

# Chemical Equilibrium

# 17





Gaseous ammonia,  $\text{NH}_3$ , and gaseous hydrogen chloride,  $\text{HCl}$ , react to form solid  $\text{NH}_4\text{Cl}$ , the white smoke. In the reverse reaction, solid  $\text{NH}_4\text{Cl}$  decomposes when heated, to form gaseous  $\text{NH}_3$  and  $\text{HCl}$ .

## OUTLINE

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| 17-3 | Variation of $K_c$ with the Form of the Balanced Equation | 17-11 | Heterogeneous Equilibria  |
| 17-4 | The Reaction Quotient                                     | 17-12 | Relationship between $\Delta G_{\text{rxn}}^0$ and the Equilibrium Constant |
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## OBJECTIVES

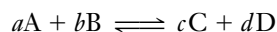
After you have studied this chapter, you should be able to

- Explain the basic ideas of chemical equilibrium
- Explain what an equilibrium constant is and what it tells us
- Explain what a reaction quotient is and what it tells us
- Use equilibrium constants to describe systems at equilibrium
- Recognize the factors that affect equilibria and predict the resulting effects
- Use the equilibrium constant expressed in terms of partial pressures ( $K_p$ ) and relate it to  $K_c$
- Describe heterogeneous equilibria and write their equilibrium constants
- Use the relationships between thermodynamics and equilibrium
- Estimate equilibrium constants at different temperatures

### 17-1 BASIC CONCEPTS

Most chemical reactions do not go to completion. That is, when reactants are mixed in stoichiometric quantities, they are not completely converted to products. Reactions that do not go to completion *and* that can occur in either direction are called **reversible reactions**.

Reversible reactions can be represented in general terms as follows, where the capital letters represent formulas and the lowercase letters represent the stoichiometric coefficients in the balanced equation.



See the *Saunders Interactive General Chemistry CD-ROM*, Screen 16.2, The Principle of Microscopic Reversibility.

The double arrow ( $\rightleftharpoons$ ) indicates that the reaction is reversible—that is, both the forward and reverse reactions occur simultaneously. In discussions of chemical equilibrium, the substances that appear on the left side of the balanced chemical equation are called the “reactants,” and those on the right side are called the “products.” In fact, the reaction can proceed in *either direction*. When A and B react to form C and D at the same rate at which C and D react to form A and B, the system is at *equilibrium*.

**Chemical equilibrium** exists when two opposing reactions occur simultaneously at the same rate.

Chemical equilibria are **dynamic equilibria**; that is, individual molecules are continually reacting, even though the overall composition of the reaction mixture does not change. In a system at equilibrium, the equilibrium is said to lie toward the right if more C and D are present than A and B, and to lie toward the left if more A and B are present.

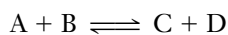
Consider a case in which the coefficients in the equation for a reaction are all 1. When substances A and B react, the rate of the forward reaction decreases as time passes because the concentration of A and B decrease.



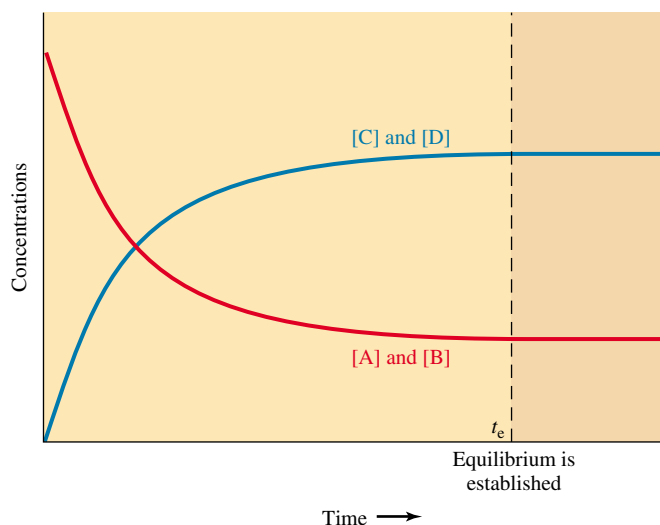
As the concentrations of C and D build up, they start to re-form A and B.




As more C and D molecules are formed, more can react, and so the rate of reaction between C and D increases with time. Eventually, the two reactions occur at the same rate, and the system is at equilibrium (Figure 17-1).



If a reaction begins with only C and D present, the rate of reaction (2) decreases with time, and the rate of reaction (1) increases with time until the two rates are equal.



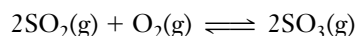
The dynamic nature of chemical equilibrium can be proved experimentally by inserting radioactive atoms into a small percentage of molecules and following them through the reaction. Even when the initial mixture is at equilibrium, radioactive atoms eventually appear in both reactant and product molecules.

 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 16.3, The Equilibrium State.

**Figure 17-1** Variation in the concentrations of species present in the  $A + B \rightleftharpoons C + D$  system as equilibrium is approached, beginning with equal concentrations of A and B only. For this reaction, production of products is favored. As we will see, this corresponds to a value of the equilibrium constant greater than 1. Brackets, [ ], represent the concentration, in moles per liter, of the species enclosed within them. The time axis may be in any convenient units—seconds, minutes, hours, and so on.

### The SO<sub>2</sub>–O<sub>2</sub>–SO<sub>3</sub> System

Consider the reversible reaction of sulfur dioxide with oxygen to form sulfur trioxide at 1500 K.



The numbers in this discussion were determined experimentally.

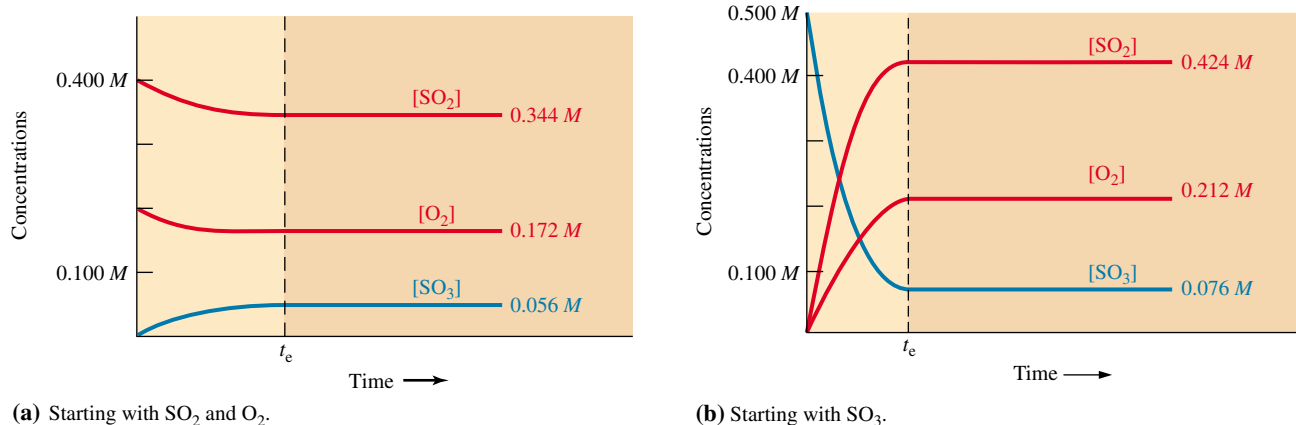
Suppose 0.400 mole of SO<sub>2</sub> and 0.200 mole of O<sub>2</sub> are injected into a closed 1.00-liter container. When equilibrium is established (at time  $t_e$ , Figure 17-2a), we find that 0.056 mole of SO<sub>3</sub> has formed and that 0.344 mole of SO<sub>2</sub> and 0.172 mole of O<sub>2</sub> remain unreacted. The reaction does not go to completion. These changes are summarized in the following reaction summary, using molarity units rather than moles. (They are numerically identical here because the volume of the reaction vessel is 1.00 liter.) The *net reaction* is represented by the *changes* in concentrations.

A setup such as this is called a “reaction summary.” The ratio in the “change due to rxn” line is determined by the coefficients in the balanced equation.

	$2\text{SO}_2(\text{g})$	+	$\text{O}_2(\text{g})$	$\rightleftharpoons$	$2\text{SO}_3(\text{g})$
initial conc'n	0.400 M		0.200 M		0
change due to rxn	–0.056 M		–0.028 M		+0.056 M
equilibrium conc'n	0.344 M		0.172 M		0.056 M

In another experiment, 0.500 mole of SO<sub>3</sub> is introduced alone into a closed 1.00-liter container. When equilibrium is established (at time  $t_e$ , Figure 17-2b), 0.076 mole of SO<sub>3</sub>, 0.212 mole of O<sub>2</sub>, and 0.424 mole of SO<sub>2</sub> are present. These equilibrium amounts differ from those in the previous case, but they are related in an important way, as we will see in the next section. This time the reaction proceeds from *right to left* as the equation is written. The changes in concentration are in the same 2 : 1 : 2 ratio as in the previous case, as required by the coefficients of the balanced equation. The time required to reach equilibrium may be longer or shorter.

	$2\text{SO}_2(\text{g})$	+	$\text{O}_2(\text{g})$	$\rightleftharpoons$	$2\text{SO}_3(\text{g})$
initial conc'n	0		0		0.500 M
change due to rxn	+0.424 M		+0.212 M		–0.424 M
equilibrium conc'n	0.424 M		0.212 M		0.076 M



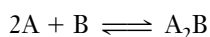
**Figure 17-2** Establishment of equilibrium in the  $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$  system. (a) Beginning with stoichiometric amounts of SO<sub>2</sub> and O<sub>2</sub> and no SO<sub>3</sub>. (b) Beginning with only SO<sub>3</sub> and no SO<sub>2</sub> or O<sub>2</sub>. Greater changes in concentrations occur to establish equilibrium when starting with SO<sub>3</sub> than when starting with SO<sub>2</sub> and O<sub>2</sub>. The equilibrium favors SO<sub>2</sub> and O<sub>2</sub>.

The results of these experiments are summarized in the following table and in Figure 17-2.

	Initial Concentrations			Equilibrium Concentrations		
	[SO <sub>2</sub> ]	[O <sub>2</sub> ]	[SO <sub>3</sub> ]	[SO <sub>2</sub> ]	[O <sub>2</sub> ]	[SO <sub>3</sub> ]
Experiment 1	0.400 M	0.200 M	0 M	0.344 M	0.172 M	0.056 M
Experiment 2	0 M	0 M	0.500 M	0.424 M	0.212 M	0.076 M

## 17-2 THE EQUILIBRIUM CONSTANT

Suppose a reversible reaction occurs by a *one-step mechanism*.



