12 Gaseous Chemical Equilibrium

The painting shows children on a seesaw in a state of dynamic equilibrium. The boy at the center can change the position of equilibrium by moving either to the left or to the right of the seesaw.

Arkell Museum at Canajoharie, Gift of Bartlett Arkell, 1932

Order is not pressure which is imposed on society from without, but an equilibrium which is set up from within.

—JOSÉ ORTEGA Y GASSET

Chapter Outline

Among the topics covered in Chapter 9 was the equilibrium between liquid and gaseous water:

$$H_2O(l) \rightleftharpoons H_2O(g)$$

The state of this equilibrium system at a given temperature can be described in a simple way by citing the equilibrium pressure of water vapor: 0.034 atm at 25°C, 1.00 atm at 100°C, and so on.

Chemical reactions involving gases carried out in closed containers resemble in many ways the $H_2O(l)$–$H_2O(g)$ system. The reactions are reversible; reactants are not completely consumed. Instead, an equilibrium mixture containing both products and reactants is obtained. At equilibrium, forward and reverse reactions take place at the same rate. As a result, the amounts of all species at equilibrium remain constant with time.

Ordinarily, where gaseous chemical equilibria are involved, more than one gaseous substance is present. We might, for example, have a system,

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$

in which the equilibrium mixture contains two gaseous products (C and D) and two gaseous reactants (A and B). To describe the position of this equilibrium, we must cite the partial pressure of each species, that is, P_C, P_D, P_A, and P_B.

Recall from Chapter 5 that the partial pressure of a gas, *i*, in a mixture is given by the expression

$$P_i = n_i RT/V$$

Reactions can often be reversed by changing the temperature or pressure.

It follows that, for an equilibrium mixture confined in a closed container of volume *V* at temperature *T*, *the partial pressure* (P_i) *of each species is directly proportional to the number of moles* (n_i) *of that species*.

It turns out that there is a relatively simple relationship between the partial pressures of different gases present at equilibrium in a reaction system. This relationship is

expressed in terms of a quantity called the *equilibrium constant*, symbol *K*.* In this chapter, you will learn how to

- write the expression for *K* corresponding to any chemical equilibrium (Section 12-2).
- calculate the value for *K* from experimental data for the equilibrium system (Section 12-3).
- use the value of *K* to predict the extent to which a reaction will take place (Section 12-4).
- use *K*, along with Le Châtelier's principle, to predict the result of disturbing an equilibrium system (Section 12-5).

Don't confuse the *equilibrium* constant *K* with the *rate* constant *k*.

12-1 The N_2O_4–NO_2 Equilibrium System

Consider what happens when a sample of N_2O_4, a colorless gas, is placed in a closed, evacuated container at 100°C. Instantly, a reddish-brown color develops. This color is due to nitrogen dioxide, NO_2, formed by decomposition of part of the N_2O_4 (Figure 12.1):

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

At first, this is the only reaction taking place. As soon as some NO_2 is formed, however, the reverse reaction can occur:

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

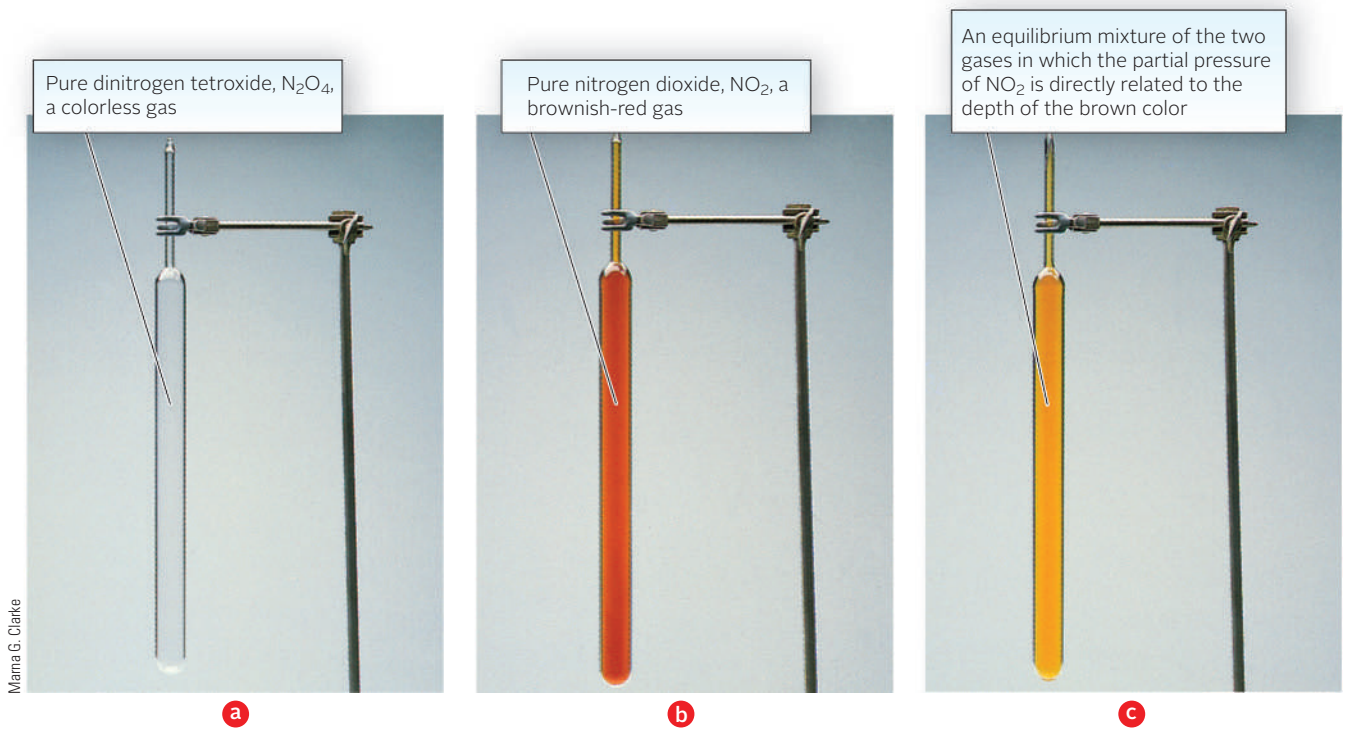

Figure 12.1 The N_2O_4–NO_2 system.

*Thermodynamically, the quantity that should appear for each species in the expression for *K* is the *activity* rather than the partial pressure. Activity is defined as the ratio of the equilibrium partial pressure to the standard pressure, 1 atm. This means that the activity and hence the equilibrium constant *K* are dimensionless, that is, pure numbers without units.

Table 12.1 Establishment of Equilibrium in the System $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ (at 100°C)

Time	0	20	40	60	80	100
$P_{N_2O_4}$ (atm)	1.00	0.60	0.35	**0.22***	**0.22**	**0.22**
P_{NO_2} (atm)	0.00	0.80	1.30	**1.56**	**1.56**	**1.56**

*Boldface numbers are equilibrium pressures.

Overall, the partial pressure of N_2O_4 drops, and the forward reaction slows down. Conversely, the partial pressure of NO_2 increases, so the rate of the reverse reaction increases. Soon these rates become equal. A dynamic equilibrium has been established.

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

At equilibrium, appreciable amounts of both gases are present. From that point on, the amounts of both NO_2 and N_2O_4 and their partial pressures remain constant, so long as the volume of the container and the temperature remain unchanged.

The characteristics just described are typical of all systems at equilibrium. First, *the forward and reverse reactions are taking place at the same rate*. This explains why *the concentrations of species present remain constant with time*. Moreover, these concentrations are independent of the direction from which equilibrium is approached.

The approach to equilibrium in the N_2O_4–NO_2 system is illustrated by the data in Table 12.1 and by Figure 12.2 (time is in arbitrary units). Originally, only N_2O_4 is present; its pressure is 1.00 atm. Because no NO_2 is around, its original pressure is zero. As equilibrium is approached, the overall reaction is

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

The amount and hence the partial pressure of N_2O_4 drop, rapidly at first, then more slowly. The partial pressure of NO_2 increases. Finally, both partial pressures level off and become constant.ⓘ At equilibrium, at 100°C,

$$P_{N_2O_4} = 0.22 \text{ atm} \qquad P_{NO_2} = 1.56 \text{ atm}$$

ⓘ These pressures don't change because forward and reverse reactions occur at the same rate.

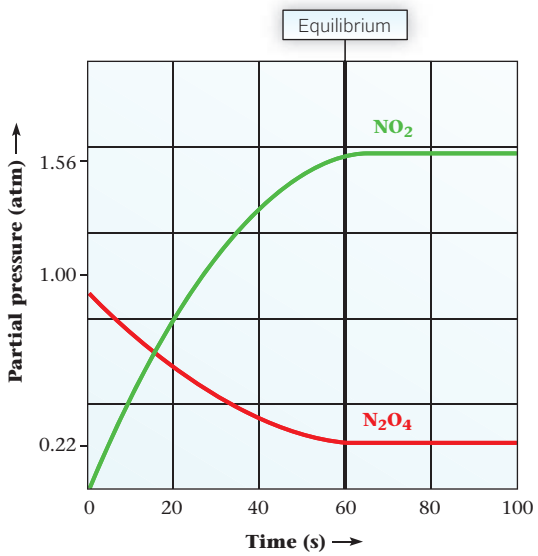

Figure 12.2 Approach to equilibrium in the N_2O_4–NO_2 system. The partial pressure of N_2O_4 starts off at 1.00 atm, drops sharply at first, and finally levels off at the equilibrium value of 0.22 atm. Meanwhile, the partial pressure of NO_2 rises from zero to its equilibrium value, 1.56 atm.

Table 12.2 Pressure Measurements at Equilibrium in the N_2O_4–NO_2 System at 100°C

		Original Pressure (atm)	Equilibrium Pressure (atm)
Expt. 1	N_2O_4	1.00	0.22
	NO_2	0.00	1.56
Expt. 2	N_2O_4	0.00	0.07
	NO_2	1.00	0.86
Expt. 3	N_2O_4	1.00	0.42
	NO_2	1.00	2.16

There are many ways to approach equilibrium in the N_2O_4–NO_2 system. Table 12.2 gives data for three experiments in which the original conditions are quite different. Experiment 1 is that just described, starting with pure N_2O_4. Experiment 2 starts with pure NO_2 at a partial pressure of 1.00 atm. As equilibrium is approached, some of the NO_2 reacts to form N_2O_4:

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

Finally, in Experiment 3, both N_2O_4 and NO_2 are present originally, each at a partial pressure of 1.00 atm.

Looking at the data in Table 12.2, you might wonder whether these three experiments have anything in common. Specifically, is there any relationship between the equilibrium partial pressures of NO_2 and N_2O_4 that is valid for all the experiments? It turns out that there is, although it is not an obvious one. The value of the quotient $(P_{NO_2})^2/P_{N_2O_4}$ is the same, about 11, in each case:

Note that this relationship holds only at equilibrium; initial pressures can have any value.

$$\text{Expt. 1} \qquad \frac{(P_{NO_2})^2}{P_{N_2O_4}} = \frac{(1.56)^2}{0.22} = 11$$

$$\text{Expt. 2} \qquad \frac{(P_{NO_2})^2}{P_{N_2O_4}} = \frac{(0.86)^2}{0.07} = 11$$

$$\text{Expt. 3} \qquad \frac{(P_{NO_2})^2}{P_{N_2O_4}} = \frac{(2.16)^2}{0.42} = 11$$

You may wonder why the equilibrium constant, 11, has no units. The reason is that each term in the reaction quotient represents the ratio of the measured pressure of the gas to the thermodynamic standard state of one atmosphere. Thus the quotient $(P_{NO_2})^2/P_{N_2O_4}$ in Experiment 1 becomes

$$K = \frac{\left(\dfrac{1.56 \text{ atm}}{1 \text{ atm}}\right)^2}{\left(\dfrac{0.22 \text{ atm}}{1 \text{ atm}}\right)} = 11$$

This relationship holds for any equilibrium mixture containing N_2O_4 and NO_2 at 100°C. More generally, it is found that, at any temperature, the quantity

$$\frac{(P_{NO_2})^2}{P_{N_2O_4}}$$

where P_{NO_2} and $P_{N_2O_4}$ are equilibrium partial pressures in atmospheres, is a constant, independent of the original composition, the volume of the container, or the

total pressure. This constant is referred to as the **equilibrium constant** (K) for the system

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

The equilibrium constant for this system, like all equilibrium constants, changes with temperature. At 100°C, K for the N_2O_4–NO_2 system is 11; at 150°C, it has a different value, about 110. Any mixture of NO_2 and N_2O_4 at 100°C will react in such a way that the ratio $(P_{NO_2})^2/P_{N_2O_4}$ becomes equal to 11. At 150°C, reaction occurs until this ratio becomes 110.

