the decomposition reaction

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$$

Le Châtelier's Principle

57. Suppose the reaction system

$$UO_2(s) + 4HF(g) \rightleftharpoons UF_4(g) + 2H_2O(g)$$

has already reached equilibrium. Predict the effect that each of the following changes will have on the equilibrium position. Tell whether the equilibrium will shift to the right, will shift to the left, or will not be affected.

- **a.** Additional $UO_2(s)$ is added to the system.
- **b.** The reaction is performed in a glass reaction vessel; $HF(g)$ attacks and reacts with glass.
- **c.** Water vapor is removed.

58. Predict the shift in the equilibrium position that will occur for each of the following reactions when the volume of the reaction container is increased.

- **a.** $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
- **b.** $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
- **c.** $H_2(g) + F_2(g) \rightleftharpoons 2HF(g)$
- **d.** $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$
- **e.** $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

59. An important reaction in the commercial production of hydrogen is

$$CO(g) + H_2O(g) \rightleftharpoons H_2(g) + CO_2(g)$$

How will this system at equilibrium shift in each of the five following cases?

- **a.** Gaseous carbon dioxide is removed.
- **b.** Water vapor is added.
- **c.** The pressure is increased by adding helium gas.
- **d.** The temperature is increased (the reaction is exothermic).
- **e.** The pressure is increased by decreasing the volume of the reaction container.

60. What will happen to the number of moles of SO_3 in equilibrium with SO_2 and O_2 in the reaction

$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g) \qquad \Delta H^\circ = 197\text{ kJ}$$

in each of the following cases?

- **a.** Oxygen gas is added.
- **b.** The pressure is increased by decreasing the volume of the reaction container.
- **c.** The pressure is increased by adding argon gas.
- **d.** The temperature is decreased.
- **e.** Gaseous sulfur dioxide is removed.

61. In which direction will the position of the equilibrium

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

be shifted for each of the following changes?

- **a.** $H_2(g)$ is added.
- **b.** $I_2(g)$ is removed.
- **c.** $HI(g)$ is removed.
- **d.** Some $Ar(g)$ is added.
- **e.** The volume of the container is doubled.
- **f.** The temperature is decreased (the reaction is exothermic).

62. Hydrogen for use in ammonia production is produced by the reaction

$$CH_4(g) + H_2O(g) \underset{750^\circ\text{C}}{\overset{\text{Ni catalyst}}{\rightleftharpoons}} CO(g) + 3H_2(g)$$

What will happen to a reaction mixture at equilibrium if

a. $H_2O(g)$ is removed?
b. the temperature is increased (the reaction is endothermic)?
c. an inert gas is added?
d. $CO(g)$ is removed?
e. the volume of the container is tripled?

63. Old-fashioned "smelling salts" consist of ammonium carbonate, $(NH_4)_2CO_3$. The reaction for the decomposition of ammonium carbonate

$$(NH_4)_2CO_3(s) \rightleftharpoons 2NH_3(g) + CO_2(g) + H_2O(g)$$

is endothermic. Would the smell of ammonia increase or decrease as the temperature is increased?

64. Ammonia is produced by the Haber process, in which nitrogen and hydrogen are reacted directly using an iron mesh impregnated with oxides as a catalyst. For the reaction

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

equilibrium constants (K_p values) as a function of temperature are

300°C,	4.34×10^{-3}
500°C,	1.45×10^{-5}
600°C,	2.25×10^{-6}

Is the reaction exothermic or endothermic?

Additional Exercises

65. Calculate a value for the equilibrium constant for the reaction

$$O_2(g) + O(g) \rightleftharpoons O_3(g)$$

given

$$NO_2(g) \overset{h\nu}{\rightleftharpoons} NO(g) + O(g) \qquad K = 6.8 \times 10^{-49}$$
$$O_3(g) + NO(g) \rightleftharpoons NO_2(g) + O_2(g) \qquad K = 5.8 \times 10^{-34}$$

Hint: When reactions are added together, the equilibrium expressions are multiplied.