The rate of the forward reaction is  $\text{Rate}_f = k_f[A]^2[B]$ ; the rate of the reverse reaction is  $\text{Rate}_r = k_r[A_2B]$ . In these expressions,  $k_f$  and  $k_r$  are the *specific rate constants* of the forward and reverse reactions, respectively. By definition, the two rates are equal *at equilibrium* ( $\text{Rate}_f = \text{Rate}_r$ ). So we write

$$k_f[A]^2[B] = k_r[A_2B] \quad (\text{at equilibrium})$$

Dividing both sides of this equation by  $k_r$  and by  $[A]^2[B]$  gives

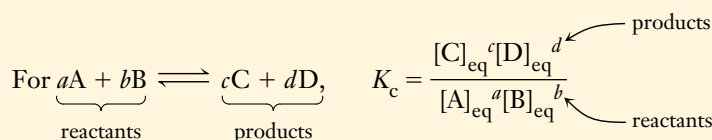
$$\frac{k_f}{k_r} = \frac{[A_2B]}{[A]^2[B]}$$

At any specific temperature, both  $k_f$  and  $k_r$  are constants, so  $k_f/k_r$  is also a constant.

This ratio is given a special name and symbol, the **equilibrium constant**,  $K_c$  or simply **K**.


$$K_c = \frac{[A_2B]}{[A]^2[B]} \quad (\text{at equilibrium})$$

Even if the overall reaction occurs by a multistep mechanism, we can show that the equilibrium constant is the product and ratio of the rate constants for each step of the mechanism. Regardless of the mechanism by which this reaction occurs, the concentrations of reaction intermediates cancel out and the equilibrium constant expression has the same form. For a reaction in general terms, the equilibrium constant can always be written as follows:




The equilibrium constant  $K_c$  is defined as the product of the *equilibrium concentrations* (moles per liter) of the products, each raised to the power that corresponds to its coefficient in the balanced equation, divided by the product of the *equilibrium concentrations* of reactants, each raised to the power that corresponds to its coefficient in the balanced equation.

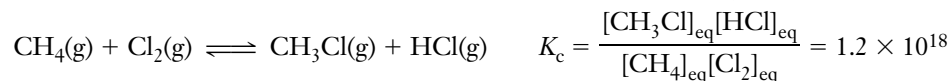
The subscript c refers to concentrations. The brackets, [ ], in this expression indicate *equilibrium concentrations* in moles per liter.

 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 16.4, The Equilibrium Constant.



 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 16.6, Writing Equilibrium Expressions.

In general, numerical values for  $K_c$  can come only from experiments. Some equilibrium constant expressions and their numerical values at 25°C are



We have used the subscript “eq” to emphasize that the concentrations in the equilibrium constant expression are those at equilibrium. For the remainder of this text, we shall omit these subscripts, remembering that calculations with  $K_c$  values always involve *equilibrium values* of concentrations.

The thermodynamic definition of the equilibrium constant involves activities rather than concentrations. The **activity** of a component of an ideal mixture is the ratio of its concentration or partial pressure to a standard concentration (1 *M*) or pressure (1 atm). For now, we can consider the activity of each species to be a dimensionless quantity whose numerical value can be determined as follows.


1. For any pure liquid or pure solid, the activity is taken as 1.
2. For components of ideal solutions, the activity of each component is taken to be the ratio of its molar concentration to a standard concentration of 1 *M*, so the units cancel.
3. For gases in an ideal mixture, the activity of each component is taken to be the ratio of its partial pressure to a standard pressure of 1 atm, so again the units cancel.

Because of the use of activities, *the equilibrium constant has no units; the values we put into  $K_c$  are numerically equal to molar concentrations, but are dimensionless*, that is, they have no units. In this text, calculations have usually included units along with numbers. Calculations involving equilibrium are frequently carried out without units; we will follow that practice in this text.

The magnitude of  $K_c$  is a measure of the extent to which reaction occurs. For any balanced chemical equation, the value of  $K_c$

1. is constant at a given temperature;
2. changes if the temperature changes;
3. does not depend on the initial concentrations.

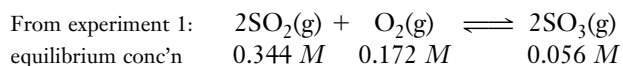
These are three very important ideas.

 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 16.5, The Meaning of the Equilibrium Constant.

A value of  $K_c$  *much* greater than 1 indicates that the “numerator concentrations” (products) would be much greater than the “denominator concentrations” (reactants); this means that at equilibrium most of the reactants would be converted into products. For example, the reaction  $\text{CH}_4(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{CH}_3\text{Cl}(\text{g}) + \text{HCl}(\text{g})$  shown earlier goes nearly to completion; in Chapter 15, we called such a reaction “product-favored.” On the other hand, if  $K_c$  is quite small, equilibrium is established when most of the reactants remain unreacted and only small amounts of products are formed. The reaction  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$  shown earlier reaches equilibrium with only a tiny amount of NO present; in Chapter 15, we called such a reaction “reactant-favored.”

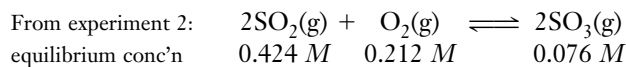
For a given chemical reaction at a specific temperature, the product of the concentrations of the products formed by the reaction, each raised to the appropriate power, divided by the product of the concentrations of the reactants, each raised to the appropriate power, always has the same value, that is,  $K_c$ . This does *not* mean that the individual equilibrium concentrations for a given reaction are always the same, but it does mean that this particular numerical combination of their values ( $K_c$ ) is constant.

Consider again the  $\text{SO}_2\text{-O}_2\text{-SO}_3$  equilibrium described in Section 17-1. We can use the *equilibrium* concentrations from either experiment to calculate the value of the equilibrium constant for this reaction at 1500 K.



Substituting the numerical values (without units) into the equilibrium expression gives the value of the equilibrium constant.

$$\text{Alternatively, } K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} = \frac{(0.056)^2}{(0.344)^2(0.172)} = 0.15$$



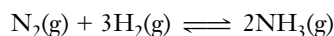
$$K_c = \frac{(0.076)^2}{(0.424)^2(0.212)} = 0.15$$

No matter what combinations of reactant and product concentrations we start with, the resulting *equilibrium* concentrations at 1500 K for this reversible reaction would always give the same value of  $K_c$ , 0.15.

For the reversible reaction written *as it is* with  $\text{SO}_2$  and  $\text{O}_2$  as reactants and  $\text{SO}_3$  as the product,  $K_c$  is 0.15 at 1500 K.

### EXAMPLE 17-1 Calculation of $K_c$

Some nitrogen and hydrogen are placed in an empty 5.00-liter container at 500°C. When equilibrium is established, 3.01 mol of  $\text{N}_2$ , 2.10 mol of  $\text{H}_2$ , and 0.565 mol of  $\text{NH}_3$  are present. Evaluate  $K_c$  for the following reaction at 500°C.



#### Plan

The *equilibrium concentrations* are obtained by dividing the number of moles of each reactant and product by the volume, 5.00 liters. Then we substitute these equilibrium concentrations into the equilibrium constant expression.

#### Solution

The equilibrium concentrations are

$$\begin{aligned} [\text{N}_2] &= 3.01 \text{ mol}/5.00 \text{ L} = 0.602 \text{ M} \\ [\text{H}_2] &= 2.10 \text{ mol}/5.00 \text{ L} = 0.420 \text{ M} \\ [\text{NH}_3] &= 0.565 \text{ mol}/5.00 \text{ L} = 0.113 \text{ M} \end{aligned}$$

We substitute these numerical values into the expression for  $K_c$ .

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(0.113)^2}{(0.602)(0.420)^3} = 0.286$$



See the *Saunders Interactive General Chemistry CD-ROM*, Screen 16.8, Determining an Equilibrium Constant.



See the *Saunders Interactive General Chemistry CD-ROM*, Screen 16.9, Systems at Equilibrium.

Remember that the concentrations in  $K_c$  calculations are *equilibrium* values of molar concentration.

Thus, for the reaction of  $\text{N}_2$  and  $\text{H}_2$  to form  $\text{NH}_3$  at  $500^\circ\text{C}$ , we can write

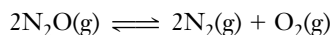
$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = 0.286$$

The small value of  $K_c$  indicates that the equilibrium lies to the left.

The value of  $K_c$  from Example 17-1 is much different from the value given earlier for the same reaction at  $25^\circ\text{C}$ . For this reaction, products are favored at the lower temperature ( $K_c = 3.6 \times 10^8$  at  $25^\circ\text{C}$ ), whereas reactants are favored at the higher temperature ( $K_c = 0.286$  at  $500^\circ\text{C}$ ). The dependence of  $K_c$  on temperature will be discussed later in this chapter; for now, we note that it can depend strongly on temperature.

### EXAMPLE 17-2 Calculation of $K_c$

We put 10.0 moles of  $\text{N}_2\text{O}$  into a 2.00-L container at some temperature, where it decomposes according to



At equilibrium, 2.20 moles of  $\text{N}_2\text{O}$  remain. Calculate the value of  $K_c$  for the reaction.

#### Plan

We express all concentrations in moles per liter. The mole ratio from the balanced chemical equation allows us to find the changes in concentrations of the other substances in the reaction. We use the reaction summary to find the equilibrium concentrations to use in the  $K_c$  expression.

#### Solution

At equilibrium, 2.20 mol  $\text{N}_2\text{O}$  remain, so

$$\begin{aligned} \text{? mol N}_2\text{O reacting} &= 10.00 \text{ mol N}_2\text{O initial} - 2.20 \text{ mol N}_2\text{O remaining} \\ &= 7.80 \text{ mol N}_2\text{O reacting} \end{aligned}$$

The initial  $[\text{N}_2\text{O}] = (10.00 \text{ mol})/(2.00 \text{ L}) = 5.00 \text{ M}$ ; the concentration of  $\text{N}_2\text{O}$  that reacts is  $(7.80 \text{ mol})/(2.00 \text{ L}) = 3.90 \text{ M}$ . From the balanced chemical equation, each 2 mol  $\text{N}_2\text{O}$  that react produces 2 mol  $\text{N}_2$  and 1 mol  $\text{O}_2$ , or a reaction ratio of

$$1 \text{ mol N}_2\text{O reacting} : 1 \text{ mol N}_2 \text{ formed} : \frac{1}{2} \text{ mol O}_2 \text{ formed}$$

We can now write the reaction summary.

	$2\text{N}_2\text{O}(\text{g})$	$\rightleftharpoons$	$2\text{N}_2(\text{g})$	+	$\text{O}_2(\text{g})$
initial	5.00 M		0		0
change due to rxn	-3.90 M		+3.90 M	+ $\frac{1}{2}$ (3.90)	= 1.95 M
equilibrium	1.10 M		3.90 M		1.95 M

We put these equilibrium concentrations into the equilibrium constant expression and evaluate  $K_c$ .

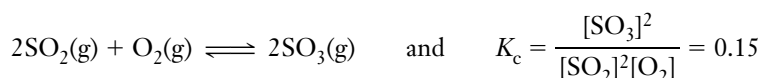
$$K_c = \frac{[\text{N}_2]^2[\text{O}_2]}{[\text{N}_2\text{O}]^2} = \frac{(3.90)^2(1.95)}{(1.10)^2} = 24.5$$

You should now work Exercises 24 and 28.