12-2 The Equilibrium Constant Expression

For every gaseous chemical system, an *equilibrium constant expression* can be written stating the condition that must be attained at equilibrium. For the general system involving only gases,

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$

where A, B, C, and D represent different substances and a, b, c, and d are their coefficients in the balanced equation,

$$K = \frac{(P_C)^c \times (P_D)^d}{(P_A)^a \times (P_B)^b} \qquad (12.1)$$

where P_C, P_D, P_A, and P_B are the partial pressures of the four gases at equilibrium. ***These partial pressures must be expressed in atmospheres.*** Notice that in the expression for K

- the equilibrium partial pressures of *products* (right side of equation) appear in the *numerator.*
- the equilibrium partial pressures of *reactants* (left side of equation) appear in the *denominator.*
- each partial pressure is raised to a *power* equal to its *coefficient* in the balanced equation.

This equilibrium constant is often given the symbol K_p to emphasize that it involves partial pressures. Other equilibrium expressions for gases are sometimes used, including K_c:

$$K_c = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b}$$

where the brackets represent equilibrium concentrations in moles per liter. The two constants, K_c and K_p, are simply related (see Problem 78):

$$K_p = K_c(RT)^{\Delta n_g}$$

where Δn_g is the change in the number of moles of gas in the equation, R is the gas law constant, 0.0821 L · atm/mol · K, and T is the Kelvin temperature. Throughout this chapter, we deal only with K_p, referring to it simply as K.

Changing the Chemical Equation

It is important to realize that ***the expression for K depends on the form of the chemical equation written to describe the equilibrium system.*** To illustrate what this statement means, consider the N_2O_4–NO_2 system:

K is meaningless unless accompanied by a chemical equation.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad K = \frac{(P_{NO_2})^2}{P_{N_2O_4}}$$

Many other equations could be written for this system, for example,

$$\tfrac{1}{2}N_2O_4(g) \rightleftharpoons NO_2(g)$$

In this case, the expression for the equilibrium constant would be

$$K' = \frac{P_{NO_2}}{(P_{N_2O_4})^{1/2}}$$

Comparing the expressions for K and K', it is clear that K' is the square root of K. This illustrates a general rule, sometimes referred to as the **coefficient rule**, which states,

> ***If the coefficients in a balanced equation are multiplied by a factor n, the equilibrium constant is raised to the nth power:***
>
> $$\boldsymbol{K' = K^n} \qquad \textbf{(12.2)}$$

In this particular case, $n = \frac{1}{2}$ because the coefficients were divided by 2. Hence K' is the square root of K. If $K = 11$, then $K' = (11)^{1/2} = 3.3$.

Another equation that might be written to describe the N_2O_4–NO_2 system is

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

for which the equilibrium constant expression is

$$K'' = \frac{P_{N_2O_4}}{(P_{NO_2})^2}$$

This chemical equation is simply the reverse of that written originally; N_2O_4 and NO_2 switch sides of the equation. Notice that K'' is the reciprocal of K; the numerator and denominator have been inverted. This illustrates the **reciprocal rule**:

> ***The equilibrium constants for forward and reverse reactions are the reciprocals of each other,***
>
> $$\boldsymbol{K'' = 1/K} \qquad \textbf{(12.3)}$$

If, for example, $K = 11$, then $K'' = 1/11 = 0.091$.

Adding Chemical Equations

A property of K that you will find very useful in this and succeeding chapters is expressed by the **rule of multiple equilibria,** which states

> ***If a reaction can be expressed as the sum of two or more reactions, K for the overall reaction is the product of the equilibrium constants of the individual reactions.***

We will use this relationship frequently in later chapters.

That is, if

$$\text{reaction 3} = \text{reaction 1} + \text{reaction 2}$$

then

$$K\ (\text{reaction 3}) = K\ (\text{reaction 1}) \times K\ (\text{reaction 2}) \qquad \textbf{(12.4)}$$

To illustrate the application of this rule, consider the following reactions at 700°C:

$$SO_2(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons SO_3(g) \qquad K = 2.2$$
$$NO_2(g) \rightleftharpoons NO(g) + \tfrac{1}{2}O_2(g) \qquad K = 4.0$$

Adding these equations eliminates $\frac{1}{2}O_2$; the result is

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

For this overall reaction, $K = 2.2 \times 4.0 = 8.8$.

Table 12.3 Dependence of K on the Form of the Chemical Reaction

$$R(g) \rightleftharpoons Y(g) \qquad K = \frac{P_Y}{P_R}$$

Form of Equation	K Expression	Relation to K	Rule
$Y(g) \rightleftharpoons R(g)$	$K' = \frac{P_R}{P_Y}$	$K' = \frac{1}{K}$	Reciprocal Rule
$nR(g) \rightleftharpoons nY(g)$	$K'' = \frac{(P_Y)^n}{(P_R)^n}$	$K'' = K^n$	Coefficient Rule
$R(g) \rightleftharpoons A(g)$	$K_1 = \frac{P_A}{P_R}$		
$A(g) \rightleftharpoons Y(g)$	$K_2 = \frac{P_Y}{P_A}$		
$R(g) \rightleftharpoons Y(g)$		$K = K_1 \times K_2$	Rule of Multiple Equilibria

The validity of this rule can be demonstrated by writing the expression for K for the individual reactions and multiplying:

$$\frac{P_{SO_3}}{(P_{SO_2})(P_{O_2})^{1/2}} \times \frac{(P_{NO})(P_{O_2})^{1/2}}{P_{NO_2}} = \frac{(P_{SO_3})(P_{NO})}{(P_{SO_2})(P_{NO_2})}$$

The product expression, at the right, is clearly the equilibrium constant for the overall reaction, as it should be according to the rule of multiple equilibria.

Table 12.3 summarizes the rules for writing the expression for the equilibrium constant.

EXAMPLE 12.1

Consider the air pollutants NO and NO_2, contributors to photochemical smog. Both can be formed by the reaction between atmospheric nitrogen and oxygen. At 25°C,

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \qquad K_1 = 4.2 \times 10^{-31} \qquad (1)$$
$$N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g) \qquad K_2 = 1.0 \times 10^{-18} \qquad (2)$$

a Write the equilibrium constant expression for the formation of two moles of NO at 25°C.

SOLUTION

K expression: $K_1 = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})}$

b Calculate K for the formation of one mole of NO at 25°C.

STRATEGY

1. Write the reaction for the formation of one mole of NO. Note that all the coefficients of the original equation are divided by two.
2. Find K. Apply the coefficient rule.

SOLUTION

1. Equation for the reaction: $\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO(g)$
2. K: $K = (K_1)^{1/2} = (4.2 \times 10^{-31})^{1/2} = 6.5 \times 10^{-16}$

continued

c Calculate K for the decomposition of one mole of NO_2 at 25°C.

STRATEGY

1. Write the reaction for the decomposition of NO_2 and note that you are asked for the decomposition of *one* mole.
2. To arrive at the equation for the decomposition of one mole of NO_2, you switch sides (reciprocal rule).
3. To arrive at the equation for the decomposition of *one* mole of NO_2, multiply the coefficients by 1/2 (coefficient rule).
4. Apply both rules.

SOLUTION

1. Equation for the reaction: $N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g) \longrightarrow 2NO_2(g) \rightleftharpoons N_2(g) + 2O_2(g) \longrightarrow NO_2(g) \rightleftharpoons \frac{1}{2}N_2(g) + O_2(g)$
2. Reciprocal rule: $K' = 1/K_2$
3. Coefficient rule: $K = (K')^{1/2} = (1/K_2)^{1/2}$
4. K: $\left(\frac{1}{1.0 \times 10^{-18}}\right)^{1/2} = 1.0 \times 10^{9}$

d Calculate K for the following reaction at 25°C:

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

STRATEGY

1. Start with two moles of NO, which is a product in Equation (1) but a reactant in the desired equation. Reverse Equation (1) and apply the reciprocal rule.
2. Focus on two moles of NO_2, which is the product in Equation (2) and in the desired equation. Change is unnecessary.
3. Add the two equations to get the overall equation.
4. Apply the rule of multiple equilibria.

SOLUTION

1. Reverse Equation (1): $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$ $\quad K'$
   Apply reciprocal rule: $K' = \frac{1}{K_1} = \frac{1}{4.2 \times 10^{-31}}$
2. Keep Equation (2): $N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)$ $\quad K_2 = 1.0 \times 10^{-18}$
3. Overall equation: $2NO(g) \rightleftharpoons \cancel{N_2(g)} + O_2(g)$ $\quad K' = \frac{1}{4.2 \times 10^{-31}}$

   $\cancel{N_2(g)} + 2O_2(g) \rightleftharpoons 2NO_2(g)$ $\quad K_2 = 1.0 \times 10^{-18}$

   $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$ $\quad K = (K')(K_2)$
4. K: $K = \left(\frac{1}{4.2 \times 10^{-31}}\right)(1.0 \times 10^{-18}) = 2.4 \times 10^{12}$

Heterogeneous Equilibria

In the reactions described so far, all the reactants and products have been gaseous; the equilibrium systems are *homogeneous*. In certain reactions, at least one of the substances involved is a pure liquid or solid; the others are gases (Figure 12.3). Such a system is *heterogeneous*, because more than one phase is present. Examples include

$$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(l)$$
$$I_2(s) \rightleftharpoons I_2(g)$$

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Figure 12.3 A heterogeneous equilibrium system: solid I_2–gaseous I_2.

Table 12.4 Equilibrium Constant Expressions for the Reaction $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(l)$

	Expt. 1	Expt. 2	Expt. 3	Expt. 4
Mass $H_2O(l)$	8 g	6 g	4 g	2 g
P_{H_2O} (atm)	3×10^{-2}	3×10^{-2}	3×10^{-2}	3×10^{-2}
K_I	9×10^{-6}	9×10^{-6}	9×10^{-6}	9×10^{-6}
K_{II}	3×10^{-4}	3×10^{-4}	3×10^{-4}	3×10^{-4}

$$K_I = \frac{P_{CO} \times P_{H_2O}}{P_{CO_2} \times P_{H_2}} \qquad K_{II} = \frac{P_{CO}}{P_{CO_2} \times P_{H_2}}$$

Experimentally, it is found that for such systems

- ***the position of the equilibrium is independent of the amount of solid or liquid, as long as some is present.***
- ***terms for pure liquids or solids need not appear in the expression for K.***

To see why this is the case, consider the data in Table 12.4 for the system

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

at 25°C. In Experiments 1 through 4, liquid water is present, so the partial pressure of water in the gas phase, P_{H_2O}, is constant at 0.03 atm, the equilibrium vapor pressure of water at 25°C.

Notice that

1. In all cases, the quantity

$$K_I = \frac{P_{CO} \times P_{H_2O}}{P_{CO_2} \times P_{H_2}}$$

is constant at 9×10^{-6}.

2. In all cases (Experiments 1 through 4), the quantity

$$K_{II} = \frac{P_{CO}}{P_{CO_2} \times P_{H_2}}$$

is constant at 3×10^{-4}. This must be true because

$$K_{II} = K_I / P_{H_2O}$$

and P_{H_2O} is constant at 3×10^{-2} atm. It follows that K_{II} is a valid equilibrium constant for the system

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

Because the expression for K_{II} is simpler than that for K_I, it is the equilibrium constant of choice for the heterogeneous system.

A similar argument can be applied to the equilibrium involved in the sublimation of iodine:

$$I_2(s) \rightleftharpoons I_2(g)$$

At a given temperature, the pressure of iodine vapor is constant, independent of the amount of solid iodine or any other factor. The equilibrium constant expression is

$$K = P_{I_2}$$

Applying the reciprocal rule, we can deduce the equilibrium constant expression for the reverse reaction

$$I_2(g) \rightleftharpoons I_2(s) \qquad K = 1/P_{I_2}$$

EXAMPLE 12.2

Write the expression for K for

(a) the reduction of black solid copper(II) oxide (1 mol) with hydrogen to form copper metal and steam.

(b) the reaction of one mole of steam with red-hot coke (carbon) to form a mixture of hydrogen and carbon monoxide, called water gas.

STRATEGY

1. Write a balanced chemical equation for the equilibrium system. Do not forget to include physical states.
2. Write the expression for K, leaving out pure solids and liquids.
3. Recall that gases are represented by their partial pressures.

SOLUTION

(a) Reaction: $CuO(s) + H_2(g) \rightleftharpoons Cu(s) + H_2O(g)$

K expression: $K = \dfrac{P_{H_2O}}{P_{H_2}}$

(b) Reaction: $H_2O(g) + C(s) \rightleftharpoons CO(g) + H_2(g)$

K expression: $K = \dfrac{(P_{H_2})(P_{CO})}{P_{H_2O}}$

In part (a) of Example 12.2, if the product were $H_2O(l)$, K would equal $1/P_{H_2}$.