66. At 25°C, $K_p \approx 1 \times 10^{-31}$ for the reaction

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

a. Calculate the concentration of NO, in molecules/cm^3, that can exist in equilibrium in air at 25°C. In air, $P_{N_2} = 0.8$ atm and $P_{O_2} = 0.2$ atm.
b. Typical concentrations of NO in relatively pristine environments range from 10^8 to 10^{10} molecules/cm^3. Why is there a discrepancy between these values and your answer to part a?

67. The gas arsine, AsH_3, decomposes as follows:

$$2AsH_3(g) \rightleftharpoons 2As(s) + 3H_2(g)$$

In an experiment at a certain temperature, pure $AsH_3(g)$ was placed in an empty, rigid, sealed flask at a pressure of 392.0 torr. After 48 hours the pressure in the flask was observed to be constant at 488.0 torr.

a. Calculate the equilibrium pressure of $H_2(g)$.
b. Calculate K_p for this reaction.

68 At a certain temperature, $K = 9.1 \times 10^{-4}$ for the reaction

$$FeSCN^{2+}(aq) \rightleftharpoons Fe^{3+}(aq) + SCN^-(aq)$$

Calculate the concentrations of Fe^{3+}, SCN^-, and $FeSCN^{2+}$ in a solution that is initially 2.0 *M* $FeSCN^{2+}$.

69. For the reaction

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

at 600. K, the equilibrium constant, K_p, is 11.5. Suppose that 2.450 g of PCl_5 is placed in an evacuated 500.-mL bulb, which is then heated to 600. K.

a. What would be the pressure of PCl_5 if it did not dissociate?
b. What is the partial pressure of PCl_5 at equilibrium?
c. What is the total pressure in the bulb at equilibrium?
d. What is the degree of dissociation of PCl_5 at equilibrium?

70. At 25°C, gaseous SO_2Cl_2 decomposes to $SO_2(g)$ and $Cl_2(g)$ to the extent that 12.5% of the original SO_2Cl_2 (by moles) has decomposed to reach equilibrium. The total pressure (at equilibrium) is 0.900 atm. Calculate the value of K_p for this system.

71. For the following reaction at a certain temperature

$$H_2(g) + F_2(g) \rightleftharpoons 2HF(g)$$

it is found that the equilibrium concentrations in a 5.00-L rigid container are $[H_2] = 0.0500$ *M*, $[F_2] = 0.0100$ *M*, and $[HF] = 0.400$ *M*. If 0.200 mol of F_2 is added to this equilibrium mixture, calculate the concentrations of all gases once equilibrium is reestablished.

72. Consider the reaction

$$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons FeSCN^{2+}(aq)$$

How will the equilibrium position shift if

a. water is added, doubling the volume?
b. $AgNO_3(aq)$ is added? (AgSCN is insoluble.)
c. $NaOH(aq)$ is added? [$Fe(OH)_3$ is insoluble.]
d. $Fe(NO_3)_3(aq)$ is added?

73. Chromium(VI) forms two different oxyanions, the orange dichromate ion, $Cr_2O_7^{2-}$, and the yellow chromate ion, CrO_4^{2-}. (See the following photos.) The equilibrium reaction between the two ions is

$$Cr_2O_7^{2-}(aq) + H_2O(l) \rightleftharpoons 2CrO_4^{2-}(aq) + 2H^+(aq)$$

Explain why orange dichromate solutions turn yellow when sodium hydroxide is added.

74. The synthesis of ammonia gas from nitrogen gas and hydrogen gas represents a classic case in which a knowledge of kinetics and equilibrium was used to make a desired chemical reaction economically feasible. Explain how each of the following conditions helps to maximize the yield of ammonia.

a. running the reaction at an elevated temperature
b. removing the ammonia from the reaction mixture as it forms
c. using a catalyst
d. running the reaction at high pressure

75. Suppose $K = 4.5 \times 10^{-3}$ at a certain temperature for the reaction

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

If it is found that the concentration of PCl_5 is twice the concentration of PCl_3, what must be the concentration of Cl_2 under these conditions?

76. For the reaction below, $K_p = 1.16$ at 800.°C.

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

If a 20.0-g sample of $CaCO_3$ is put into a 10.0-L container and heated to 800.°C, what percentage by mass of the $CaCO_3$ will react to reach equilibrium?