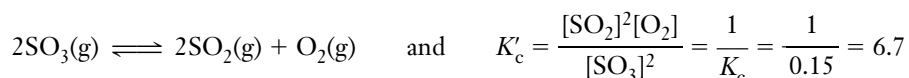


### 17-3 VARIATION OF $K_c$ WITH THE FORM OF THE BALANCED EQUATION

The value of  $K_c$  depends on the form of the balanced equation for the reaction. We wrote the equation for the reaction of  $\text{SO}_2$  and  $\text{O}_2$  to form  $\text{SO}_3$ , and its equilibrium constant expression as



Suppose we write the equation for the same reaction in reverse. The equation and its equilibrium constant, written this way, are



We see that  $K'_c$ , the equilibrium constant for the reaction written in reverse, is the *reciprocal* of  $K_c$ , the equilibrium constant for the original reaction.


If the equation for the reaction were written as



If an *equation* for a reaction is *multiplied* by any factor,  $n$ , then the *original value* of  $K_c$  is raised to the  $n$ th power. Thus, we must always write the balanced chemical equation to accompany the value of  $K_c$  for a chemical reaction.

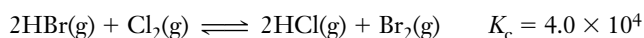
Reversing an equation is the same as multiplying all coefficients by  $-1$ . This reverses the roles of “reactants” and “products.”

We see that  $K''_c$  is the square root of  $K_c$ .  $K_c^{1/2}$  means the square root of  $K_c$ .

 See the Saunders Interactive General Chemistry CD-ROM, Screen 16.7, Manipulating Equilibrium Expressions.

#### EXAMPLE 17-3 Variation of the Form of $K_c$

You are given the following reaction and its equilibrium constant at a given temperature.



Write the expression for, and calculate the numerical value of, the equilibrium constant for each of the following at the same temperature.

- (a)  $4\text{HBr}(\text{g}) + 2\text{Cl}_2(\text{g}) \rightleftharpoons 4\text{HCl}(\text{g}) + 2\text{Br}_2(\text{g})$   
 (b)  $\text{HBr}(\text{g}) + \frac{1}{2}\text{Cl}_2(\text{g}) \rightleftharpoons \text{HCl}(\text{g}) + \frac{1}{2}\text{Br}_2(\text{g})$

A coefficient of  $\frac{1}{2}$  refers to  $\frac{1}{2}$  of a mole, *not*  $\frac{1}{2}$  of a molecule.

#### Plan

We recall the definition of the equilibrium constant. For the original equation,

$$K_c = \frac{[\text{HCl}]^2[\text{Br}_2]}{[\text{HBr}]^2[\text{Cl}_2]} = 4.0 \times 10^4$$

#### Solution

(a) The original equation has been multiplied by 2, so  $K_c$  must be squared.

$$K'_c = \frac{[\text{HCl}]^4[\text{Br}_2]^2}{[\text{HBr}]^4[\text{Cl}_2]^2} \quad K'_c = (K_c)^2 = (4.0 \times 10^4)^2 = 1.6 \times 10^9$$

(b) The original equation has been multiplied by  $\frac{1}{2}$  (divided by 2), so  $K_c$  must be raised to the  $\frac{1}{2}$  power. The value of  $K'_c$  is the square root of the original  $K_c$  value.

$$K_c'' = \frac{[\text{HCl}][\text{Br}_2]^{1/2}}{[\text{HBr}][\text{Cl}_2]^{1/2}} = \sqrt{K_c} = \sqrt{4.0 \times 10^4} = 2.0 \times 10^2$$

You should now work Exercise 30.

## 17-4 THE REACTION QUOTIENT

The reaction quotient is sometimes called the **mass action expression**.

The **reaction quotient**,  $Q$ , for the general reaction is given as follows.

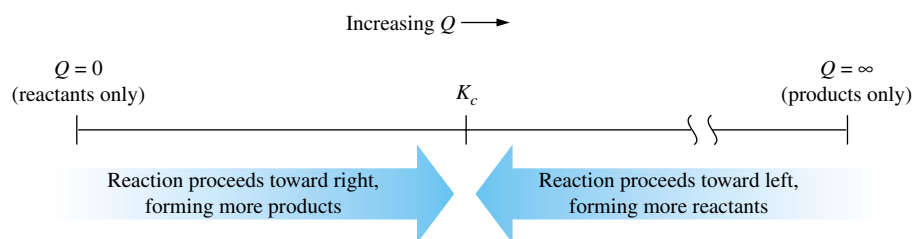
$$\text{For } aA + bB \rightleftharpoons cC + dD, \quad Q = \frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b} \quad \left\{ \begin{array}{l} \text{not necessarily} \\ \text{equilibrium} \\ \text{concentrations} \end{array} \right.$$

When the forward reaction occurs to a greater extent than the reverse reaction, we say that a *net* forward reaction has occurred.

The reaction quotient has the same *form* as the equilibrium constant, but it involves specific values that are not *necessarily* equilibrium concentrations. If they *are* equilibrium concentrations, then  $Q = K_c$ . The concept of the reaction quotient is very useful. We can compare the magnitude of  $Q$  with that of  $K_c$  for a reaction under given conditions to decide whether the forward or the reverse reaction must occur to a greater extent to establish equilibrium.

We can think of the reaction quotient,  $Q$ , as a measure of the progress of the reaction. When the mixture contains *only* reactants, the concentrations in the numerator are zero, so  $Q = 0$ . As the reaction proceeds to the right, the product concentrations (numerator) increase and the reactant concentrations (denominator) decrease, so  $Q$  increases to an infinitely large value when all reactants have been consumed and only products remain. The value of  $K_c$  is a particular value of  $Q$  that represents equilibrium mixtures for the reaction.

If at any time  $Q < K_c$ , the forward reaction must occur to a greater extent than the reverse reaction for equilibrium to be established. This is because when  $Q < K_c$ , the numerator of  $Q$  is too small and the denominator is too large. To increase the numerator and to reduce the denominator, A and B must react to produce C and D. Conversely, if  $Q > K_c$ , the reverse reaction must occur to a greater extent than the forward reaction for equilibrium to be reached. When the value of  $Q$  reaches the value of  $K_c$ , the system is at equilibrium, so no further *net* reaction occurs.



$Q < K_c$  Forward reaction predominates until equilibrium is established.

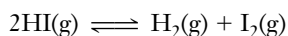
$Q = K_c$  System is at equilibrium.

$Q > K_c$  Reverse reaction predominates until equilibrium is established.

In Example 17-4 we calculate the value for  $Q$  and compare it with the *known* value of  $K_c$  to predict the direction of the reaction that leads to equilibrium.

### EXAMPLE 17-4 The Reaction Quotient

At a very high temperature,  $K_c = 65.0$  for the following reaction.



The following concentrations were detected in a mixture. Is the system at equilibrium? If not, in which direction must the reaction proceed for equilibrium to be established?

$$[\text{HI}] = 0.500 \text{ M}, \quad [\text{H}_2] = 2.80 \text{ M}, \quad \text{and} \quad [\text{I}_2] = 3.40 \text{ M}$$

#### Plan

We substitute these concentrations into the expression for the reaction quotient to calculate  $Q$ . Then we compare  $Q$  with  $K_c$  to see whether the system is at equilibrium.

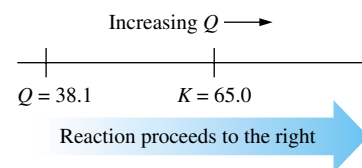
#### Solution

$$Q = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = \frac{(2.80)(3.40)}{(0.500)^2} = 38.1$$

But  $K_c = 65.0$ , so  $Q < K_c$ . The system is *not* at equilibrium. For equilibrium to be established, the value of  $Q$  must *increase* until it equals  $K_c$ . This can occur only if the numerator *increases* and the denominator *decreases*. Thus, the forward (left-to-right) reaction must occur to a greater extent than the reverse reaction; that is, some HI must react to form more  $\text{H}_2$  and  $\text{I}_2$  to reach equilibrium.

You should now work Exercises 38, 40, and 42.

These concentrations could be present if we started with a mixture of HI,  $\text{H}_2$ , and  $\text{I}_2$ .



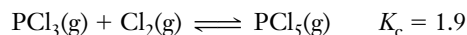
## 17-5 USES OF THE EQUILIBRIUM CONSTANT, $K_c$

We have seen (Section 17-2) how to calculate the value of  $K_c$  from one set of equilibrium concentrations. Once that value has been obtained, the process can be turned around to calculate equilibrium *concentrations* from the equilibrium *constant*.

The equilibrium constant is a “constant” only if the temperature does not change.

### EXAMPLE 17-5 Finding Equilibrium Concentrations

The equation for the following reaction and the value of  $K_c$  at a given temperature are given. An equilibrium mixture in a 1.00-liter container contains 0.25 mol of  $\text{PCl}_5$  and 0.16 mol of  $\text{PCl}_3$ . What equilibrium concentration of  $\text{Cl}_2$  must be present?




#### Plan

We write the equilibrium constant expression and its value. Only one term,  $[\text{Cl}_2]$ , is unknown. We solve for it.

#### Solution

Because the volume of the container is 1.00 liter, the molar concentration (mol/L) of each substance is numerically equal to the number of moles. The equilibrium constant expression and its numeric value are

 See the Saunders Interactive General Chemistry CD-ROM, Screen 16.10, Estimating Equilibrium Concentrations.

$$K_c = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]} = 1.9$$

$$[\text{Cl}_2] = \frac{[\text{PCl}_5]}{K_c[\text{PCl}_3]} = \frac{(0.25)}{(1.9)(0.16)} = 0.82 \text{ M}$$

Often we know the starting concentrations and want to know how much of each reactant and each product would be present at equilibrium. The next two examples illustrate this important kind of calculation.

### EXAMPLE 17-6 Finding Equilibrium Concentrations

For the following reaction, the equilibrium constant is 49.0 at a certain temperature. If 0.400 mol each of A and B are placed in a 2.00-liter container at that temperature, what concentrations of all species are present at equilibrium?



We have represented chemical formulas by single letters to simplify the notation in these calculations.

#### Plan

First we find the initial concentrations. Then we write the reaction summary and represent the equilibrium concentrations algebraically. Finally we substitute the algebraic representations of equilibrium concentrations into the  $K_c$  expression and find the equilibrium concentrations.

#### Solution

The initial concentrations are

$$[\text{A}] = \frac{0.400 \text{ mol}}{2.00 \text{ L}} = 0.200 \text{ M} \quad [\text{C}] = 0 \text{ M}$$

$$[\text{B}] = \frac{0.400 \text{ mol}}{2.00 \text{ L}} = 0.200 \text{ M} \quad [\text{D}] = 0 \text{ M}$$

We know that the reaction can only proceed to the right because only “reactants” are present. The reaction summary includes the values, or symbols for the values, of (1) initial concentrations, (2) changes in concentrations, and (3) concentrations at equilibrium.

Let  $x$  = moles per liter of A that react; then  $x$  = moles per liter of B that react and  $x$  = moles per liter of C and D that are formed.