In this and succeeding chapters, a wide variety of different types of equilibria will be covered. They may involve gases, pure liquids or solids, and species in aqueous solution. It will always be true that in the expression for the equilibrium constant

- ***gases enter as their partial pressures in atmospheres.***
- ***pure liquids or solids do not appear; neither does the solvent for a reaction in dilute solution.***
- ***species (ions or molecules) in water solution enter as their molar concentrations.***

Thus for the equilibrium attained when zinc metal reacts with acid,

$$Zn(s) + 2H^+(aq) \rightleftharpoons Zn^{2+}(aq) + H_2(g)$$

$$K = \frac{P_{H_2} \times [Zn^{2+}]}{[H^+]^2}$$

We will have more to say in later chapters about equilibria involving species in aqueous solution.

12-3 Determination of *K*

Numerical values of equilibrium constants can be calculated if the partial pressures of products and reactants at equilibrium are known. Sometimes you will be given equilibrium partial pressures directly (Example 12.3). At other times you will be given the original partial pressures and the equilibrium partial pressure of one species (Example 12.4). In that case, the calculation of K is a bit more difficult, because you have to calculate the equilibrium partial pressures of all the species.

EXAMPLE 12.3

Ammonium chloride is sometimes used as a flux in soldering because it decomposes on heating:

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

The HCl formed removes oxide films from metals to be soldered. In a certain equilibrium system at 400°C, 22.6 g of NH_4Cl is present; the partial pressures of NH_3 and HCl are 2.5 atm and 4.8 atm, respectively. Calculate K at 400°C.

ANALYSIS

Information given:	equation for the reaction at T = 400°C mass of NH_4Cl (22.6 g) partial pressures of NH_3 (2.5 atm) and HCl (4.8 atm)
Asked for:	K at 400°C

STRATEGY

1. Write the expression for K. Recall that pure liquids and solids are not included in the expression.
2. Substitute the partial pressures of the gases into the expression for K.

SOLUTION

1. K expression	$K = (P_{NH_3})(P_{HCl})$
2. K	K = (2.5 atm)(4.8 atm) = 12

END POINT

Note that the mass of NH_4Cl is not relevant to the calculation because NH_4Cl is a solid and hence is not included in the expression for K.

EXAMPLE 12.4

Consider the equilibrium system

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

Originally, an evacuated flask contains only HI at a pressure of 1.00 atm at 520°C. At equilibrium the partial pressure of H_2 is found to be 0.10 atm.

a What are P_{I_2} and P_{HI} at equilibrium?

ANALYSIS

Information given:	initial pressure (P_o) for HI (1.00 atm) equilibrium pressure (P_{eq}) for H_2 (0.10 atm)
Information implied:	initial pressures (P_o) for H_2 and I_2
Asked for:	equilibrium partial pressures (P_{eq}) for I_2 and HI

STRATEGY AND SOLUTION

1. Create a table (shown below) and enter the pertinent information (both explicit and implied) from the statement of the problem. Note that the problem states that *only* HI is initially present. Your table looks like this:

	$2HI(g)$	$\rightleftharpoons$	$H_2(g)$	+	$I_2(g)$
P_o (atm)	1.00		0		0
ΔP (atm)					
P_{eq} (atm)			0.10		

continued

2. Find a column where only one entry is missing. In this case it is the $H_2(g)$ column. The missing entry can be determined algebraically. By noting that initially the pressure is 0 atm and at equilibrium, the pressure is 0.10 atm. The change, ΔP, must be +0.10 atm. All changes will be shaded in green.

	$2HI(g)$	$\rightleftharpoons$	$H_2(g)$	+	$I_2(g)$
P_o (atm)	1.00		0		0
ΔP (atm)			+0.10		
P_{eq} (atm)			0.10		

3. Since the system is at constant volume and temperature, the number of moles must be directly proportional to the pressure. Use the coefficients of the reaction to determine stoichiometric ratios. (Recall Chapter 3.) Fill in the rest of the row labeled ΔP with 0.10 atm multiplied by the stoichiometric ratios:

$$1 \text{ mol } I_2/1 \text{ mol } H_2 \qquad 2 \text{ mol HI}/1 \text{ mol } H_2$$

Use + signs for species produced and − signs for species used up.

	$2HI(g)$	$\rightleftharpoons$	$H_2(g)$	+	$I_2(g)$
P_o (atm)	1.00		0		0
ΔP (atm)	$-(\frac{2}{1})(0.10)$		+0.10		$+(\frac{1}{1})(0.10)$
P_{eq} (atm)			0.10		

4. Fill in the row P_{eq} by performing the indicated calculation for each column.

	$2HI(g)$	$\rightleftharpoons$	$H_2(g)$	+	$I_2(g)$
P_o (atm)	1.00		0		0
ΔP (atm)	$-(\frac{2}{1})(0.10)$		+0.10		$+(\frac{1}{1})(0.10)$
P_{eq} (atm)	0.80		0.10		0.10

5. Thus from the row P_{eq}, the equilibrium partial pressure for HI is 0.80 atm, and that for I_2 is 0.10 atm.

b What is K for the system?

ANALYSIS

Information given:	from part (a): equilibrium pressures for HI (0.80 atm) and for I_2 (0.10 atm); equilibrium pressure (P_{eq}) for H_2 (0.10 atm)
Information implied:	K expression
Asked for:	equilibrium constant K at 520°C

STRATEGY

1. Write the equilibrium expression.
2. Substitute into the expression for K.

SOLUTION

1. equilibrium expression

$$K = \frac{(P_{H_2})(P_{I_2})}{(P_{HI})^2}$$

2. K

$$K = \frac{(0.10)(0.10)}{(0.80)^2} = 0.016$$

END POINT

You should expect K to be rather small (0.016). Recall that at equilibrium, P_{H_2} is 0.10 atm, only one tenth of the original pressure of HI (1.00 atm).

Example 12.4 illustrates a principle that you will find very useful in solving equilibrium problems throughout this (and later) chapters. ***As a system approaches equilibrium, changes in partial pressures of reactants and products—like changes in molar amounts—are related to one another through the coefficients of the balanced equation.***

12-4 Applications of the Equilibrium Constant

Sometimes, knowing only the magnitude of the equilibrium constant, it is possible to decide on the feasibility of a reaction. Consider, for example, a possible method for "fixing" atmospheric nitrogen—converting it to a compound—by reaction with oxygen:

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

$$K = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})} = 1 \times 10^{-30} \text{ at } 25°C$$

Because K is so small, the partial pressure of NO in equilibrium with N_2 and O_2, and hence the amount of NO, must be extremely small, approaching zero. Clearly, this would not be a suitable way to fix nitrogen, at least at 25°C.

An alternative approach to nitrogen fixation involves reacting it with hydrogen:

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

$$K = \frac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3} = 6 \times 10^5 \text{ at } 25°C$$

In this case, the equilibrium system must contain mostly ammonia. A mixture of N_2 and H_2 should be almost completely converted to NH_3 at equilibrium.

In general, if K is a very small number, the equilibrium mixture will contain mostly unreacted starting materials; for all practical purposes, the forward reaction does not go. Conversely, a large K implies a reaction that, at least in principle, is feasible; products should be formed in high yield.◂ Frequently, K has an intermediate value, in which case you must make quantitative calculations concerning the *direction* or *extent* of reaction.

The concept of equilibrium is most useful when K is neither very large nor very small.

Direction of Reaction; the Reaction Quotient (Q)

Consider the general gas-phase reaction

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$

for which

$$K = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$$

As we have seen, for a given system at a particular temperature, the value of K is fixed.

In contrast, the actual pressure ratio, Q,

$$Q = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$$

can have any value at all.◂ If you start with pure reactants (A and B), P_C and P_D are zero, and the value of Q is zero:

Q can have any value; K is fixed.

$$Q = \frac{(0)(0)}{(P_A)^a(P_B)^b} = 0$$

Conversely, starting with only C and D, the value of Q becomes infinite as the values of P_A and P_B approach zero:

$$Q = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b \to 0} \longrightarrow \infty$$

If all four substances are present, Q can have any value between zero and infinity.

The form of the expression for Q, known as the **reaction quotient,** is the same as that for the equilibrium constant, K. The difference is that the partial pressures that appear in Q are those that apply at a particular moment, not necessarily when the system is at equilibrium. By comparing the numerical value of Q with that of K, it is possible to decide in which direction the system will move to achieve equilibrium.

1. If $Q < K$ the reaction proceeds from left to right:

$$aA(g) + bB(g) \longrightarrow cC(g) + dD(g)$$

$Q < K; \longrightarrow$

In this way, the partial pressures of products increase, while those of reactants decrease. As this happens, the reaction quotient Q increases and eventually at equilibrium becomes equal to K.

2. If $Q > K$ the partial pressures of products are "too high" and those of the reactants "too low" to meet the equilibrium condition. Reaction proceeds in the reverse direction:

$Q > K; \longleftarrow$

$$aA(g) + bB(g) \longleftarrow cC(g) + dD(g)$$

increasing the partial pressures of A and B while reducing those of C and D. This lowers Q to its equilibrium value, K.

3. If perchance $Q = K$, the system is already at equilibrium, so the amounts of products and reactants remain unchanged.

As equilibrium is approached, Q approaches K.

To illustrate these statements, consider the simple system shown in Table 12.5.

Table 12.5 Approach to Equilibrium in the System A $\rightleftharpoons$ B for which $K = 1.00$

The direction of the reaction may change, but the expression for the equilibrium constant does not.

	Experiment 1*				Experiment 2*			
t	0	20	40	60	0	20	40	60
[B]	1.00	1.35	1.50	1.50	2.00	1.65	1.50	1.50
[A]	2.00	1.65	1.50	1.50	1.00	1.35	1.50	1.50
Q = [B]/[A]	0.500	0.818	1.00	1.00	2.00	1.22	1.00	1.00
	$Q < K$		$Q = K$		$Q > K$		$Q = K$	

*In both experiments, systems to the right of the broken line have reached equilibrium.

EXAMPLE 12.5

Consider the following system at 100°C:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad K = 11$$

Predict the direction in which reaction will occur to reach equilibrium, starting with 0.10 mol of N_2O_4 and 0.20 mol of NO_2 in a 2.0-L container.

ANALYSIS

Information given:	reaction and K at 100°C (11) initial amounts of N_2O_4 (0.10 mol) and NO_2 (0.20 mol) volume of the container (2.0 L)
Information implied:	R value
Asked for:	direction of the reaction

continued

STRATEGY

1. Calculate the partial pressures of all species using the ideal gas law and stoichiometric ratios.
2. Write the expression for Q and find its value.
3. Compare Q with K to predict the direction of the reaction.

SOLUTION

1. $P_{N_2O_4}$

$$P = \frac{nRT}{V} = \frac{(0.10)(0.0821)(373)}{2.0} = 1.5 \text{ atm}$$

P_{NO_2}

Since V and T are constant, n is proportional to P, and P can be obtained using the stoichioimetric ratio of NO_2 and N_2O_4.

$$1.5 \text{ atm for } N_2O_4 \times \frac{2 \text{ mol } NO_2}{1 \text{ mol } N_2O_4} = 3.0 \text{ atm}$$

2. Q

$$Q = \frac{(P_{NO_2})^2}{P_{N_2O_4}} = \frac{(3.0)^2}{1.5} = 6.0$$

3. Direction

$Q(6.0) < K(11)$ The reaction proceeds from left to right (→).

END POINT

When we say that the reaction proceeds from left to right or in the forward direction, we refer to the reaction as written. In this case, the partial pressure of NO_2 increases while that of N_2O_4 decreases until the system reaches equilibrium.

Extent of Reaction; Equilibrium Partial Pressures

The equilibrium constant for a chemical system can be used to calculate the partial pressures of the species present at equilibrium. In the simplest case, one equilibrium pressure can be calculated, knowing all the others. Consider, for example, the system

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

$$K = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})} = 1 \times 10^{-30} \text{ at } 25°C$$

In air, the partial pressures of N_2 and O_2 are about 0.78 and 0.21 atm, respectively. The expression for K can be used to calculate the equilibrium partial pressure of NO under these conditions:

$$(P_{NO})^2 = (P_{N_2})(P_{O_2})(K)$$
$$= (0.78)(0.21)(1 \times 10^{-30}) = 1.6 \times 10^{-31}$$
$$P_{NO} = (1.6 \times 10^{-31})^{1/2} = 4 \times 10^{-16} \text{ atm}$$

This is an extremely small pressure, as you might have guessed from the small magnitude of the equilibrium constant.

That's just as well; if N_2 and O_2 in the atmosphere were converted to NO, we'd be in big trouble.

More commonly K is used to determine the equilibrium partial pressures of all species, reactants, and products, knowing their original pressures. To do this, it helps to follow this path.