77. A 2.4156-g sample of PCl_5 was placed in an empty 2.000-L flask and allowed to decompose to PCl_3 and Cl_2 at 250.0°C:

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

At equilibrium the total pressure inside the flask was observed to be 358.7 torr. Calculate the partial pressure of each gas at equilibrium and the value of K_p at 250.0°C.

78. Consider the decomposition of the compound $C_5H_6O_3$ as follows:

$$C_5H_6O_3(g) \longrightarrow C_2H_6(g) + 3CO(g)$$

When a 5.63-g sample of pure $C_5H_6O_3(g)$ was sealed into an otherwise empty 2.50-L flask and heated to 200.°C, the pressure in the flask gradually rose to 1.63 atm and remained at that value. Calculate K for this reaction.

Challenge Problems

79. At 35°C, $K = 1.6 \times 10^{-5}$ for the reaction

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

If 2.0 mol NO and 1.0 mol Cl_2 are placed into a 1.0-L flask, calculate the equilibrium concentrations of all species.

80. Nitric oxide and bromine at initial partial pressures of 98.4 and 41.3 torr, respectively, were allowed to react at 300. K. At equilibrium the total pressure was 110.5 torr. The reaction is

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

a. Calculate the value of K_p.
b. What would be the partial pressures of all species if NO and Br_2, both at an initial partial pressure of 0.30 atm, were allowed to come to equilibrium at this temperature?

81. At 25°C, $K_p = 5.3 \times 10^5$ for the reaction

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

When a certain partial pressure of $NH_3(g)$ is put into an otherwise empty rigid vessel at 25°C, equilibrium is reached when 50.0% of the original ammonia has decomposed. What was the original partial pressure of ammonia before any decomposition occurred?

82. Consider the reaction

$$P_4(g) \longrightarrow 2P_2(g)$$

where $K_p = 1.00 \times 10^{-1}$ at 1325 K. In an experiment where $P_4(g)$ is placed into a container at 1325 K, the equilibrium mixture of $P_4(g)$ and $P_2(g)$ has a total pressure of 1.00 atm. Calculate the equilibrium pressures of $P_4(g)$ and $P_2(g)$. Calculate the fraction (by moles) of $P_4(g)$ that has dissociated to reach equilibrium.

83. The partial pressures of an equilibrium mixture of $N_2O_4(g)$ and $NO_2(g)$ are $P_{N_2O_4} = 0.34$ atm and $P_{NO_2} = 1.20$ atm at a certain temperature. The volume of the container is doubled. Find the partial pressures of the two gases when a new equilibrium is established.

84. At 125°C, $K_p = 0.25$ for the reaction

$$2NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + CO_2(g) + H_2O(g)$$

A 1.00-L flask containing 10.0 g $NaHCO_3$ is evacuated and heated to 125°C.

a. Calculate the partial pressures of CO_2 and H_2O after equilibrium is established.
b. Calculate the masses of $NaHCO_3$ and Na_2CO_3 present at equilibrium.
c. Calculate the minimum container volume necessary for all of the $NaHCO_3$ to decompose.

85. An 8.00-g sample of SO_3 was placed in an evacuated container, where it decomposed at 600°C according to the following reaction:

$$SO_3(g) \rightleftharpoons SO_2(g) + \tfrac{1}{2}O_2(g)$$

At equilibrium the total pressure and the density of the gaseous mixture were 1.80 atm and 1.60 g/L, respectively. Calculate K_p for this reaction.

86. A sample of iron(II) sulfate was heated in an evacuated container to 920 K, where the following reactions occurred:

$$2FeSO_4(s) \rightleftharpoons Fe_2O_3(s) + SO_3(g) + SO_2(g)$$
$$SO_3(g) \rightleftharpoons SO_2(g) + \tfrac{1}{2}O_2(g)$$

After equilibrium was reached, the total pressure was 0.836 atm and the partial pressure of oxygen was 0.0275 atm. Calculate K_p for each of these reactions.