	A	+	B	$\rightleftharpoons$	C	+	D
initial	0.200 M		0.200 M		0 M		0 M
change due to rxn	$-x \text{ M}$		$-x \text{ M}$		$+x \text{ M}$		$+x \text{ M}$
at equilibrium	$(0.200 - x) \text{ M}$		$(0.200 - x) \text{ M}$		$x \text{ M}$		$x \text{ M}$

Now  $K_c$  is known, but concentrations are not. But the equilibrium concentrations have all been expressed in terms of the single variable  $x$ . We substitute the equilibrium concentrations (*not* the initial ones) into the  $K_c$  expression and solve for  $x$ .

$$K_c = \frac{[\text{C}][\text{D}]}{[\text{A}][\text{B}]} = 49.0$$

$$\frac{(x)(x)}{(0.200 - x)(0.200 - x)} = \frac{x^2}{(0.200 - x)^2} = 49.0$$

This quadratic equation has a perfect square on both sides. We solve it by taking the square roots of both sides of the equation and then rearranging for  $x$ .

The coefficients in the equation are all 1's, so the reaction ratio must be 1:1:1:1.

$$\frac{x}{0.200 - x} = 7.00$$

$$x = 1.40 - 7.00x \quad 8.00x = 1.40 \quad x = \frac{1.40}{8.00} = 0.175$$

Now we know the value of  $x$ , so the equilibrium concentrations are

$$[A] = (0.200 - x) M = 0.025 M; \quad [C] = x M = 0.175 M$$

$$[B] = (0.200 - x) M = 0.025 M; \quad [D] = x M = 0.175 M$$

We see that the equilibrium concentrations of products are much greater than those of reactants because  $K_c$  is much greater than 1.

To check our answers we use the equilibrium concentrations to calculate  $Q$  and verify that its value is equal to  $K_c$ .

$$Q = \frac{[C][D]}{[A][B]} = \frac{(0.175)(0.175)}{(0.025)(0.025)} = 49 \quad \text{Recall that } K_c = 49.0$$

The ideas developed in Example 17-6 may be applied to cases in which the reactants are mixed in nonstoichiometric amounts. This is shown in Example 17-7.

### EXAMPLE 17-7 Finding Equilibrium Concentrations

Consider the same system as in Example 17-6 at the same temperature. If 0.600 mol of A and 0.200 mol of B are mixed in a 2.00-liter container and allowed to reach equilibrium, what are the equilibrium concentrations of all species?

#### Plan

We proceed as we did in Example 17-6. The only difference is that now we have *nonstoichiometric* amounts of reactants.

#### Solution

As in Example 17-6, we let  $x = \text{mol/L}$  of A that react; then  $x = \text{mol/L}$  of B that react, and  $x = \text{mol/L}$  of C and D formed.

	A	+	B	$\rightleftharpoons$	C	+	D
initial	0.300 M		0.100 M		0 M		0 M
change due to rxn	$-x M$		$-x M$		$+x M$		$+x M$
equilibrium	$(0.300 - x) M$		$(0.100 - x) M$		$x M$		$x M$

The initial concentrations are governed by the amounts of reactants mixed together. But *changes in concentrations* due to reaction must occur in the 1:1:1:1 ratio required by the coefficients in the balanced equation.

$$K_c = \frac{[C][D]}{[A][B]} = 49.0 \quad \text{so} \quad \frac{(x)(x)}{(0.300 - x)(0.100 - x)} = 49.0$$

The left side of this equation is *not* a perfect square.

We can arrange this quadratic equation into the standard form.

$$\frac{x^2}{0.0300 - 0.400x + x^2} = 49.0$$

$$x^2 = 1.47 - 19.6x + 49.0x^2$$

$$48.0x^2 - 19.6x + 1.47 = 0$$

Quadratic equations can be solved by use of the quadratic formula.

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

In this case  $a = 48.0$ ,  $b = -19.6$ , and  $c = 1.47$ . Substituting these values gives

$$\begin{aligned} x &= \frac{-(-19.6) \pm \sqrt{(-19.6)^2 - 4(48.0)(1.47)}}{2(48.0)} \\ &= \frac{19.6 \pm 10.1}{96.0} = 0.309 \quad \text{or} \quad 0.099 \end{aligned}$$

Solving a quadratic equation always yields two roots. One root (the answer) has physical meaning. The other root, while mathematically correct, is extraneous; that is, it has no physical meaning. The value of  $x$  is defined as the number of moles of A per liter that react and the number of moles of B per liter that react. No more B can be consumed than was initially present (0.100 M), so  $x = 0.309$  is the extraneous root. Thus,  $x = 0.099$  is the root that has physical meaning, and the extraneous root is 0.309. The equilibrium concentrations are

$$\begin{aligned} [\text{A}] &= (0.300 - x) \text{ M} = 0.201 \text{ M}; & [\text{B}] &= (0.100 - x) \text{ M} = 0.001 \text{ M}; \\ [\text{C}] &= [\text{D}] = x \text{ M} = 0.099 \text{ M} \end{aligned}$$

You should now work Exercises 34, 44, and 46.



### Problem-Solving Tip: Solving Quadratic Equations—Which Root Shall We Use?

Quadratic equations can be rearranged into standard form.

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

All can be solved by the quadratic formula, which is

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad (\text{Appendix A})$$

This formula gives *two* roots, both of which are *mathematically* correct. A foolproof way to determine which root of the equation has physical meaning is to substitute the value of the variable into the expressions for the equilibrium concentrations. For the extraneous root, one or more of these substitutions will lead to a negative concentration, which is physically impossible (there cannot be *less than none* of a substance present!). The correct root will give all positive concentrations. In Example 17-7, substitution of the extraneous root  $x = 0.309$  would give  $[\text{A}] = (0.300 - 0.309) \text{ M} = -0.009 \text{ M}$  and  $[\text{B}] = (0.100 - 0.309) \text{ M} = -0.209 \text{ M}$ . Either of these concentration values is impossible, so we would know that 0.309 is an extraneous root. You should apply this check to subsequent calculations that involve solving a quadratic equation.

Check Example 17-6:

$$\begin{aligned} Q &= \frac{[\text{C}][\text{D}]}{[\text{A}][\text{B}]} = \frac{(0.175)(0.175)}{(0.025)(0.025)} \\ Q &= 49 = K_c \end{aligned}$$

Check Example 17-7

$$\begin{aligned} Q &= \frac{(0.099)(0.099)}{(0.201)(0.001)} \\ Q &= 49 = K_c \end{aligned}$$

The following table summarizes Examples 17-6 and 17-7.

	Initial Concentrations (M)				Equilibrium Concentrations (M)			
	[A]	[B]	[C]	[D]	[A]	[B]	[C]	[D]
Example 17-6	0.200	0.200	0	0	0.025	0.025	0.175	0.175
Example 17-7	0.300	0.100	0	0	0.201	0.001	0.099	0.099



The data from the table can be substituted into the reaction quotient expression,  $Q$ , as a check. Even though the reaction is initiated by different relative amounts of reactants in the two cases, the ratios of equilibrium concentrations of products to reactants (each raised to the first power) agree within roundoff error.

## 17-6 FACTORS THAT AFFECT EQUILIBRIA

Once a reacting system has reached equilibrium, it remains at equilibrium until it is disturbed by some change of conditions. The guiding principle is known as **LeChatelier's Principle** (Section 13-6).

If a change of conditions (stress) is applied to a system at equilibrium, the system shifts in the direction that reduces the stress to move toward a new state of equilibrium.

*LeChatelier* is pronounced "le-SHOT-lee-ay."

Remember that the *value* of an equilibrium constant changes only with temperature.

The reaction quotient,  $Q$ , helps us predict the direction of this shift. Three types of changes can disturb the equilibrium of a reaction.

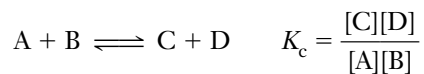
1. Changes in concentration
2. Changes in pressure or volume (for reactions that involve gases)
3. Changes in temperature

We now study the effects of these types of stresses from a qualitative, or descriptive, point of view. In Section 17-8 we expand our discussion with quantitative examples.

For reactions involving gases at constant temperature, changes in volume cause changes in pressure, and vice versa.


### Changes in Concentration


Consider the following system *starting at equilibrium*.



When more of any reactant or product is *added* to the system, the value of  $Q$  changes, so it no longer matches  $K_c$ , and the reaction is no longer at equilibrium. The stress due to the added substance is relieved by shifting the equilibrium in the direction that consumes some of the added substance, moving the value of  $Q$  back toward  $K_c$ . Let us compare the mass action expressions for  $Q$  and  $K_c$ . If more A or B is added, then  $Q < K_c$ , and the forward reaction occurs more rapidly and to a greater extent than the reverse reaction until equilibrium is reestablished. If more C or D is added,  $Q > K_c$ , and the reverse reaction occurs more rapidly and to a greater extent until equilibrium is reestablished.

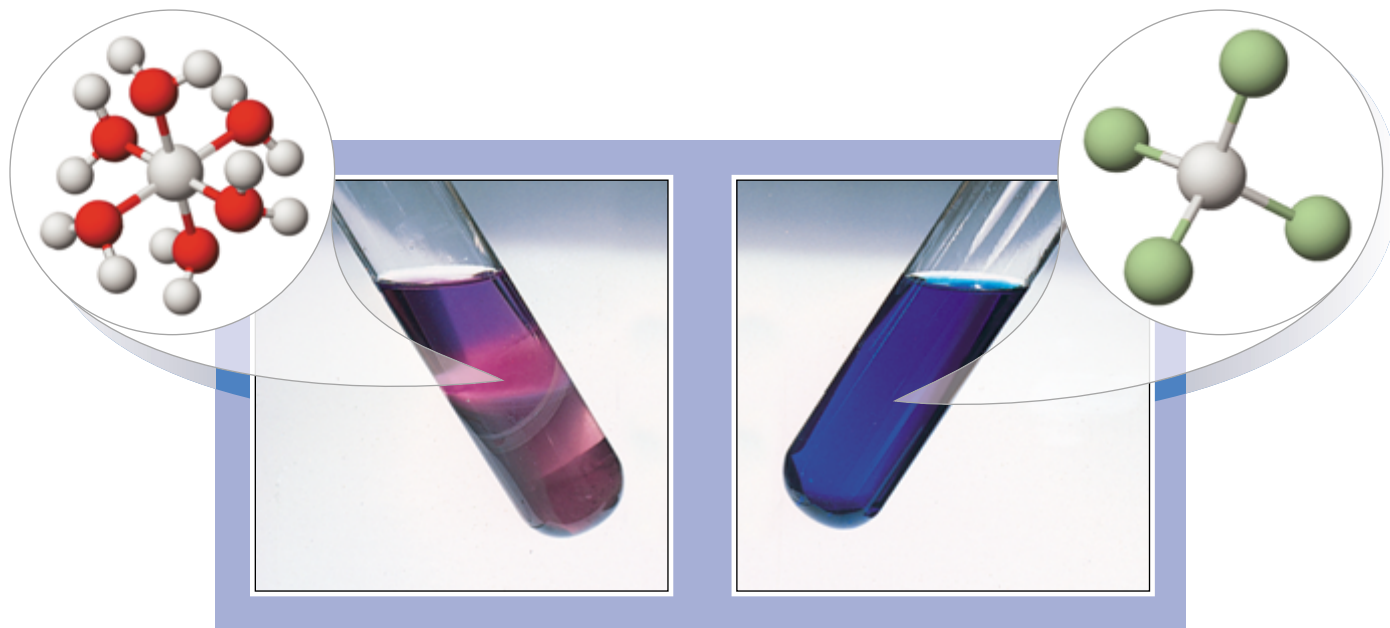
Adding or removing reactants or products changes the value of  $Q$ . It *does not change* the value of  $K_c$ .