1. ***Create a table to keep track of all information.*** This was illustrated in Example 12.4.

2. ***Choose ΔP for one of the species to be represented by x.*** A good choice would be a species that has a coefficient of 1 in its balanced equation and/or a

species that is not present initially. Relate ΔP of the chosen species to the other species by using the stoichiometric ratios provided by the coefficients in the balanced equation.

3. ***Determine the direction of the reaction and assign + or − signs to the entries in the row for ΔP.***
   —The reaction proceeds in the direction where initial pressure is 0.
   —If all the species have initial partial pressures, find Q.
4. ***Fill in the row for equilibrium partial pressures.***
5. ***Write the expression for K and substitute the entries for equilibrium partial pressure into the expression.*** Solve for x.
6. ***Having found x, refer back to the table and calculate the equilibrium partial pressures of all species.***

EXAMPLE 12.6 GRADED

For the system

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

K is 0.64 at 900 K.

a Calculate the equilibrium partial pressures of all species, starting with

$$P_{CO_2} = P_{H_2} = 1.00 \text{ atm}; P_{CO} = P_{H_2O} = 0$$

ANALYSIS

Information given:	initial partial pressures for CO_2 (1.00 atm), H_2 (1.00 atm), CO (0 atm), and H_2O (0 atm); K (0.64) at 900 K
Information implied:	direction of the reaction
Asked for:	equilibrium partial pressures of all species

STRATEGY AND SOLUTION

1. Create a table.

	$CO_2(g)$	+	$H_2(g)$	$\rightleftharpoons$	$CO(g)$	+	$H_2O(g)$
P_o (atm)	1.00		1.00		0		0
ΔP (atm)							
P_{eq} (atm)							

2. Choose ΔP for CO as x. Since all the coefficients of the reaction are 1, all the species have x for ΔP.

	$CO_2(g)$	+	$H_2(g)$	$\rightleftharpoons$	$CO(g)$	+	$H_2O(g)$
P_o (atm)	1.00		1.00		0		0
ΔP (atm)	x		x		x		x
P_{eq} (atm)							

3. Direction of the reaction (→)

	$CO_2(g)$	+	$H_2(g)$	$\rightleftharpoons$	$CO(g)$	+	$H_2O(g)$
P_o (atm)	1.00		1.00		0		0
ΔP (atm)	$-x$		$-x$		$+x$		$+x$
P_{eq} (atm)							

continued

4. Equilibrium partial pressures

	$CO_2(g)$	+	$H_2(g)$	$\rightleftharpoons$	$CO(g)$	+	$H_2O(g)$
P_o (atm)	1.00		1.00		0		0
ΔP (atm)	$-x$		$-x$		$+x$		$+x$
P_{eq} (atm)	$1.00 - x$		$1.00 - x$		x		x

5. K expression $$K = \frac{(P_{CO})(P_{H_2O})}{(P_{CO_2})(P_{H_2})} = \frac{(x)(x)}{(1.00 - x)(1.00 - x)} = 0.64$$

Solve for x Take the square root of both sides: $0.80 = \dfrac{x}{1.00 - x} \longrightarrow x = 0.44$

6. P_{eq} $P_{CO} = P_{H_2O} = x =$ 0.44 atm; $P_{CO_2} = P_{H_2} = 1.00 - x = (1.00 - 0.44)$ atm $=$ 0.56 atm

b Calculate the equilibrium partial pressures of all species, starting with

$$P_{CO_2} = 2.00 \text{ atm}, P_{H_2} = 1.00 \text{ atm}; P_{CO} = P_{H_2O} = 0$$

ANALYSIS

Information given:	initial partial pressures for CO_2 (2.00 atm), H_2 (1.00 atm), CO (0.500 atm), and H_2O (0.500 atm); K (0.64) at 900 K
Information implied:	direction of the reaction
Asked for:	equilibrium partial pressures of all species

STRATEGY

1. Determine Q so you know the direction of the reaction.
2. Make a table. Follow the first four steps (shown in detail in part (a)).
3. Substitute into the K expression.
4. Solve for the equilibrium pressure of all species.

ANALYSIS

1. Q $$Q = \frac{(2.00)(1.00)}{(0.500)(0.500)} = 0.125$$

$0.125 < 0.64$; direction of reaction $\longrightarrow$

2. Table

	$CO_2(g)$	+	$H_2(g)$	$\rightleftharpoons$	$CO(g)$	+	$H_2O(g)$
P_o (atm)	2.00		1.00		0.500		0.500
ΔP (atm)	$-x$		$-x$		$+x$		$+x$
P_{eq} (atm)	$2.00 - x$		$1.00 - x$		$0.500 + x$		$0.500 + x$

3. K expression $$K = \frac{(P_{CO})(P_{H_2O})}{(P_{CO_2})(P_{H_2})} = \frac{(0.500 + x)(0.500 + x)}{(2.00 - x)(1.00 - x)} = 0.64$$

For the most part, we'll avoid tedious calculations of this type (Example 12.6b).

It is not useful to take the square root of both sides, so rearrange the equation to the standard form for using the quadratic equation: $ax^2 + bx + c = 0 \longrightarrow 0.36\,x^2 + 2.92\,x - 1.03 = 0$

Apply the **quadratic formula**: $x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$  $\longrightarrow x = 0.34$ or -8.40

0.34 atm is plausible; -8.40 atm would imply a negative partial pressure.

continued

4. P_{eq} $P_{CO} = P_{H_2O} = 0.500 + x = 0.500 + 0.34 = 0.84$ atm

$P_{CO_2} = 2.00 - 0.34 = 1.66$ atm $\quad P_{H_2} = 1.00 - 0.34 = 0.66$ atm

END POINT

Check your algebra by substituting the equilibrium partial pressures back into the expression for K.

$$K = \frac{(P_{CO})(P_{H_2O})}{(P_{CO_2})(P_{H_2})} = \frac{(0.84)(0.84)}{(1.66)(0.66)} = 0.64 \qquad \text{Voila!}$$

We should point out that the calculations in Example 12.6 assume ideal gas behavior. At the conditions specified (1 atm, relatively high temperatures), this assumption is a good one. However, many industrial gas-phase reactions are carried out at very high pressures. In that case, intermolecular forces become important, and calculated yields based on ideal gas behavior may be seriously in error.

12-5 Effect of Changes in Conditions on an Equilibrium System

Once a system has attained equilibrium, it is possible to change the ratio of products to reactants by changing the external conditions. We will consider three ways in which a chemical equilibrium can be disturbed:

1. Adding or removing a gaseous reactant or product.
2. Compressing or expanding the system.
3. Changing the temperature.

You can deduce the direction in which an equilibrium will shift when one of these changes is made by applying the following principle:

> ***If a system at equilibrium is disturbed by a change in concentration, pressure, or temperature, the system will, if possible, shift to partially counteract the change.*** 

Equilibrium systems, like people, resist change.

This law was first stated, in a more complex form, in 1884 by Henri Le Châtelier (1850–1936), a French chemist who had studied a variety of industrial equilibria, including those involved in the production of iron in the blast furnace. The statement is commonly referred to as **Le Châtelier's principle.**

Adding or Removing a Gaseous Species

According to Le Châtelier's principle, ***if a chemical system at equilibrium is disturbed by adding a gaseous species (reactant or product), the reaction will proceed in such a direction as to consume part of the added species. Conversely, if a gaseous species is removed, the system shifts to restore part of that species.*** In that way, the change in concentration brought about by adding or removing a gaseous species is partially counteracted when equilibrium is restored.

To apply this general rule, consider the reaction

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

Suppose this system has reached equilibrium at a certain temperature. This equilibrium could be disturbed by

- *adding* N_2O_4. Reaction will occur in the forward direction (left to right). In this way, part of the N_2O_4 will be consumed.
- *adding* NO_2, which causes the reverse reaction (right to left) to occur, using up part of the NO_2 added.

- *removing* N_2O_4. Reaction occurs in the reverse direction to restore part of the N_2O_4.
- *removing* NO_2, which causes the forward reaction to occur, restoring part of the NO_2 removed.

It is possible to use K to calculate the extent to which reaction occurs when an equilibrium is disturbed by adding or removing a product or reactant. To see how this is done, consider the effect of adding hydrogen iodide to the HI–H_2–I_2 system (Example 12.7).

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

The system does *not* return to its original equilibrium state.

EXAMPLE 12.7

In Example 12.4 you found that the HI–H_2–I_2 system is in equilibrium at 520°C when $P_{HI} = 0.80$ atm and $P_{H_2} = P_{I_2} = 0.10$ atm. Suppose enough HI is added to raise its pressure temporarily to 1.00 atm. When equilibrium is restored, what are P_{HI}, P_{H_2}, and P_{I_2}?

ANALYSIS

Information given:	equilibrium pressures for HI (0.80 atm), I_2 (0.10 atm), and H_2 (0.10 atm) from Example 12.4; K (0.016) equilibrium disturbed by adding HI (now 1.00 atm)
Information implied:	direction of the reaction
Asked for:	equilibrium pressures when equilibrium is reestablished

STRATEGY

1. Create a table. Note that the equilibrium partial pressures now become initial pressures for HI and I_2. P_o for HI is now 1.00 atm.
2. Since HI is added, the reaction goes in the direction of using up the HI, thus to the right.
3. Write the K expression and solve for x.
4. Substitute the value for x into the equilibrium pressures for all species.

SOLUTION

Table

	$2HI(g)$	$\rightleftharpoons$	$H_2(g)$	+	$I_2(g)$
P_o (atm)	1.00		0.10		0.10
ΔP (atm)	$-2x$		$+x$		$+x$
P_{eq} (atm)	$1.00 - 2x$		$0.10 + x$		$0.10 + x$

K expression

$$K = 0.016 = \frac{(P_{H_2})(P_{I_2})}{(P_{HI})^2} = \frac{(0.10 + x)(0.10 + x)}{(1.00 - 2x)^2} = \frac{(0.10 + x)^2}{(1.00 - 2x)^2}$$

x

Take the square root of both sides: $0.13 = \dfrac{(0.10 + x)}{(1.00 - 2x)} \longrightarrow x = 0.024$ atm

Equilibrium pressures

$P_{I_2} = P_{H_2} = 0.10 + 0.024 = 0.12$ atm; $P_{HI} = 1.00 - 2(0.024) = 0.95$ atm

END POINT

Note that the equilibrium partial pressure of HI is intermediate between its value before equilibrium was established (0.80 atm) and that immediately afterward (1.00 atm). This is exactly what LeChâtelier's principle predicts: part of the added HI is consumed to reestablish equilibrium!

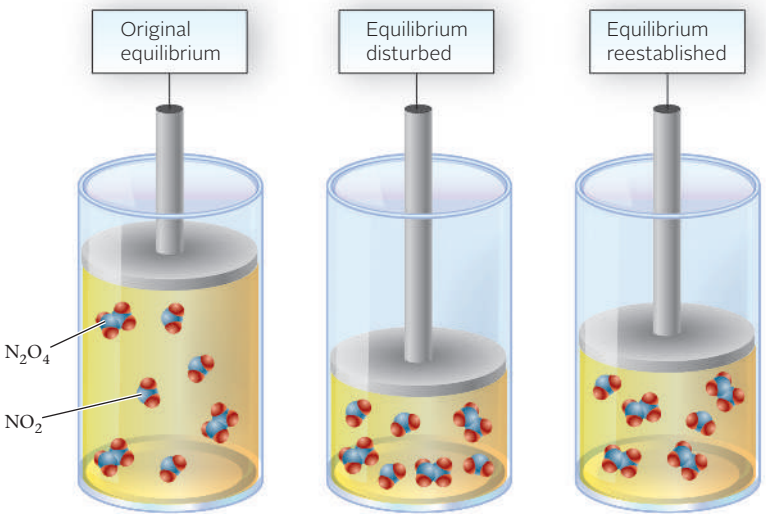


Figure 12.4 Effect of compression on the $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ system at equilibrium. The immediate effect (middle cylinder) is to crowd the same number of moles of gas into a smaller volume and thus increase the total pressure. This is partially compensated for by the conversion of some of the NO_2 to N_2O_4, thereby reducing the total number of moles of gas.

We should emphasize that adding a pure liquid or solid has no effect on a system at equilibrium. The rule is a simple one: *For a species to shift the position of an equilibrium, it must appear in the expression for K.*

Compression or Expansion

To understand how a change in pressure can change the position of an equilibrium, consider again the N_2O_4–NO_2 system:

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

Suppose the system is compressed by pushing down the piston shown in Figure 12.4. The immediate effect is to increase the gas pressure because the same number of molecules are crowded into a smaller volume ($P = nRT/V$). According to Le Châtelier's principle, the system will shift to partially counteract this change. There is a simple way in which the gas pressure can be reduced. Some of the NO_2 molecules combine with each other to form N_2O_4 (cylinder at right of Figure 12.4). That is, reaction occurs in the reverse direction:

When V decreases, NO_2 is converted to N_2O_4.