87. At 5000 K and 1.000 atm, 83.00% of the oxygen molecules in a sample have dissociated to atomic oxygen. At what pressure will 95.0% of the molecules dissociate at this temperature?

88. A sample of $N_2O_4(g)$ is placed in an empty cylinder at 25°C. After equilibrium is reached the total pressure is 1.5 atm and 16% (by moles) of the original $N_2O_4(g)$ has dissociated to $NO_2(g)$.

a. Calculate the value of K_p for this dissociation reaction at 25°C.
b. If the volume of the cylinder is increased until the total pressure is 1.0 atm (the temperature of the system remains constant), calculate the equilibrium pressure of $N_2O_4(g)$ and $NO_2(g)$.
c. What percentage (by moles) of the original $N_2O_4(g)$ is dissociated at the new equilibrium position (total pressure = 1.00 atm)?

89. A sample of gaseous nitrosyl bromide, NOBr, was placed in a rigid flask, where it decomposed at 25°C according to the following reaction:

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

At equilibrium the total pressure and the density of the gaseous mixture were found to be 0.0515 atm and 0.1861 g/L, respectively. Calculate the value of K_p for this reaction.

90. The equilibrium constant K_p for the reaction

$$CCl_4(g) \rightleftharpoons C(s) + 2Cl_2(g)$$

at 700°C is 0.76 atm. Determine the initial pressure of carbon tetrachloride that will produce a total equilibrium pressure of 1.20 atm at 700°C.

Integrative Problems

These problems require the integration of multiple concepts to find the solutions.

91. For the reaction

$$NH_3(g) + H_2S(g) \rightleftharpoons NH_4HS(s)$$

$K = 400.$ at 35.0°C. If 2.00 mol each of NH_3, H_2S, and NH_4HS are placed in a 5.00-L vessel, what mass of NH_4HS will be present at equilibrium? What is the pressure of H_2S at equilibrium?

92. Given $K = 3.50$ at 45°C for the reaction

$$A(g) + B(g) \rightleftharpoons C(g)$$

and $K = 7.10$ at 45°C for the reaction

$$2A(g) + D(g) \rightleftharpoons C(g)$$

what is the value of K at the same temperature for the reaction

$$C(g) + D(g) \rightleftharpoons 2B(g)$$

What is the value of K_p at 45°C for the reaction? Starting with 1.50 atm partial pressures of both C and D, what is the mole fraction of B once equilibrium is reached?

93. The hydrocarbon naphthalene was frequently used in mothballs until recently, when it was discovered that human inhalation of naphthalene vapors can lead to hemolytic anemia. Naphthalene is 93.71% carbon by mass and a 0.256-mol sample of naphthalene has a mass of 32.8 g. What is the molecular formula of naphthalene? This compound works as a pesticide in mothballs by sublimation of the solid so that it fumigates enclosed spaces with its vapors according to the equation

$$\text{naphthalene}(s) \rightleftharpoons \text{naphthalene}(g) \quad K = 4.29 \times 10^{-6} \text{ (at 298 K)}$$

If 3.00 g of solid naphthalene is placed into an enclosed space with a volume of 5.00 L at 25°C, what percentage of the naphthalene will have sublimed once equilibrium has been established?

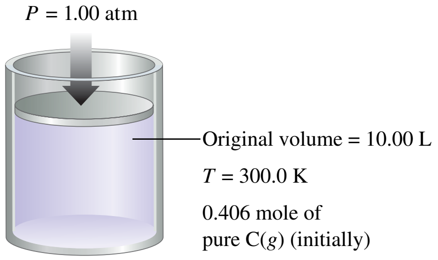
Marathon Problem*

This problem is designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

94. Consider the reaction

$$A(g) + B(g) \rightleftharpoons C(g)$$

for which $K = 1.30 \times 10^2$. Assume that 0.406 mol C(g) is placed in the cylinder represented below. The temperature is 300.0 K, and the barometric pressure on the piston (which is assumed to be massless and frictionless) is constant at 1.00 atm. The original volume (before the 0.406 mol C(g) begins to decompose) is 10.00 L. What is the volume in the cylinder at equilibrium?



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