 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 16.11, Disturbing a Chemical Equilibrium (1): LeChatelier's Principle.

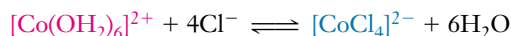
 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 16.13, Disturbing a Chemical Equilibrium (3): Addition or Removal of a Reagent.

We can understand LeChatelier's Principle in the kinetic terms we used to introduce equilibrium. The rate of the forward reaction is proportional to the reactant concentrations raised to some powers,

$$\text{Rate}_f = k_f[A]^x[B]^y$$



Effects of changes in concentration on the equilibrium



A solution of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  in isopropyl alcohol and water is purple (not shown) due to the mixture of  $[\text{Co}(\text{OH}_2)_6]^{2+}$  (pink) and  $[\text{CoCl}_4]^{2-}$  (blue). When we add concentrated  $\text{HCl}$ , the excess  $\text{Cl}^-$  shifts the reaction to the right (blue, right). Adding  $\text{AgNO}_3(\text{aq})$  removes some  $\text{Cl}^-$  by precipitation of  $\text{AgCl}(\text{s})$  and favors the reaction to the left (produces more  $[\text{Co}(\text{OH}_2)_6]^{2+}$ ; the resulting solution is pink (left). Each insert shows the structure of the cobalt complex species present in higher concentration; other ions and solvent molecules are not shown.

The terminology used here is not as precise as we might like, but it is widely used. When we say that the equilibrium is “shifted to the left,” we mean that the reaction to the left occurs to a greater extent than the reaction to the right.

When we add more A to an equilibrium mixture, this rate increases so that it no longer matches the rate of the reverse reaction. As the reaction proceeds to the right, consuming some A and B and forming more C and D, the forward rate diminishes and the reverse rate increases until they are again equal. At that point, a new equilibrium condition has been reached, with more C and D than were present in the *original* equilibrium mixture. Not all of the added A has been consumed when the new equilibrium is reached, however.

If a reactant or product is *removed* from a system at equilibrium, the reaction that produces *that* substance occurs more rapidly and to a greater extent than its reverse. If some C or D is removed, then  $Q < K_c$ , and the forward reaction is favored until equilibrium is reestablished. If some A or B is removed, the reverse reaction is favored.

This tabulation summarizes a lot of useful information. Study it carefully.

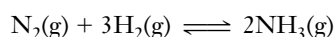
Stress	$Q$	Direction of Shift of $\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D}$
Increase concentration of A or B	$Q < K$	→ right
Increase concentration of C or D	$Q > K$	← left
Decrease concentration of A or B	$Q > K$	← left
Decrease concentration of C or D	$Q < K$	→ right

When a new equilibrium condition is established, (1) the rates of the forward and reverse reactions are again equal; and (2)  $K_c$  is again satisfied by the new concentrations of reactants and products.

Practical applications of changes of this type are of great economic importance. Removing a product of a reversible reaction forces the reaction to produce more product than could be obtained if the reaction were simply allowed to reach equilibrium.

### EXAMPLE 17-8 Applying a Stress to a System at Equilibrium

Given the following reaction at equilibrium in a closed container at 500°C, predict the effect of each of the following changes on the amount of  $\text{NH}_3$  present at equilibrium: (a) forcing more  $\text{H}_2$  into the system; (b) removing some  $\text{NH}_3$  from the system.



#### Plan

We apply LeChatelier's Principle to each part of the question individually.

#### Solution

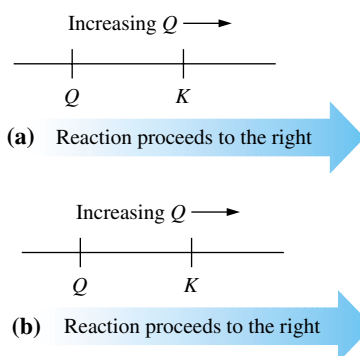
(a) Adding a substance favors the reaction that uses up that substance (forward in this case).

More  $\text{NH}_3$  is formed.

(b) Removing a substance favors the reaction that produces that substance (forward in this case).

More  $\text{NH}_3$  is formed.

Note that at the new equilibrium, the *concentration*  $[\text{NH}_3]$  would still be less than at the *original* equilibrium.



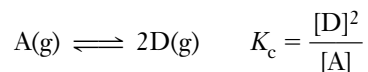
### Changes in Volume and Pressure


Changes in pressure have little effect on the concentrations of solids or liquids because they are only slightly compressible. Changes in pressure do cause significant changes in concentrations of gases, however. Such changes therefore affect the value of  $Q$  for reactions in which the number of moles of gaseous reactants differs from the number of moles of gaseous products. For an ideal gas,

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

The term  $(n/V)$  represents concentration, that is, mol/L. At constant temperature,  $n$ ,  $R$ , and  $T$  are constants. Thus, if the volume occupied by a gas decreases, its partial pressure increases and its concentration  $(n/V)$  increases. If the volume of a gas increases, both its partial pressure and its concentration decrease.

Consider the following gaseous system at equilibrium.



 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 16.14, Disturbing a Chemical Equilibrium (4): Volume Changes.

At constant temperature, a decrease in volume (increase in pressure) increases the concentrations of both A and D. In the expression for  $Q$ , the concentration of D is squared and the concentration of A is raised to the first power. As a result, the numerator of  $Q$  increases more than the denominator as pressure increases. Thus,  $Q > K_c$ , and this equilibrium shifts to the left. Conversely, an increase in volume (decrease in pressure) shifts this reaction to the right until equilibrium is reestablished, because  $Q < K_c$ . We can summarize the effect of pressure (volume) changes on *this* gas-phase system at equilibrium.

Study this tabulation carefully. How would these conclusions change for a reaction in which there are more moles of gaseous reactants than moles of gaseous products?

Stress	$Q^*$	Direction of Shift of $A(g) \rightleftharpoons 2D(g)$
Volume decrease, pressure increase	$Q > K_c$	Toward smaller number of moles of gas (left for <i>this</i> reaction)
Volume increase, pressure decrease	$Q < K_c$	Toward larger number of moles of gas (right for <i>this</i> reaction)

\*In  $Q$  for this reaction, there are more moles of gaseous product than gaseous reactant.

In general, for reactions that involve gaseous reactants or products, LeChatelier's Principle allows us to predict the following results.

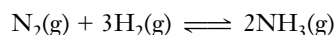
1. If there is *no change in the total number of moles of gases in a reaction*, a volume (pressure) change does not affect the position of equilibrium;  $Q$  is unchanged by the volume (or pressure) change.
2. If a reaction *involves a change in the total number of moles of gases*, changing the volume (or pressure) of a reaction mixture changes the value of  $Q$ ; it *does not change* the value of  $K_c$ . For such a reaction:
  - (a) A decrease in volume (increase in pressure) shifts a reaction in the direction that produces the *smaller total number of moles of gas*, until  $Q$  again equals  $K_c$ .
  - (b) An increase in volume (decrease in pressure) shifts a reaction in the direction that produces the *larger total number of moles of gas*, until  $Q$  again equals  $K_c$ .

One practical application of these ideas is illustrated in the next section by the Haber process.

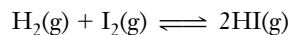
The foregoing argument applies only when pressure changes are due to volume changes. It *does not apply* if the total pressure of a gaseous system is raised by merely pumping in an inert gas, for example, He. If the gas that is introduced is not involved in the reaction, the *partial pressure* of each reacting gas remains constant, so the system remains at equilibrium.

### EXAMPLE 17-9 Applying a Stress to a System at Equilibrium

(a) Given the following reaction at equilibrium in a closed container at 500°C, predict the effect of increasing the pressure by decreasing the volume.



(b) Make the same prediction for the following reaction at high temperature.



#### Plan

We apply LeChatelier's Principle to predict the effect on each reaction.

**Solution**

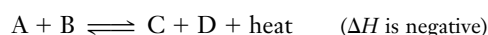
(a) Increasing the pressure favors the reaction that produces the smaller number of moles of gas (forward in this case).

More  $\text{NH}_3$  is formed.

(b) This reaction involves the same number of moles of gas on both sides, so a pressure (volume) change does not disturb the equilibrium. There is no effect on the position of equilibrium.

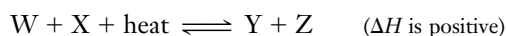
**Changes in Temperature**


Consider the following exothermic reaction at equilibrium:

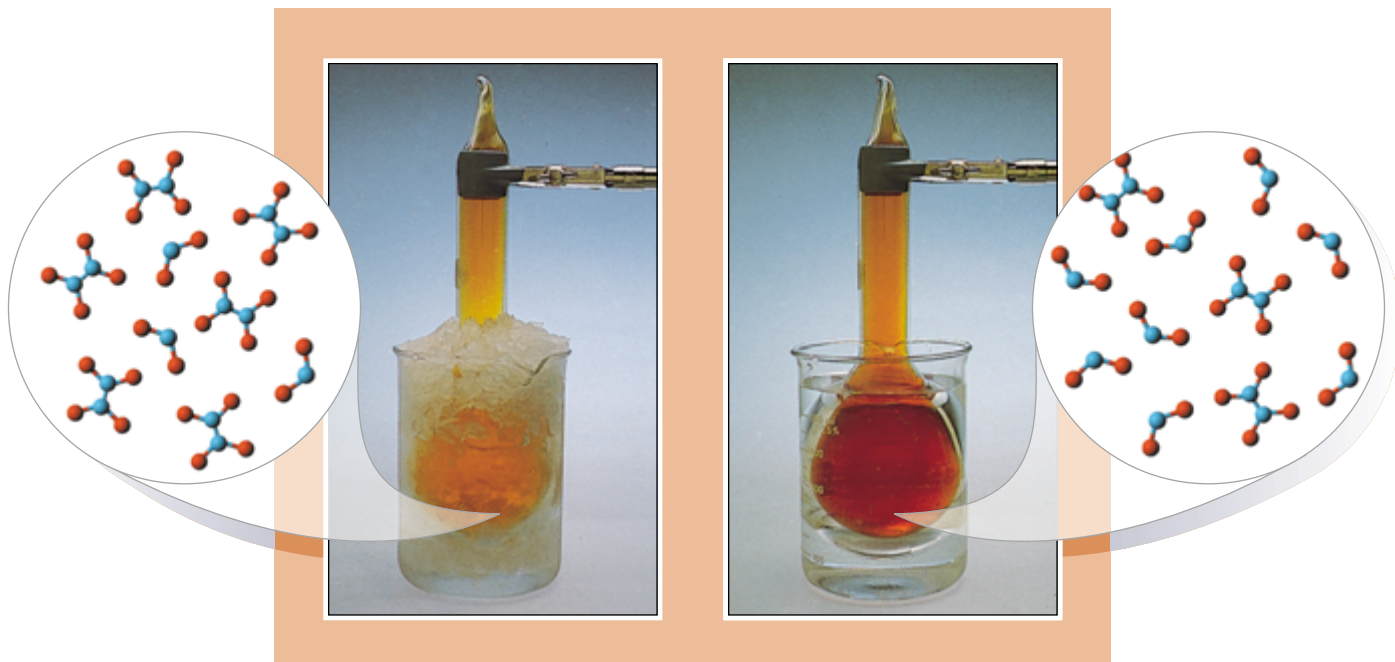


Heat is produced by the forward (exothermic) reaction. Suppose we increase the temperature at constant pressure by adding heat to the system. This favors the reaction to the left, removing some of the extra heat. Lowering the temperature favors the reaction to the right as the system replaces some of the heat that was removed.