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

This reduces the number of moles, n, and hence the pressure, P.

It is possible (but not easy) to calculate from K the extent to which NO_2 is converted to N_2O_4 when the system is compressed. The results of such calculations are given in Table 12.6. As the pressure is increased from 1.0 to 10.0 atm, more and more of the NO_2 is converted to N_2O_4. Notice that the total number of moles of gas decreases steadily as a result of this conversion.

Table 12.6 Effect of Compression on the Equilibrium System $N_2O_4(g) \rightleftharpoons 2NO_2(g)$; $K = 11$ at 100°C

P_{tot} (atm)	n_{NO_2}	$n_{N_2O_4}$	n_{tot}
1.0	0.92	0.08	1.00
2.0	0.82	0.13	0.95
5.0	0.64	0.22	0.86
10.0	0.50	0.29	0.79

Table 12.7 Effect of Pressure on the Position of Gaseous Equilibria

System	Δn_{gas}*	P_{tot} Increases	P_{tot} Decreases
1. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$	+1	←	→
2. $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$	$-\frac{1}{2}$	→	←
3. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	−2	→	←
4. $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$	+1	←	→
5. $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$	0	0	0

*Δn_{gas} is the change in the number of moles of gas as the forward reaction occurs.

The analysis we have just gone through for the N_2O_4–NO_2 system can be applied to any equilibrium system involving gases

- ***When the system is compressed, thereby increasing the total pressure, reaction takes place in the direction that decreases the total number of moles of gas.***
- ***When the system is expanded, thereby decreasing the total pressure, reaction takes place in the direction that increases the total number of moles of gas.***

The application of this principle to several different systems is shown in Table 12.7. In system 2, the number of moles of gas decreases from $\frac{3}{2}$ to 1 as the reaction goes to the right. Hence increasing the pressure causes the forward reaction to occur; a decrease in pressure has the reverse effect. Notice that it is the change in the number of moles of *gas* that determines which way the equilibrium shifts (system 4). When there is no change in the number of moles of gas (system 5), a change in pressure has no effect on the position of the equilibrium.

We should emphasize that in applying this principle it is important to realize that an "increase in pressure" means that the system is compressed; that is, the volume is decreased. Similarly, a "decrease in pressure" corresponds to expanding the system by increasing its volume. There are other ways in which pressure can be changed. One way is to add an unreactive gas such as helium at constant volume. This increases the total number of moles and hence the total pressure. It has no effect, however, on the position of the equilibrium, because it does not change the partial pressures of any of the gases taking part in the reaction. Remember that the partial pressure of a gas A is given by the expression

$$P_A = n_A RT/V \qquad (n_A = \text{no. of moles of A})$$

Adding a different gas at constant volume does not change any of the quantities on the right side of this equation, so P_A stays the same.

Mama G. Clarke

Figure 12.5 Effect of temperature on the N_2O_4–NO_2 system at equilibrium. At 0°C *(tube at right)*, N_2O_4, which is colorless, predominates. At 50°C *(tube at left)*, some of the N_2O_4 has dissociated to give the deep brown color of NO_2.

Change in Temperature

Le Châtelier's principle can be used to predict the effect of a change in temperature on the position of an equilibrium. In general, ***an increase in temperature causes the endothermic reaction to occur.*** This absorbs heat and so tends to reduce the temperature of the system, partially compensating for the original temperature increase.

Applying this principle to the N_2O_4–NO_2 system,

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad \Delta H^\circ = +57.2 \text{ kJ}$$

it follows that raising the temperature causes the forward reaction to occur, because that reaction absorbs heat. This is confirmed by experiment (Figure 12.5). At higher temperatures, more NO_2 is produced, and the reddish-brown color of that gas becomes more intense.

For the synthesis of ammonia,

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H^\circ = -92.2 \text{ kJ}$$

an increase in temperature shifts the equilibrium to the left; some ammonia decomposes to the elements. This reflects the fact that the reverse reaction is endothermic:

$$2NH_3(g) \longrightarrow N_2(g) + 3H_2(g) \qquad \Delta H^\circ = +92.2 \text{ kJ}$$

As pointed out earlier, the equilibrium constant of a system changes with temperature. The form of the equation relating K to T is a familiar one, similar to the Clausius-Clapeyron equation (Chapter 9) and the Arrhenius equation (Chapter 11). This one is called the *van't Hoff equation*, honoring Jacobus van't Hoff (1852–1911), who was the first to use the equilibrium constant, K. Coincidentally, van't Hoff was a good friend of Arrhenius. The equation is

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \tag{12.5}$$

where K_2 and K_1 are the equilibrium constants at T_2 and T_1, respectively, ΔH° is the standard enthalpy change for the forward reaction, and R is the gas constant, 8.31 J/mol·K.

To illustrate how this equation is used, let us apply it to calculate the equilibrium constant at 100°C for the system

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H^\circ = -92.2 \text{ kJ}$$

given that $K = 6 \times 10^5$ at 25°C. The relation is

$$\ln \frac{K \text{ at } 100^\circ\text{C}}{6 \times 10^5} = \frac{-92{,}200 \text{ J/mol}}{8.31 \text{ J/mol} \cdot \text{K}}\left[\frac{1}{298 \text{ K}} - \frac{1}{373 \text{ K}}\right] = -7.5$$

Taking inverse logarithms,

$$\frac{K \text{ at } 100^\circ\text{C}}{6 \times 10^5} = 6 \times 10^{-4}$$

$$K \text{ at } 100^\circ\text{C} = 4 \times 10^2$$

Notice that the equilibrium constant becomes smaller as the temperature increases. In general,

- if the forward reaction is exothermic, as is the case here ($\Delta H^\circ = -92.2$ kJ), K decreases as T increases.
- if the forward reaction is endothermic as in the decomposition of N_2O_4,

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad \Delta H^\circ = +57.2 \text{ kJ}$$

K increases as T increases. For this reaction K is 0.11 at 25°C and 11 at 100°C.

EXAMPLE 12.8

Consider the following systems:

(a) $2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$ $\quad \Delta H = -566$ kJ

(b) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ $\quad \Delta H = -2.7$ kJ

(c) $H_2(g) + I_2(s) \rightleftharpoons 2HI(g)$ $\quad \Delta H = +53.0$ kJ

(d) $I_2(g) \rightleftharpoons 2I(g)$ $\quad \Delta H = +36.2$ kJ

What will happen to the position of the equilibrium if the system is compressed (at constant temperature)? Heated at constant pressure?

continued

STRATEGY	
1. An increase in pressure tends to drive the equilbrium in a direction where there are fewer moles of gas.	
2. An increase in temperature favors an endothermic reaction ($\Delta H > 0$), i.e., creates more products.	
SOLUTION	
(a) Increase in P Increase in T	(3 mol of gas on the left; 2 mol of gas on the right) $\longrightarrow$ exothermic reaction $\longleftarrow$
(b) Increase in P Increase in T	(2 mol of gas on the left; 2 mol of gas on the right) no effect exothermic reaction $\longleftarrow$ (slightly)
(c) Increase in P Increase in T	(1 mol of gas on the left; 2 mol of gas on the right) $\longleftarrow$ endothermic reaction $\longrightarrow$
(d) Increase in P Increase in T	(1 mol of gas on the left; 2 mol of gas on the right) $\longleftarrow$ endothermic reaction $\longrightarrow$

We should emphasize that of the three changes in conditions described in this section

- adding or removing a gaseous species
- compressing or expanding the system
- changing the temperature

the only one that changes the value of the equilibrium constant is a change in temperature. In the other two cases, K remains constant.

CHEMISTRY **BEYOND** THE CLASSROOM

An Industrial Application of Gaseous Equilibrium

A wide variety of materials, both pure substances and mixtures, are made by processes that involve one or more gas-phase reactions. Among these is one of the most important industrial chemicals, ammonia.

The process used to make this chemical applies many of the principles of chemical equilibrium, discussed in this chapter, and chemical kinetics (Chapter 11).

Haber Process for Ammonia

Combined ("fixed") nitrogen in the form of protein is essential to all forms of life. There is more than enough elementary nitrogen in the air, about 4×10^{18} kg, to meet all our needs. The problem is to convert the element to compounds that can be used by plants to make proteins. At room temperature and atmospheric pressure, N_2 does not react with any nonmetal. However, in 1908 in Germany, Fritz Haber (Figure A) showed that nitrogen does react with hydrogen at high temperatures and pressures to form ammonia in good yield:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H^\circ = -92.2 \text{ kJ}$$

The **Haber process**, represented by this equation, is now the main source of fixed nitrogen. Its feasibility depends on choosing conditions under which nitrogen and hydrogen react rapidly to give a high yield of ammonia. At 25°C and atmospheric pressure, the position of the equilibrium favors the formation of NH_3 ($K = 6 \times 10^5$). Unfortunately, however, the rate of reaction is virtually zero. Equilibrium is reached more rapidly by raising the temperature. However, because the synthesis of ammonia is exothermic, high temperatures reduce K and hence the yield of ammonia. High pressures, on the other hand, have a favorable effect on both the rate of the reaction and the position of the equilibrium (Table A).

Figure A Fritz Haber (1868–1934).

The values of the equilibrium constant K listed in Table A are those obtained from data at low pressures, where the gases behave ideally. At higher pressures the mole percent of ammonia observed is generally larger than the calculated value. For example, at 400°C and 300 atm, the observed mole percent of NH_3 is 47; the calculated value is only 41.

Table A Effect of Temperature and Pressure on the Yield of Ammonia in the Haber Process ($P_{H_2} = 3P_{N_2}$)

		Mole Percent NH_3 in Equilibrium Mixture				
°C	*K*	10 atm	50 atm	100 atm	300 atm	1000 atm
200	0.30	51	74	82	90	98
300	3.7×10^{-3}	15	39	52	71	93
400	1.5×10^{-4}	4	15	25	47	80
500	1.4×10^{-5}	1	6	11	26	57
600	2.1×10^{-6}	0.5	2	5	14	31

The goal of Haber's research was to find a catalyst to synthesize ammonia at a reasonable rate without going to very high temperatures. These days two different catalysts are used. One consists of a mixture of iron, potassium oxide, K_2O, and aluminum oxide, Al_2O_3. The other, which uses finely divided ruthenium, Ru, metal on a graphite surface, is less susceptible to poisoning by impurities. Reaction takes place at 450°C and a pressure of 200 to 600 atm. The ammonia formed is passed through a cooling chamber. Ammonia boils at −33°C, so it is condensed out as a liquid, separating it from unreacted nitrogen and hydrogen. The yield is typically less than 50%, so the reactants are recycled to produce more ammonia.

Fritz Haber

Haber had a distinguished scientific career. He received, among other honors, the 1918 Nobel Prize in chemistry. For more than 20 years, he was director of the prestigious Kaiser Wilhelm Institute for Physical Chemistry at Dahlem, Germany, a suburb of Berlin. Presumably because of Haber's Jewish ancestry, he was forced to resign that position when Adolf Hitler came to power in 1933. A contributing factor may have been his comment after listening to a radio broadcast of one of Hitler's hysterical harangues. When asked what he thought of it, Haber replied, "Give me a gun so I can shoot him."

Haber, like all of us, suffered disappointment and tragedy in his life. In the years after World War I, he devised a scheme to pay Germany's war debts by extracting gold from seawater. The project, which occupied Haber for several years, was a total failure because the concentration of gold turned out to be only about one thousandth of the literature value.

During World War I, Haber was in charge of the German poison gas program. In April of 1915, the Germans used chlorine for the first time on the Western front, causing 5000 fatalities. Haber's wife, Clara, was aghast; she pleaded with her husband to forsake poison gas. When he adamantly refused to do so, she committed suicide.

On a lighter note, there is an amusing anecdote told by the author Morris Goran (*The Story of Fritz Haber*, 1967). It seems that in a Ph.D. examination, Haber asked the candidate how iodine was prepared. The student made a wild guess that it was obtained from a tree (it isn't). Haber played along with him, asking where the iodine tree grew, what it looked like, and, finally, when it bloomed. "In the fall," was the answer. Haber smiled, put his arm around the student, and said, "Well, my friend, I'll see you again when the iodine blossoms appear once more."