By contrast, for an endothermic reaction at equilibrium,



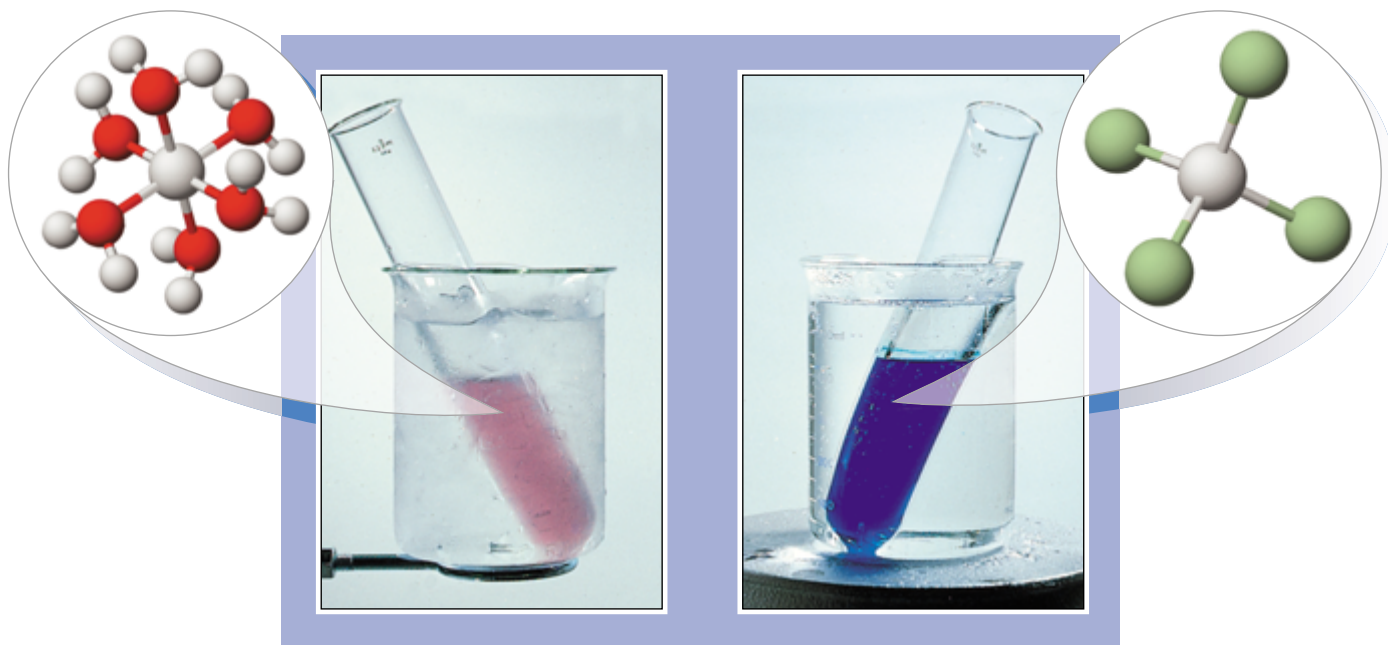
 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 16.12, Disturbing a Chemical Equilibrium (2): Temperature Changes.



The gas-phase equilibrium for the *exothermic* reaction



The two flasks contain the same *total* amounts of gas.  $\text{NO}_2$  is brown, whereas  $\text{N}_2\text{O}_4$  is colorless. The higher temperature ( $50^{\circ}\text{C}$ ) of the flask on the right favors the reverse reaction; this mixture is more highly colored because it contains more  $\text{NO}_2$ . The flask on the left, at the temperature of ice water, contains less brown  $\text{NO}_2$  gas.



Effect of temperature changes on the equilibrium of the *endothermic* reaction



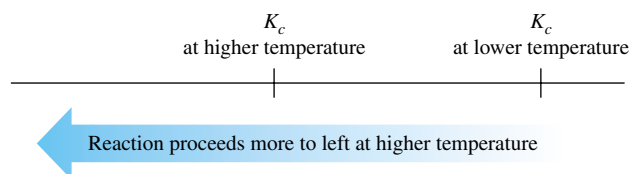
We begin with a purple equilibrium mixture of the pink and blue complexes at room temperature (not shown). In hot water the forward reaction (endothermic) is favored and  $K_c$  is higher, so the solution is blue (*right*). At 0°C, the reverse reaction (exothermic) is favored and  $K_c$  is lower, so the solution is pink (*left*). Each insert shows the structure of the cobalt complex species present in highest concentration; other ions and solvent molecules are not shown.

an increase in temperature at constant pressure favors the reaction to the right. A decrease in temperature favors the reaction to the left.

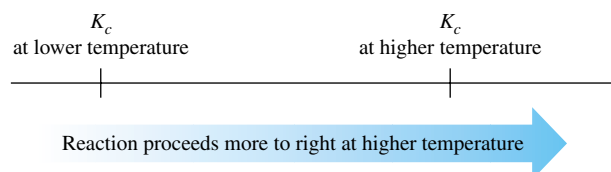
The *value of any equilibrium constant changes* as the temperature changes. Changing the temperature of a reaction at equilibrium thus causes  $Q$  to differ from  $K_c$ , but this is now because  $K_c$  has changed. The reaction then proceeds in the direction that moves  $Q$  toward the new value of  $K_c$ . As we will see in Section 17-13,

the  $K_c$  values of exothermic reactions decrease with increasing  $T$ , and the  $K_c$  values of endothermic reactions increase with increasing  $T$ . No other stresses affect the value of  $K_c$ .

For an exothermic reaction



For an endothermic reaction





## Addition of a Catalyst

Adding a catalyst to a system changes the rate of the reaction (Section 16-9), but this *cannot* shift the equilibrium in favor of either products or reactants. Because a catalyst affects the activation energy of *both* forward and reverse reactions equally, it changes both rate constants by the same factor, so their ratio,  $K_c$ , does not change.

Can you use the Arrhenius equation (Section 16-8) to show that lowering the activation energy barrier increases forward and reverse rates by the same factor?

Adding a catalyst to a reaction at equilibrium has no effect; it changes neither  $Q$  nor  $K_c$ .

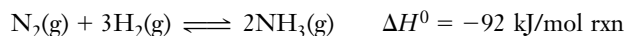
The same equilibrium mixture is achieved with or without the catalyst, but the equilibrium is established more quickly in the presence of a catalyst.

Not all reactions attain equilibrium; they may occur too slowly, or else products or reactants may be continually added or removed. Such is the case with most reactions in biological systems. On the other hand, some reactions, such as typical acid–base neutralizations, achieve equilibrium very rapidly.

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### EXAMPLE 17-10 *Applying a Stress to a System at Equilibrium*

Given the following reaction at equilibrium in a closed container at 500°C, predict the effect of each of the following changes on the amount of  $\text{NH}_3$  present at equilibrium: (a) increasing the temperature; (b) lowering the temperature; (c) introducing some platinum catalyst.



#### Plan

We apply LeChatelier's Principle to each part of the question individually.

#### Solution

(a) The negative value for  $\Delta H$  tells us that the forward reaction is exothermic. Increasing the temperature favors the endothermic reaction (reverse in this case).

Some  $\text{NH}_3$  is used up.

(b) Lowering the temperature favors the exothermic reaction (forward in this case).

More  $\text{NH}_3$  is formed.

(c) A catalyst does not favor either reaction.

It would have no effect on the amount of  $\text{NH}_3$ .

*You should now work Exercises 54, 57, and 58.*

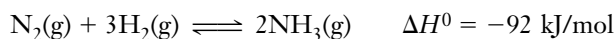
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Now we shall illustrate the commercial importance of these changes.

### 17-7 THE HABER PROCESS: A PRACTICAL APPLICATION OF EQUILIBRIUM

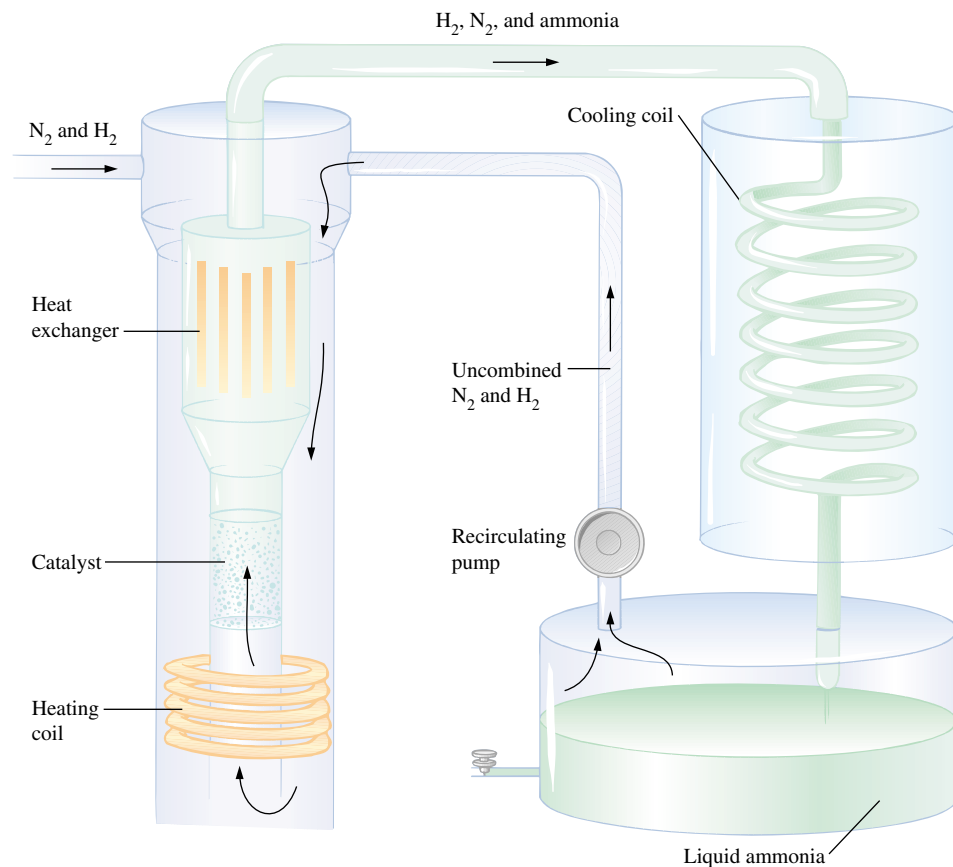
Fritz Haber (1868–1934) developed the process to provide a cheaper and more reliable source of explosives as Germany prepared for World War I. (Britain controlled the seas and thus the access to the natural nitrates in India and Chile that were needed to prepare explosives.) The current use of the process is more humanitarian: most  $\text{NH}_3$  is used to produce fertilizers. In the United States, approximately 135 pounds of  $\text{NH}_3$  is required per person per year.

Nitrogen,  $\text{N}_2$ , is very unreactive. The Haber process is the economically important industrial process by which atmospheric  $\text{N}_2$  is converted to ammonia,  $\text{NH}_3$ , a soluble, reactive compound. Innumerable dyes, plastics, explosives, fertilizers, and synthetic fibers are made from ammonia. The Haber process provides insight into kinetic and thermodynamic factors that influence reaction rates and the positions of equilibria. In this process the reaction between  $\text{N}_2$  and  $\text{H}_2$  to produce  $\text{NH}_3$  is never allowed to reach equilibrium, but moves toward it.



$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = 3.6 \times 10^8 \quad (\text{at } 25^\circ\text{C})$$

The process is diagrammed in Figure 17-3. The reaction is carried out at about  $450^\circ\text{C}$  under pressures ranging from 200 to 1000 atmospheres. Hydrogen is obtained from coal gas or petroleum refining and nitrogen from liquefied air.



**Figure 17-3** A simplified representation of the Haber process for synthesizing ammonia.

**TABLE 17-1** Effect of  $T$  and  $P$  on Yield of Ammonia

°C	$K_c$	Mole % $\text{NH}_3$ in Equilibrium Mixture		
		10 atm	100 atm	1000 atm
209	650	51	82	98
467	0.5	4	25	80
758	0.014	0.5	5	13

The value of  $K_c$  is  $3.6 \times 10^8$  at 25°C. This very large value of  $K_c$  indicates that *at equilibrium* virtually all of the  $\text{N}_2$  and  $\text{H}_2$  (mixed in a 1:3 mole ratio) would be converted into  $\text{NH}_3$ . At 25°C, the reaction occurs so slowly, however, that no measurable amount of  $\text{NH}_3$  is produced within a reasonable time. Thus, the large equilibrium constant (a thermodynamic factor) indicates that the reaction proceeds toward the right almost completely. It tells us *nothing*, however, about how fast the reaction occurs (a kinetic factor).

There are four moles of gas on the left side of the equation and only two moles of gas on the right, so increasing the pressure favors the production of  $\text{NH}_3$ . The Haber process is therefore carried out at very high pressures, as high as the equipment will safely stand.

The reaction is exothermic ( $\Delta H_{\text{rxn}}^0$  is negative), so increasing the temperature favors the *decomposition* of  $\text{NH}_3$  (the reverse reaction). But, the rates of both forward and reverse reactions increase as the temperature increases.

The addition of a catalyst of finely divided iron and small amounts of selected oxides also speeds up both the forward and reverse reactions. This allows  $\text{NH}_3$  to be produced not only faster but at a lower temperature, which increases the yield of  $\text{NH}_3$  and extends the life of the equipment.

Table 17-1 shows the effects of increases in temperature and pressure on the equilibrium yield of  $\text{NH}_3$ , starting with 1:3 mole ratios of  $\text{N}_2$ : $\text{H}_2$ .  $K_c$  decreases by more than ten orders of magnitude, from  $3.6 \times 10^8$  at 25°C to only  $1.4 \times 10^{-2}$  at 758°C. This tells us that the reaction proceeds *very far to the left* at high temperatures. Casual examination of the data might suggest that the reaction should be run at lower temperatures, because a higher percentage of the  $\text{N}_2$  and  $\text{H}_2$  is converted into  $\text{NH}_3$ . The reaction occurs so slowly, however, even in the presence of a catalyst, that it cannot be run economically at temperatures below about 450°C.

The emerging reaction mixture is cooled down, and  $\text{NH}_3$  (bp =  $-33.43^\circ\text{C}$ ) is removed as a liquid. This prevents the reaction from reaching equilibrium and favors the forward reaction. The unreacted  $\text{N}_2$  and  $\text{H}_2$  are recycled. Excess  $\text{N}_2$  is used to favor the reaction to the right.

## 17-8 APPLICATION OF STRESS TO A SYSTEM AT EQUILIBRIUM

We can use equilibrium constants to determine new equilibrium concentrations that result from adding one or more species to, or removing one or more species from, a system at equilibrium.



A nighttime photo of a large plant for the commercial production of ammonia,  $\text{NH}_3$ . Such an installation can produce up to 7000 metric tons of ammonia per day. There are nearly 100 such plants in the world.

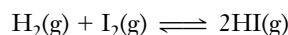
In practice, the mixed reactants are compressed by special pumps and injected into the heated reaction vessel.

Ten orders of magnitude is  $10^{10}$ , that is, 10 billion.

$$1 \times 10^{10} = 10,000,000,000$$

**EXAMPLE 17-11** *Applying a Stress to a System at Equilibrium*

Some hydrogen and iodine are mixed at 229°C in a 1.00-liter container. When equilibrium is established, the following concentrations are present:  $[\text{HI}] = 0.490\text{ M}$ ,  $[\text{H}_2] = 0.080\text{ M}$ , and  $[\text{I}_2] = 0.060\text{ M}$ . If an additional 0.300 mol of HI is then added, what concentrations will be present when the new equilibrium is established?

**Plan**

We use the initial equilibrium concentrations to calculate the value of  $K_c$ . Then we determine the new concentrations after some HI has been added and calculate  $Q$ . The value of  $Q$  tells us which reaction is favored. Then we can represent the new equilibrium concentrations. We substitute these representations into the  $K_c$  expression and solve for the new equilibrium concentrations.

**Solution**

Calculate the value of  $K_c$  from the first set of equilibrium concentrations.

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(0.490)^2}{(0.080)(0.060)} = 50$$

When we add 0.300 mol of HI to the 1.00-liter container, the  $[\text{HI}]$  instantaneously increases by 0.300 M.

	$\text{H}_2(\text{g})$	+	$\text{I}_2(\text{g})$	$\rightleftharpoons$	$2\text{HI}(\text{g})$
equilibrium	0.080 M		0.060 M		0.490 M
mol/L added	0 M		0 M		+0.300 M
new initial conc'n	0.080 M		0.060 M		0.790 M

It is obvious that adding some HI favors the reaction to the left. If more than one substance is added to the reaction mixture, it might not be obvious which reaction will be favored. Calculating  $Q$  always lets us make the decision.

Substitution of these *new initial* concentrations into the reaction quotient gives

$$Q = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(0.790)^2}{(0.080)(0.060)} = 130$$

Because  $Q > K_c$ , the reaction proceeds to the left to establish a new equilibrium. The new equilibrium concentrations can be determined as follows. Let  $x = \text{mol/L}$  of  $\text{H}_2$  formed; so  $x = \text{mol/L}$  of  $\text{I}_2$  formed, and  $2x = \text{mol/L}$  of HI consumed.

	$\text{H}_2(\text{g})$	+	$\text{I}_2(\text{g})$	$\rightleftharpoons$	$2\text{HI}(\text{g})$
new initial conc'n	0.080 M		0.060 M		0.790 M
change due to rxn	+x M		+x M		-2x M
new equilibrium	$(0.080 + x)\text{ M}$		$(0.060 + x)\text{ M}$		$(0.790 - 2x)\text{ M}$

Equal concentrations of  $\text{H}_2$  and  $\text{I}_2$  must be formed by the *new progress* of the reaction.

Substitution of these values into  $K_c$  allows us to evaluate  $x$ .

$$K_c = 50 = \frac{(0.790 - 2x)^2}{(0.080 + x)(0.060 + x)} = \frac{0.624 - 3.16x + 4x^2}{0.0048 + 0.14x + x^2}$$

$$0.24 + 7.0x + 50x^2 = 0.624 - 3.16x + 4x^2$$

$$46x^2 + 10.2x - 0.38 = 0$$

To “consume a negative quantity of HI” would be to form HI. The value  $x = -0.25$  would lead to  $[\text{H}_2] = (0.080 + x)\text{ M} = (0.080 - 0.25)\text{ M} = -0.17\text{ M}$ . A negative concentration is impossible, so  $x = -0.25$  is the extraneous root.

Solution by the quadratic formula gives  $x = 0.032$  and  $-0.25$ .

Clearly,  $x = -0.25$  is the extraneous root, because  $x$  cannot be less than zero in this case. This reaction does not consume a negative quantity of HI, because the reaction is proceeding toward the left. Thus,  $x = 0.032$  is the root with physical meaning, so the new equilibrium concentrations are

$$[\text{H}_2] = (0.080 + x) M = (0.080 + 0.032) M = 0.112 M$$

$$[\text{I}_2] = (0.060 + x) M = (0.060 + 0.032) M = 0.092 M$$

$$[\text{HI}] = (0.790 - 2x) M = (0.790 - 0.064) M = 0.726 M$$

In summary,

Original Equilibrium	Stress Applied	New Equilibrium
$\left\{ \begin{array}{l} [\text{H}_2] = 0.080 M \\ [\text{I}_2] = 0.060 M \\ [\text{HI}] = 0.490 M \end{array} \right.$	Add 0.300 M HI	$\left\{ \begin{array}{l} [\text{H}_2] = 0.112 M \\ [\text{I}_2] = 0.092 M \\ [\text{HI}] = 0.726 M \end{array} \right.$

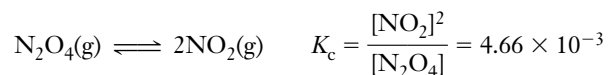
We see that some of the additional HI is consumed, but not all of it. More HI remains after the new equilibrium is established than was present before the stress was imposed. The new equilibrium  $[\text{H}_2]$  and  $[\text{I}_2]$  are substantially greater than the original equilibrium concentrations, however.

You should now work Exercise 64.

We can also use the equilibrium constant to calculate new equilibrium concentrations that result from decreasing the volume (increasing the pressure) of a gaseous system that was initially at equilibrium.

### EXAMPLE 17-12 Applying a Stress to a System at Equilibrium

At 22°C the equilibrium constant,  $K_c$ , for the following reaction is  $4.66 \times 10^{-3}$ . (a) If 0.800 mol of  $\text{N}_2\text{O}_4$  were injected into a closed 1.00-liter container at 22°C, how many moles of each gas would be present at equilibrium? (b) If the volume were halved (to 0.500 L) at constant temperature, how many moles of each gas would be present after the new equilibrium has been established?