Key Concepts

1. Relate the expression for *K* to the corresponding chemical equation.
   (Examples 12.1, 12.2; Problems 5–14)
2. Calculate *K*, knowing
   - appropriate *K*'s for other reactions.
     (Example 12.1; Problems 15–20)
   - all the equilibrium partial pressures.
     (Example 12.3; Problems 21–24)
   - all the original and one equilibrium partial pressure.
     (Example 12.4; Problems 25, 26)
3. Use the value of *K* to determine
   - the direction of reaction.
     (Example 12.5; Problems 27–32)
   - equilibrium partial pressures of all species.
     (Examples 12.6, 12.7; Problems 33–46)
4. Use Le Châtelier's principle to predict what will happen when the conditions on an equilibrium system are changed.
   (Examples 12.7, 12.8; Problems 47–60)

Key Equations

Expression for K

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$

$$K = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$$

Coefficient rule $K' = K^n$

Reciprocal rule $K'' = 1/K$

Multiple equilibrium $K_3 = K_1 \times K_2$

van't Hoff equation $\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$

Key Terms

equilibrium constant Le Châtelier's principle reaction quotient

Summary Problem

Consider phosgene, $COCl_2(g)$. It is an important intermediate in the manufacture of some plastics. It can decompose into carbon monoxide and chlorine gases. Its molar heat of formation (ΔH_f°) is −220.1 kJ/mol.

(a) Write the chemical equation for the decomposition of phosgene using simplest whole-number coefficients.

(b) Write the equilibrium expression for the decompostion.

(c) At 500°C, after the reaction has reached equilibrium, the partial pressures of CO, Cl_2, and $COCl_2$ are 0.413 atm, 0.237 atm, and 0.217 atm, respectively. Calculate K at 500°C.

(d) Initially, a 5.00-L flask contains $COCl_2$, Cl_2, and CO at partial pressures of 0.689 atm, 0.250 atm, and 0.333 atm, respectively. After equilibrium is established at 500°C, the partial pressure of $COCl_2$ is 0.501 atm. Calculate the equilibrium partial pressures of chlorine and carbon monoxide gases.

(e) Initially, a reaction vessel contains Cl_2, CO, and $COCl_2$ at 500°C, where both Cl_2 and CO gases have partial pressures of 0.750 atm. The partial pressure of phosgene is 0.500 atm.

1. In what direction will the reaction proceed at that temperature?
2. What is the partial pressure of each gas when equilibrium is established?
3. Suppose enough phosgene is added to raise its pressure temporarily to 2.00 atm. In which direction will the equilibrium shift?
4. When equilibrium is restored, what is the partial pressure of each gas?

(f) In which direction will this system shift if at equilibrium

1. the system is expanded?
2. helium gas is added?
3. the temperature is increased?

(g) What is the equilibrium constant at 375°C?

Answers

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

(b) $K = \dfrac{P_{CO} \times P_{Cl_2}}{P_{COCl_2}}$

(c) 0.451

(d) $P_{Cl_2} = 0.438$ atm; $P_{CO} = 0.521$ atm

(e) 1. ⟵ 2. $P_{Cl_2} = P_{CO} = 0.558$ atm; $P_{COCl_2} = 0.692$ atm
3. ⟶ 4. $P_{Cl_2} = P_{CO} = 0.872$ atm; $P_{COCl_2} = 1.686$ atm

(f) 1. ⟶ 2. no change 3. ⟶

(g) 0.0168

Questions and Problems

Even-numbered questions and Challenge Problems have answers in Appendix 5 and fully worked solutions in the *Student Solutions Manual*.

12-1 The N_2O_4–NO_2 Equilibrium System

1. The following data are for the system

$$A(g) \rightleftharpoons 2B(g)$$

Time (s)	0	20	40	60	80	100
P_A (atm)	1.00	0.83	0.72	0.65	0.62	0.62
P_B (atm)	0.00	0.34	0.56	0.70	0.76	0.76

(a) How long does it take the system to reach equilibrium?
(b) How does the rate of the forward reaction compare with the rate of the reverse reaction after 30 s? After 90 s?

2. The following data are for the system

$$A(g) \rightleftharpoons 2B(g)$$

Time (s)	0	30	45	60	75	90
P_A (atm)	0.500	0.390	0.360	0.340	0.325	0.325
P_B (atm)	0.000	0.220	0.280	0.320	0.350	0.350

(a) How long does it take the system to reach equilibrium?
(b) How does the rate of the forward reaction compare with the rate of the reverse reaction after 45 s? After 90 s?

3. Complete the table below for the reaction

$$2A(g) + B(g) \longrightarrow 3C(g)$$
$$A + B \longrightarrow \text{products}$$

Time (s)	0	10	20	30	40	50	60
P_A (atm)	1.850	_____	1.500	_____	1.100	_____	0.920
P_B (atm)	0.900	_____	_____	0.600	_____	0.435	_____
P_C (atm)	0.000	0.0850	_____	_____	_____	_____	_____

4. Complete the table below for the reaction:

$$3A(g) + B(g) \rightleftharpoons 2C(g)$$

Time (min)	0	1	2	3	4	5	6
P_A (atm)	1.000	0.778	_____	_____	_____	0.325	_____
P_B (atm)	0.400	_____	0.260	_____	0.185	_____	0.175
P_C (atm)	0.000	_____	_____	0.390	_____	_____	_____

12-2 The Equilibrium Constant Expression

5. Write the equilibrium expressions (K) for the following reactions:

(a) $CH_4(g) + H_2O(l) \rightleftharpoons CO(g) + 3H_2(g)$
(b) $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$
(c) $BaCO_3(s) \rightleftharpoons BaO(s) + CO_2(g)$
(d) $NH_3(g) + HCl(g) \rightleftharpoons NH_4Cl(s)$

6. Write equilibrium constant (K) expressions for the following reactions:

(a) $Na_2CO_3(s) \rightleftharpoons 2NaO(s) + CO_2(g)$
(b) $C_2H_6(g) + 2H_2O(l) \rightleftharpoons 2CO(g) + 5H_2(g)$
(c) $4NO(g) + 6H_2O(g) \rightleftharpoons 4NH_3(g) + 5O_2(g)$
(d) $NH_3(g) + HI(l) \rightleftharpoons NH_4I(s)$

7. Write equilibrium constant expressions (K) for the following reactions:

(a) $2NO_3^-(aq) + 8H^+(aq) + 3Cu(s) \rightleftharpoons 2NO(g) + 3Cu^{2+}(aq) + 4H_2O(l)$
(b) $2PbS(s) + 3O_2(g) \rightleftharpoons 2PbO(s) + 2SO_2(g)$
(c) $Ca^{2+}(aq) + CO_3^{2-}(aq) \rightleftharpoons CaCO_3(s)$

8. Write equilibrium constant (K) expressions for the following reactions:

(a) $I_2(s) + 2Cl^-(g) \rightleftharpoons Cl_2(g) + 2I^-(aq)$
(b) $CH_3NH_2(aq) + H^+(aq) \rightleftharpoons CH_3NH_3^+(aq)$
(c) $Au^{2+}(aq) + 4CN^-(aq) \rightleftharpoons Au(CN)_4^{2-}(aq)$

9. Given the following descriptions of reversible reactions, write a balanced equation (smallest whole-number coefficients) and the equilibrium constant expression for each.

(a) Nickel metal reacts with carbon monoxide to form nickel tetracarbonyl ($Ni(CO)_4$) gas.
(b) Aqueous nitrous acid in equilibrium with hydrogen and nitrite ions.
(c) Chlorine gas and bromide ions in equilibrium with liquid bromine and chloride ions.

10. Given the following descriptions of reversible reactions, write a balanced net ionic equation (simplest whole-number coefficients) and the equilibrium constant expression (K) for each.

(a) Liquid acetone (C_3H_6O) is in equilibrium with its vapor.
(b) Hydrogen gas reduces nitrogen dioxide gas to form ammonia and steam.
(c) Hydrogen sulfide gas (H_2S) bubbled into an aqueous solution of lead(II) ions produces lead sulfide precipitate and hydrogen ions.

11. Write an equation for an equilibrium system that would lead to the following expressions (a–c) for K.

(a) $K = \dfrac{(P_{CO})^2(P_{H_2})^5}{(P_{C_2H_6})(P_{H_2O})^2}$

(b) $K = \dfrac{(P_{NH_3})^4(P_{O_2})^5}{(P_{NO})^4(P_{H_2O})^6}$

(c) $K = \dfrac{[ClO_3^-]^2[Mn^{2+}]^2}{(P_{Cl_2})[MnO_4^-]^2[H^+]^4}$; liquid water is a product

12. Write a chemical equation for an equilibrium system that would lead to the following expressions (a–d) for K.

(a) $K = \dfrac{(P_{H_2S})^2\,(P_{O_2})^3}{(P_{SO_2})^2\,(P_{H_2O})^2}$ **(b)** $K = \dfrac{(P_{F_2})^{1/2}\,(P_{I_2})^{1/2}}{P_{IF}}$

(c) $K = \dfrac{[Cl^-]^2}{(P_{Cl_2})[Br^-]^2}$ **(d)** $K = \dfrac{(P_{NO})^2(P_{H_2O})^4[Cu^{2+}]^3}{[NO_3^-]^2[H^+]^8}$

13. Consider the following reaction at 250°C:

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

(**a**) Write an equilibrium constant expression for the reaction. Call the equilibrium constant K_1.
(**b**) Write an equilibrium constant expression for the formation of one mole of B(g) and call the equilibrium constant K_2.
(**c**) Relate K_1 and K_2.

14. Consider the following reaction at 100°C:

$$NO(g) + \tfrac{1}{2}Cl_2(g) \rightleftharpoons NOCl(g)$$

(**a**) Write an equilibrium constant expression for the reaction and call it K'.
(**b**) Write an equilibrium constant expression for the decomposition of NOCl to produce one mole of chlorine gas. Call the constant K''.
(**c**) Relate K' and K''.

12-3 Determination of *K*

15. At 627°C, $K = 0.76$ for the reaction

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

Calculate K at 627°C for
(**a**) the synthesis of one mole of sulfur trioxide gas.
(**b**) the decomposition of two moles of SO_3.

16. At 800°C, $K = 2.2 \times 10^{-4}$ for the following reaction

$$2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$$

Calculate K at 800°C for
(**a**) the synthesis of one mole of H_2S from H_2 and S_2 gases.
(**b**) the decomposition of one mole of H_2S gas.

17. Given the following reactions and their equilibrium constants,

$$H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g) \qquad K = 1.6$$
$$FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g) \qquad K = 0.67$$

calculate K for the reaction

$$Fe(s) + H_2O(g) \rightleftharpoons FeO(s) + H_2(g)$$

18. Given the following data at 25°C

$$2NO(g) \rightleftharpoons N_2(g) + O_2(g) \qquad K = 1 \times 10^{-30}$$
$$2NO(g) + Br_2(g) \rightleftharpoons 2NOBr(g) \qquad K = 8 \times 10^{1}$$

Calculate K for the formation of one mole of NOBr from its elements in the gaseous state.

19. Given the following data at a certain temperature,

$$2N_2(g) + O_2(g) \rightleftharpoons 2N_2O(g) \qquad K = 1.2 \times 10^{-35}$$
$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad K = 4.6 \times 10^{-3}$$
$$\tfrac{1}{2}N_2(g) + O_2(g) \rightleftharpoons NO_2(g) \qquad K = 4.1 \times 10^{-9}$$

calculate K for the reaction between one mole of dinitrogen oxide gas and oxygen gas to give dinitrogen tetroxide gas.

20. Consider the following hypothetical reactions and their equilibrium constants at 75°C,

$$3A(g) \rightleftharpoons 3B(g) + 2C(g) \qquad K_1 = 0.31$$
$$3D(g) + 2B(g) \rightleftharpoons 2C(g) \qquad K_2 = 2.8$$

Find the equilibrium constant at 75°C for the following reaction

$$A(g) \rightleftharpoons D(g) + \tfrac{5}{3}B(g)$$

21. When one mole of carbon disulfide gas reacts with hydrogen gas, methane and hydrogen sulfide gases are formed. When equilibrium is reached at 900°C, analysis shows that $P_{CH_4} = 0.0833$ atm, $P_{H_2S} = 0.163$ atm, $P_{CS_2} = 1.27$ atm, and $P_{H_2} = 0.873$ atm.
(**a**) Write a balanced equation (smallest whole-number coefficients) for the reaction.
(**b**) Find K at 900°C.

22. Calculate K for the formation of methyl alcohol at 100°C:

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

given that at equilibrium, the partial pressures of the gases are $P_{CO} = 0.814$ atm, $P_{H_2} = 0.274$ atm, and $P_{CH_3OH} = 0.0512$ atm.

23. Ammonium carbamate solid ($NH_4CO_2NH_2$) decomposes at 313 K into ammonia and carbon dioxide gases. At equilibrium, analysis shows that there are 0.0451 atm of CO_2, 0.0961 atm of ammonia, and 0.159 g of ammonium carbamate.
(**a**) Write a balanced equation for the decomposition of one mole of $NH_4CO_2NH_2$.
(**b**) Calculate K at 313 K.

24. Consider the decomposition at 25°C of one mole of NOBr gas into NO and Br_2 gases. At equilibrium, the concentrations of NOBr, NO, and Br_2 gases are 0.0162 M, 0.0011 M, and 0.072 M, respectively.
(**a**) Write a balanced equation for the reaction.
(**b**) Calculate K for the reaction at 25°C. (Note that the gases need to be expressed as pressure in atm.)

25. Consider the decomposition of ammonium hydrogen sulfide:

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

In a sealed flask at 25°C are 10.0 g of NH_4HS, ammonia with a partial pressure of 0.692 atm, and H_2S with a partial pressure of 0.0532 atm. When equilibrium is established, it is found that the partial pressure of ammonia has increased by 12.4%. Calculate K for the decomposition of NH_4HS at 25°C.

26. A sealed flask has 0.541 atm of SO_3 at 1000 K. The following equilibrium is established.

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

At equilibrium, the partial pressure of oxygen is measured to be 0.216 atm. Calculate K for the decomposition of SO_3 at 1000 K.

12-4 Applications of the Equilibrium Constant

K; Direction of the Reaction

27. A gaseous reaction mixture contains 0.30 atm SO_2, 0.16 atm Cl_2, and 0.50 atm SO_2Cl_2 in a 2.0-L container. $K = 0.011$ for the equilibrium system

$$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$$

(**a**) Is the system at equilibrium? Explain.
(**b**) If it is not at equilibrium, in which direction will the system move to reach equilibrium?

28. For the system

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

K is 26 at 300°C. In a 10.0-L flask at 300°C, a gaseous mixture consists of all three gases with the following partial pressures: $P_{PCl_5} = 0.026$ atm, $P_{PCl_3} = 0.65$ atm, $P_{Cl_2} = 0.33$ atm

(**a**) Is the system at equilibrium? Explain.

(**b**) If the system is not at equilibrium, in which direction will the system move to reach equilibrium?

29. The reversible reaction between hydrogen chloride gas and one mole of oxygen gas produces steam and chlorine gas:

$$4HCl(g) + O_2(g) \rightleftharpoons 2Cl_2(g) + 2H_2O(g) \qquad K = 0.79$$

Predict the direction in which the system will move to reach equilibrium if one starts with

(**a**) $P_{H_2O} = P_{HCl} = P_{O_2} = 0.20$ atm

(**b**) $P_{HCl} = 0.30$ atm, $P_{H_2O} = 0.35$ atm, $P_{Cl_2} = 0.2$ atm, $P_{O_2} = 0.15$ atm

30. For the reaction

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

K at a certain temperature is 3.7×10^{-4}. Predict the direction in which the system will move to reach equilibrium if one starts with

(**a**) $P_{N_2} = P_{H_2} = P_{NH_3} = 0.01$ atm

(**b**) $P_{NH_3} = 0.0045$ atm

(**c**) $P_{N_2} = 1.2$ atm, $P_{H_2} = 1.88$ atm, $P_{NH_3} = 0.0058$ atm

31. A compound, X, decomposes at 131°C according to the following equation:

$$2X(g) \rightleftharpoons A(g) + 3C(g) \qquad K = 1.1 \times 10^{-3}$$

If a flask initially contains X, A, and C, all at partial pressures of 0.250 atm, in which direction will the reaction proceed?

32. Consider the following reaction at 75°C:

$$3R(s) + 2Q(g) \rightleftharpoons A(g) + 5B(l) \qquad K = 9.4$$

A 10.0-L sample contains 0.30 mol of R and Q and 0.50 mol of A and B. In which direction will the reaction proceed?

K; Extent of the Reaction

33. Consider the reaction between nitrogen and steam:

$$2N_2(g) + 6H_2O(g) \rightleftharpoons 4NH_3(g) + 3O_2(g)$$

At a certain temperature, $K = 28.6$. Calculate the equilibrium partial pressure of steam if $P_{NH_3} = 1.75$ atm, $P_{O_2} = 0.963$ atm, and $P_{N_2} = 0.996$ atm at equilibrium.

34. At 500°C, K for the formation of ammonia from nitrogen and hydrogen gases is 1.5×10^{-5}.

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

Calculate the equilibrium partial pressure of hydrogen if the equilibrium partial pressures of ammonia and nitrogen are 0.015 atm and 1.2 atm, respectively.

35. At a certain temperature, K is 4.9 for the formation of one mole of bromine chloride gas (BrCl) from its elements. A mixture at equilibrium at this temperature contains all three gases. The partial pressures at equilibrium of bromine and chlorine gas is 0.19 atm. What is the partial pressure of bromine chloride in this mixture at equilibrium?

36. At a certain temperature, $K = 0.29$ for the decomposition of two moles of iodine trichloride, $ICl_3(s)$, to chlorine and iodine gases. The partial pressure of chlorine gas at equilibrium is three times that of iodine gas. What are the partial pressures of iodine and chlorine at equilibrium?

37. For the reaction

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

K is 1.54×10^{-3}. When equilibrium is established, the partial pressure of nitrogen is 0.168 atm, and that of NO is 0.225 atm. The total pressure of the system at equilibrium is 1.87 atm. What are the equilibrium partial pressures of hydrogen and steam?

38. Nitrogen dioxide can decompose to nitrogen oxide and oxygen.

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

K is 0.87 at a certain temperature. A 5.0-L flask at equilibrium is determined to have a total pressure of 1.25 atm and oxygen to have a partial pressure of 0.515 atm. Calculate P_{NO} and P_{NO_2} at equilibrium.

39. Consider the following reaction:

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

At a certain temperature, the equilibrium constant for the reaction is 0.0639. What are the partial pressures of all gases at equilibrium if the initial partial pressure of the gases (both products and reactants) is 0.400 atm?

40. Consider the hypothetical reaction at 325°C

$$R(g) + Q(g) \rightleftharpoons 2Z(g) \qquad K = 2.71$$

What are the equilibrium partial pressures of all the gases if all the gases (products and reactants) have an initial partial pressure of 0.228 atm?

41. At a certain temperature, the equilibrium constant for the following reaction is 0.0472.

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

All gases are at an initial pressure of 0.862 atm.

(**a**) Calculate the partial pressure of each gas at equilibrium.

(**b**) Compare the initial total pressure with the total pressure of the gases at equilibrium. Would that relation be true of all gaseous systems?

42. At 460°C, the reaction

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

has $K = 84.7$. All gases are at an initial pressure of 1.25 atm.

(**a**) Calculate the partial pressure of each gas at equilibrium.

(**b**) Compare the total pressure initially with the total pressure at equilibrium. Would that relation be true of all gaseous systems?

43. Solid ammonium iodide decomposes to ammonia and hydrogen gases at sufficiently high temperatures.

$$NH_4I(s) \rightleftharpoons NH_3(g) + HI(g)$$

The equilibrium constant for the decomposition at 400°C is 0.215. Twenty grams of ammonium iodide are sealed in a 7.50-L flask and heated to 400°C.

(**a**) What is the total pressure in the flask at equilibrium?

(**b**) How much solid NH_4I is left after the decomposition?

44. Consider the following decomposition at 80°C.

$$PH_3BCl_3(s) \rightleftharpoons PH_3(g) + BCl_3(g) \qquad K = 0.054$$

Twenty grams of PH_3BCl_3 are sealed in a 5.0-L flask and heated to 80°C.

(a) What is the total pressure in the flask at equilibrium?

(b) How many grams of PH_3BCl_3 are left in the flask at equilibrium?

45. Hydrogen cyanide, a highly toxic gas, can decompose to cyanogen and hydrogen gases,

$$2HCN(g) \rightleftharpoons C_2N_2(g) + H_2(g)$$

At a certain temperature, K for this decomposition is 0.17. What are the partial pressures of all gases at equilibrium if initially the partial pressures are $P_{C_2N_2} = P_{H_2} = 0.32$ atm, $P_{HCN} = 0.45$ atm?

46. At 800 K, hydrogen iodide can decompose into hydrogen and iodine gases.

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

At this temperature, $K = 0.0169$. What are the partial pressures at equilibrium of the hydrogen and iodine if initially a sealed flask at 800 K contains only HI at a pressure of 0.200 atm?

12-5 Effect of Changes in Conditions on an Equilibrium System

Changing Reaction Conditions; Le Châtelier's Principle

47. For the following reactions, predict whether the pressure of the reactants or products increases or remains the same when the volume of the reaction vessel is increased.

(a) $H_2O(l) \rightleftharpoons H_2O(g)$

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

(c) $C_2H_4(g) + H_2O(g) \rightleftharpoons C_2H_5OH(g)$

48. Follow the directions of Question 47 for the following reactions:

(a) $2H_2O(g) + O_2(g) \rightleftharpoons 2H_2O_2(g)$

(b) $2CH_4(g) \rightleftharpoons C_2H_2(g) + 3H_2(g)$

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

49. Consider the system

$$SO_3(g) \rightleftharpoons SO_2(g) + \tfrac{1}{2}O_2(g) \qquad \Delta H = 98.9 \text{ kJ}$$

(a) Predict whether the forward or reverse reaction will occur when the equilibrium is disturbed by

1. adding oxygen gas.

2. compressing the system at constant temperature.

3. adding argon gas.

4. removing $SO_2(g)$.

5. decreasing the temperature.

(b) Which of the above factors will increase the value of K? Which will decrease it?

50. Consider the system

$$4NH_3(g) + 3O_2(g) \rightleftharpoons 2N_2(g) + 6H_2O(l) \qquad \Delta H = -1530.4 \text{ kJ}$$

(a) How will the amount of ammonia at equilibrium be affected by

1. removing $O_2(g)$?

2. adding $N_2(g)$?

3. adding water?

4. expanding the container at constant pressure?

5. increasing the temperature?

(b) Which of the above factors will increase the value of K? Which will decrease it?

51. Predict the direction in which each of the following equilibria will shift if the pressure on the system is decreased by expansion.

(a) $Ni(s) + 4CO(g) \rightleftharpoons Ni(CO)_4(g)$

(b) $2CH_4(g) \rightleftharpoons C_2H_2(g) + 3H_2(g)$

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

52. Predict the direction in which each of the following equilibria will shift if the pressure on the system is decreased by expansion.

(a) $2H_2O_2(l) \rightleftharpoons O_2(g) + 2H_2O(l)$

(b) $2CH_4(g) \rightleftharpoons C_2H_2(g) + 3H_2(g)$

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

53. At a certain temperature, nitrogen and oxygen gases combine to form nitrogen oxide gas.

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

When equilibrium is established, the partial pressures of the gases are: $P_{N_2} = 1.200$ atm, $P_{O_2} = 0.800$ atm, $P_{NO} = 0.0220$ atm.

(a) Calculate K at the temperature of the reaction.

(b) After equilibrium is reached, more oxygen is added to make its partial pressure 1.200 atm. Calculate the partial pressure of all gases when equilibrium is reestablished.

54. Consider the following hypothetical reaction:

$$X_2(g) + R(s) \rightleftharpoons X_2R(g)$$

R has a molar mass of 73 g/mol. When equilibrium is established, a 2.5-L reaction vessel at 125°C contains 15.0 g of R, 4.3 atm of X_2, and 0.98 atm of X_2R.

(a) Calculate K for the reaction at 125°C.

(b) The mass of R is doubled. What are the partial pressures of X_2 and X_2R when equilibrium is reestablished?

(c) The partial pressure of X_2 is decreased to 2.0 atm. What are the partial pressures of X_2 and X_2R when equilibrium is reestablished?

55. Iodine chloride decomposes at high temperatures to iodine and chlorine gases.

$$2ICl(g) \rightleftharpoons I_2(g) + Cl_2(g)$$

Equilibrium is established at a certain temperature when the partial pressures of ICl, I_2, and Cl_2 are (in atm) 0.43, 0.16, and 0.27, respectively.

(a) Calculate K.

(b) If enough iodine condenses to decrease its partial pressure to 0.10 atm, in which direction will the reaction proceed? What is the partial pressure of iodine when equilibrium is reestablished?

56. Sulfur oxychloride, SO_2Cl_2, decomposes to sulfur dioxide and chlorine gases.

$$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$$

At a certain temperature, the equilibrium partial pressures of SO_2, Cl_2, and SO_2Cl_2 are 1.88 atm, 0.84 atm, and 0.27 atm, respectively.

(a) What is K at that temperature?

(b) Enough Cl_2 condenses to reduce its partial pressure to 0.68 atm. What are the partial pressures of all gases when equilibrium is reestablished?

57. For the following reaction

$$C(s) + 2H_2(g) \rightleftharpoons CH_4(g)$$

$K = 0.26$ at 1000°C (3 significant figures). What is the equilibrium constant at 750°C (3 significant figures)?

58. For the system

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

$K = 1.32$ at 627°C. What is the equilibrium constant at 555°C?

59. For a certain reaction, $\Delta H°$ is +33 kJ. What is the ratio of the equilibrium constant at 400 K to that at 200 K?

60. What is the value of $\Delta H°$ for a reaction in which K at 37°C is 48% of K at 27°C?

Unclassified

61. Hemoglobin (Hb) binds to both oxygen and carbon monoxide. When the carbon monoxide replaces the oxygen in an organism, the following reaction occurs:

$$HbO_2(aq) + CO(g) \rightleftharpoons HbCO(aq) + O_2(g)$$

At 37°C, K is about 200. When equal concentrations of HbO_2 and HbCO are present, the effect of CO inhalation is fatal. Assuming $P_{O_2} = 0.21$ atm, what is P_{CO} when $[HbO_2] = [HbCO]$?

62. Mustard gas, used in chemical warfare in World War I, has been found to be an effective agent in the chemotherapy of Hodgkin's disease. It can be produced according to the following reaction:

$$SCl_2(g) + 2C_2H_4(g) \rightleftharpoons S(CH_2CH_2Cl)_2(g)$$

An evacuated 5.0-L flask at 20.0°C is filled with 0.258 mol SCl_2 and 0.592 mol C_2H_4. After equilibrium is established, 0.0349 mol mustard gas is present.

(**a**) What is the partial pressure of each gas at equilibrium?

(**b**) What is K at 20.0°C?

63. At 1000 K, hydrogen dissociates into gaseous atoms:

$$H_2(g) \rightleftharpoons 2H(g)$$

where K is 5.0×10^{-18}. Ten moles of hydrogen gas are pumped into an evacuated 15.0-L flask and heated to 1000 K.

(**a**) How many atoms of H are in the flask when equilibrium is reached?

(**b**) What percent (in moles) of H_2 dissociated?

64. For the decomposition of $CaCO_3$ at 900°C, $K = 1.04$.

$$CaCO_3(s) \rightleftharpoons CaO(s) + O_2(g)$$

Find the smallest mass of $CaCO_3$ needed to reach equilibrium in a 5.00-L vessel at 900°C.

65. Isopropyl alcohol is the main ingredient in rubbing alcohol. It can decompose into acetone (the main ingredient in nail polish remover) and hydrogen gas according to the following reaction:

$$C_3H_7OH(g) \rightleftharpoons C_2H_6CO(g) + H_2(g)$$

At 180°C, the equilibrium constant for the decomposition is 0.45. If 20.0 mL ($d = 0.785$ g/mL) of isopropyl alcohol is placed in a 5.00-L vessel and heated to 180°C, what percentage remains undissociated at equilibrium?

66. Consider the equilibrium

$$H_2(g) + S(s) \rightleftharpoons H_2S(g)$$

When this system is at equilibrium at 25°C in a 2.00-L container, 0.120 mol of H_2, 0.034 mol of H_2S, and 0.4000 mol of S are present. When the temperature is increased to 35°C, the partial pressure of H_2 increases to 1.56 atm.

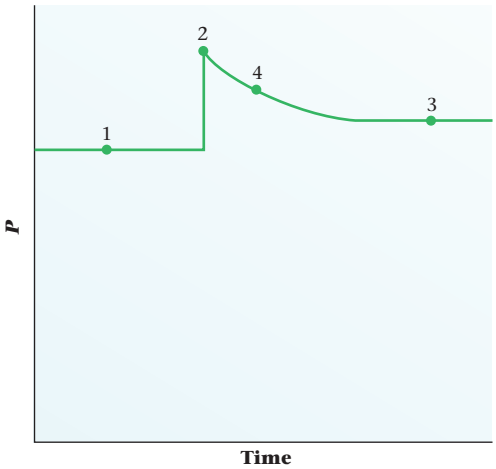
(**a**) What is K for the reaction at 25°C?

(**b**) What is K for the reaction at 35°C?

Conceptual Problems

67. Consider the following graph representing the progression of a reaction with time.

$$A(g) \rightleftharpoons 2B(g)$$



(**a**) What is the relationship between Q and K at Points 1, 3, and 4?

(**b**) What caused the disturbance at Point 2?

(**c**) Draw a similar graph for the same reaction, but increase the pressure in A.

68. The following data apply to the *unbalanced* equation

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

Time (s)	0	50	100	150	200	250
P_A (atm)	2.00	1.25	0.95	0.80	0.71	0.68
P_B (atm)	0.10	0.60	0.80	0.90	0.96	0.98

(**a**) On the basis of the data, balance the equation (simplest whole-number coefficients).

(**b**) Has the system reached equilibrium? Explain.

69. Consider the reaction:

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

At 25°C, only A, B, and C are present. The partial pressures of A, B, and D are given as P_A, P_B, and P_D. Equilibrium is established 18 minutes after the reaction starts. Use terms is less than (**LT**), is greater than (**GT**), is equal to (**EQ**), or insufficient information (**X**) to answer the following questions.

(**a**) P_D at 5 min _____ P_A.

(**b**) P_A at 21 min _____ P_A at 27 min.

(**c**) P_B at 7 min _____ P_B at 13 min.

(**d**) After 20 min, more B is added. When equilibrium is reestablished, K before the addition _____ K after the addition.

(e) After 20 min, the temperature is increased to 35°C. P_A before the temperature increase _____ P_A after the temperature increase after equilibrium is reestablished.

70. For the reaction

$$C(s) + CO_2(g) \rightleftharpoons 2CO(g)$$

$K = 168$ at 1273 K. If one starts with 0.3 atm of CO_2 and 12.0 g of C at 1273 K, will the equilibrium mixture contain

(a) mostly CO_2?
(b) mostly CO?
(c) roughly equal amounts of CO_2 and CO?
(d) only C?

71. Consider the system

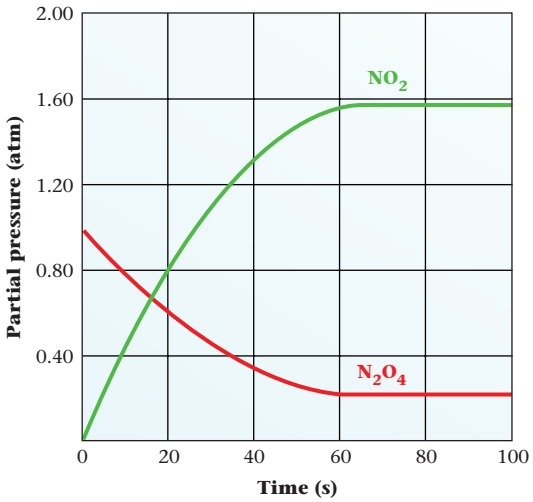
$$A(g) + 2B(g) + C(s) \rightleftharpoons 2D(g)$$

at 25°C. At zero time, only A, B, and C are present. The reaction reaches equilibrium 10 min after the reaction is initiated. Partial pressures of A, B, and D are written as P_A, P_B, and P_D.

Answer the questions below, using **LT** (for *is less than*), **GT** (for *is greater than*), **EQ** (for *is equal to*), or **MI** (for *more information required*).

(a) P_D at 11 min _____ P_D at 12 min.
(b) P_A at 5 min _____ P_A at 7 min.
(c) K for the forward reaction _____ K for the reverse reaction.
(d) At equilibrium, K _____ Q.
(e) After the system is at equilibrium, more of gas B is added. After the system returns to equilibrium, K before the addition of B _____ K after the addition of B.
(f) The same reaction is initiated, this time with a catalyst. K for the system without a catalyst _____ K for the system with a catalyst.
(g) K for the formation of one mole of D _____ K for the formation of two moles of D.
(h) The temperature of the system is increased to 35°C. P_B at equilibrium at 25°C _____ P_B at equilibrium at 35°C.
(i) Ten more grams of C are added to the system. P_B before the addition of C _____ P_B after the addition of C.

72. The graph below is similar to that of Figure 12.2.



If after 100 s have elapsed the partial pressure of N_2O_4 is increased to 1.0 atm, what will the graph for N_2O_4 look like beyond 100 s?

73. The system

$$3Z(g) + Q(g) \rightleftharpoons 2R(g)$$

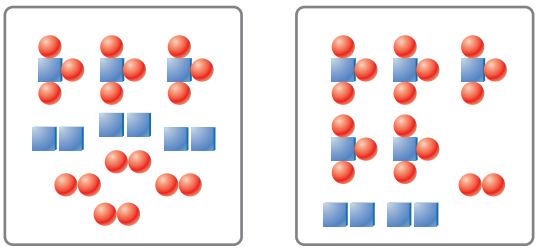
is at equilibrium when the partial pressure of Q is 0.44 atm. Sufficient R is added to increase the partial pressure of Q temporarily to 1.5 atm. When equilibrium is reestablished, the partial pressure of Q could be which of the following?

(a) 1.5 atm (b) 1.2 atm (c) 0.80 atm
(d) 0.44 atm (e) 0.40 atm

74. The figures below represent the following reaction at equilibrium at different temperatures.

$$A_2(g) + 3B_2(g) \rightleftharpoons 2AB_3(g)$$

where squares represent atom A and circles represent atom B. Is the reaction exothermic?



75. Criticize the statement "The rate of most reactions increases as the temperature rises. Thus, the equilibrium constant of most reactions increases as temperature rises."

76. Consider the statement "The equilibrium constant for a mixture of hydrogen, nitrogen, and ammonia is 3.41." What information is missing from this statement?

Challenge Problems

77. Consider the following reaction at a certain temperature:

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

A reaction mixture contains 0.70 atm of O_2 and 0.81 atm of NO. When equilibrium is established, the total pressure in the reaction vessel is 1.20 atm. Find K.

78. Derive the relationship

$$K = K_c \times (RT)^{\Delta n_g}$$

where K_c is the equilibrium constant using molarities and Δn_g is the change in the number of moles of gas in the reaction (see page 310). (*Hint:* Recall that $P_A = n_A RT/V$ and $n_A/V = [A]$.)

79. Ammonia can decompose into its constituent elements according to the reaction

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

The equilibrium constant for the decomposition at a certain temperature is 2.5. Calculate the partial pressures of all the gases at equilibrium if ammonia with a pressure of 1.00 atm is sealed in a 3.0-L flask.

80. Hydrogen iodide gas decomposes to hydrogen gas and iodine gas:

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

To determine the equilibrium constant of the system, identical one-liter glass bulbs are filled with 3.20 g of HI and maintained at a certain temperature. Each bulb is periodically

opened and analyzed for iodine formation by titration with sodium thiosulfate, $Na_2S_2O_3$.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$$

It is determined that when equilibrium is reached, 37.0 mL of 0.200 *M* $Na_2S_2O_3$ is required to titrate the iodine. What is *K* at the temperature of the experiment?

81. For the system

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

at 1000 K, $K = 0.45$. Sulfur trioxide, originally at 1.00 atm pressure, partially dissociates to SO_2 and O_2 at 1000 K. What is its partial pressure at equilibrium?

82. A student studies the equilibrium

$$I_2(g) \rightleftharpoons 2I(g)$$

at a high temperature. She finds that the total pressure at equilibrium is 40% greater than it was originally, when only I_2 was present. What is *K* for this reaction at that temperature?

83. At a certain temperature, the reaction

$$Xe(g) + 2F_2(g) \rightleftharpoons XeF_4(g)$$

gives a 50.0% yield of XeF_4, starting with Xe ($P_{Xe} = 0.20$ atm) and F_2 ($P_{F_2} = 0.40$ atm). Calculate *K* at this temperature. What must the initial pressure of F_2 be to convert 75.0% of the xenon to XeF_4?

84. Benzaldehyde, a flavoring agent, is obtained by the dehydrogenation of benzyl alcohol.

$$C_6H_5CH_2OH(g) \rightleftharpoons C_6H_5CHO(g) + H_2(g)$$

K for the reaction at 250°C is 0.56. If 1.50 g of benzyl alcohol is placed in a 2.0-L flask and heated to 250°C,

(**a**) what is the partial pressure of the benzaldehyde when equilibrium is established?

(**b**) how many grams of benzyl alcohol remain at equilibrium?

85. Hydrogen and nitrogen react to form NH_3

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

At a certain temperature, it is determined that an equilibrium mixture of N_2, H_2, and NH_3 has a total pressure of 3.065 atm. The mixture has 20.4% NH_3. What is *K* at that temperature?

86. At 165°C, a solid chloride (X) reacts with 0.0417 mol of steam to form the solid oxychloride, Y, and HCl gas. Steam and HCl have a 1:2 stoichiometric ratio in the reaction

$$X(s) + H_2O(g) \rightleftharpoons Y(s) + 2HCl(g)$$

When the reaction reaches equilibrium, the gases are transferred without loss to a 2.50-L vessel. The temperature is kept at 165°C. Sufficient silver(I) ion is added to precipitate the chloride as AgCl. If 7.29 g of AgCl are obtained, what is *K* for the reaction of the chloride with steam at 165°C?