#### Plan

(a) We are given the value of  $K_c$  and the initial concentration of  $\text{N}_2\text{O}_4$ . We write the reaction summary, which gives the representation of the equilibrium concentrations. Then we substitute these into the  $K_c$  expression and solve for the new equilibrium concentrations.

(b) We obtain the new *initial* concentrations by adjusting the equilibrium concentrations from part (a) for the volume change. Then we solve for the *new* equilibrium concentrations as we did in part (a).

#### Solution

(a) Let  $x = \text{mol/L}$  of  $\text{N}_2\text{O}_4$  consumed and  $2x = \text{mol/L}$  of  $\text{NO}_2$  formed.

	$\text{N}_2\text{O}_4(\text{g})$	$\rightleftharpoons$	$2\text{NO}_2(\text{g})$
initial	0.800 M		0 M
change due to rxn	$-x M$		$+2x M$
equilibrium	$(0.800 - x) M$		$2x M$

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = 4.66 \times 10^{-3} = \frac{(2x)^2}{0.800 - x} = \frac{4x^2}{0.800 - x}$$

$$3.73 \times 10^{-3} - 4.66 \times 10^{-3}x = 4x^2$$

$$4x^2 + 4.66 \times 10^{-3}x - 3.73 \times 10^{-3} = 0$$

The value of  $x$  is the number of moles per liter of  $\text{N}_2\text{O}_4$  that react. So  $x$  must be positive and cannot be greater than  $0.800 M$ .

$$0 < x < 0.800 M$$

Solving by the quadratic formula gives  $x = 3.00 \times 10^{-2}$  and  $x = -3.11 \times 10^{-2}$ . We use  $x = 3.00 \times 10^{-2}$ .

The original equilibrium concentrations are

$$[\text{NO}_2] = 2x M = 6.00 \times 10^{-2} M$$

$$[\text{N}_2\text{O}_4] = (0.800 - x) M = (0.800 - 3.00 \times 10^{-2}) M = 0.770 M$$

$$\underline{\quad} \text{ mol NO}_2 = 1.00 \text{ L} \times \frac{6.00 \times 10^{-2} \text{ mol NO}_2}{\text{L}} = 6.00 \times 10^{-2} \text{ mol NO}_2$$

$$\underline{\quad} \text{ mol N}_2\text{O}_4 = 1.00 \text{ L} \times \frac{0.770 \text{ mol N}_2\text{O}_4}{\text{L}} = 0.770 \text{ mol N}_2\text{O}_4$$

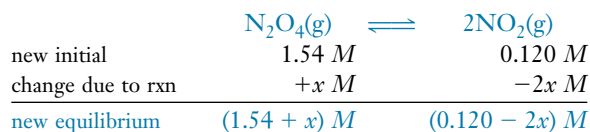
LeChatelier's Principle tells us that a decrease in volume (increase in pressure) favors the production of  $\text{N}_2\text{O}_4$ .

$$Q = \frac{(0.120)^2}{1.54} = 9.35 \times 10^{-3}$$

$$Q > K$$

$\therefore$   $\xleftarrow{\text{shift left}}$

(b) When the volume of the reaction vessel is halved, the concentrations are doubled, so the new *initial* concentrations of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  are  $2(0.770 M) = 1.54 M$  and  $2(6.00 \times 10^{-2} M) = 0.120 M$ , respectively.



$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = 4.66 \times 10^{-3} = \frac{(0.120 - 2x)^2}{1.54 + x}$$

Rearranging into the standard form of a quadratic equation gives

$$x^2 - 0.121x + 1.81 \times 10^{-3} = 0$$

Solving as before gives  $x = 0.104$  and  $x = 0.017$ .

The maximum value of  $x$  is  $0.060 M$ , because  $2x$  may not exceed the concentration of  $\text{NO}_2$  that was present after the volume was halved. Thus,  $x = 0.017 M$  is the root with physical significance. The new equilibrium concentrations in the 0.500-liter container are

$$[\text{NO}_2] = (0.120 - 2x) M = (0.120 - 0.034) M = 0.086 M$$

$$[\text{N}_2\text{O}_4] = (1.54 + x) M = (1.54 + 0.017) M = 1.56 M$$

$$\underline{\quad} \text{ mol NO}_2 = 0.500 \text{ L} \times \frac{0.086 \text{ mol NO}_2}{\text{L}} = 0.043 \text{ mol NO}_2$$

$$\underline{\quad} \text{ mol N}_2\text{O}_4 = 0.500 \text{ L} \times \frac{1.56 \text{ mol N}_2\text{O}_4}{\text{L}} = 0.780 \text{ mol N}_2\text{O}_4$$

The root  $x = 0.104$  would give a *negative* concentration for  $\text{NO}_2$ , which is impossible.

In summary,

First Equilibrium	Stress	New Equilibrium
0.770 mol of $\text{N}_2\text{O}_4$ 0.0600 mol of $\text{NO}_2$	Decrease volume from 1.00 L to 0.500 L	0.780 mol of $\text{N}_2\text{O}_4$ 0.043 mol of $\text{NO}_2$



Both  $[\text{N}_2\text{O}_4]$  and  $[\text{NO}_2]$  *increase* because of the large decrease in volume. However, the *number of moles* of  $\text{N}_2\text{O}_4$  increases, while the *number of moles* of  $\text{NO}_2$  decreases. We predict this from LeChatelier's Principle.

You should now work Exercise 66.



### Problem-Solving Tip: There Are Several Ways to Solve Equilibrium Problems

When a stress is applied to a system originally at equilibrium, it is no longer at equilibrium. As we did in Example 17-12(b), we can apply the stress to the *old equilibrium values* and then treat these as the new "initial values." Alternatively, we could adjust the *original concentrations values* to reflect the stress, and then treat these as the new "initial values." We could consider  $[\text{N}_2\text{O}_4]_{\text{initial}}$  in Example 17-12(b) as the *original* 0.800 mol of  $\text{N}_2\text{O}_4$  from part (a) in the *new* volume, 0.500 L. That is,  $[\text{N}_2\text{O}_4]_{\text{initial}} = 0.800 \text{ mol}/0.500 \text{ L} = 1.60 \text{ M}$ , with no  $\text{NO}_2$  having yet been formed.  $[\text{NO}_2]_{\text{initial}} = 0 \text{ M}$ . From that starting point, the reaction would proceed to the *right*.

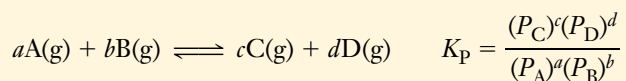
## 17-9 PARTIAL PRESSURES AND THE EQUILIBRIUM CONSTANT

It is often more convenient to measure pressures rather than concentrations of gases. Solving the ideal gas equation,  $PV = nRT$ , for pressure gives

$$P = \frac{n}{V}(RT) \quad \text{or} \quad P = M(RT) \quad \left(\frac{n}{V}\right) \text{ is } \left(\frac{\text{no. mol}}{\text{L}}\right)$$

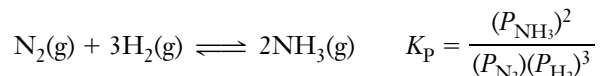
The pressure of a gas is directly proportional to its concentration ( $n/V$ ). For reactions in which all substances that appear in the equilibrium constant expression are gases, we sometimes prefer to express the equilibrium constant in terms of partial pressures *in atmospheres* ( $K_p$ ) rather than in terms of concentrations ( $K_c$ ).

In general for a reaction involving gases,



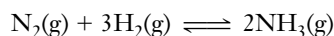
$K_p$  has no units for the same reasons that  $K_c$  has no units.

For instance, for the following reversible reaction,



### EXAMPLE 17-13 Calculation of $K_p$

In an equilibrium mixture at  $500^\circ\text{C}$ , we find  $P_{\text{NH}_3} = 0.147 \text{ atm}$ ,  $P_{\text{N}_2} = 6.00 \text{ atm}$ , and  $P_{\text{H}_2} = 3.70 \text{ atm}$ . Evaluate  $K_p$  at  $500^\circ\text{C}$  for the following reaction.



**Plan**

We are given equilibrium partial pressures of all reactants and products. So we write the expression for  $K_p$  and substitute partial pressures in atmospheres into it.

**Solution**

$$K_p = \frac{(P_{\text{NH}_3})^2}{(P_{\text{N}_2})(P_{\text{H}_2})^3} = \frac{(0.147)^2}{(6.00)(3.70)^3} = 7.11 \times 10^{-5}$$

You should now work Exercises 70 and 73.



**Problem-Solving Tip:** In  $K_p$  Calculations, Gas Pressures Must Be Expressed in Atmospheres

One error that students sometimes make when solving  $K_p$  problems is to express pressures in torr. Remember that these pressures must be expressed in atmospheres.

**17-10** RELATIONSHIP BETWEEN  $K_p$  AND  $K_c$

If the ideal gas equation is rearranged, the molar concentration of a gas is

$$\left(\frac{n}{V}\right) = \frac{P}{RT} \quad \text{or} \quad M = \frac{P}{RT}$$

Substituting  $P/RT$  for  $n/V$  in the  $K_c$  expression for the  $\text{N}_2\text{-H}_2\text{-NH}_3$  equilibrium gives the relationship between  $K_c$  and  $K_p$  for *this* reaction.

$$\begin{aligned} K_c &= \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{\left(\frac{P_{\text{NH}_3}}{RT}\right)^2}{\left(\frac{P_{\text{N}_2}}{RT}\right)\left(\frac{P_{\text{H}_2}}{RT}\right)^3} = \frac{(P_{\text{NH}_3})^2}{(P_{\text{N}_2})(P_{\text{H}_2})^3} \times \frac{\left(\frac{1}{RT}\right)^2}{\left(\frac{1}{RT}\right)^4} \\ &= K_p (RT)^2 \quad \text{and} \quad K_p = K_c (RT)^{-2} \end{aligned}$$

In general the relationship between  $K_c$  and  $K_p$  is

$$K_p = K_c(RT)^{\Delta n} \quad \text{or} \quad K_c = K_p(RT)^{-\Delta n} \quad \Delta n = (n_{\text{gas prod}}) - (n_{\text{gas react}})$$

$\Delta n$  refers to the numbers of moles of gaseous substances in the balanced equation, *not* in the reaction vessel.

For reactions in which equal numbers of moles of gases appear on both sides of the equation,  $\Delta n = 0$  and  $K_p = K_c$ .

In Example 17-1, we saw that for the ammonia reaction at 500°C (or 773 K),  $K_c = 0.286$ . We can describe this equilibrium in terms of partial pressures using  $K_p$ .

$$\begin{aligned} \text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) &\rightleftharpoons 2\text{NH}_3(\text{g}) \quad \Delta n = 2 - 4 = -2 \\ K_p &= K_c(RT)^{\Delta n} = (0.286)[(0.0821)(773)]^{-2} = 7.10 \times 10^{-5} \end{aligned}$$

This is essentially the same value we obtained in Example 17-13.

 **Problem-Solving Tip: Be Careful About the Value of  $R$**

To decide which value of  $R$  to use when you convert between  $K_c$  and  $K_p$ , you can reason as follows.  $K_c$  involves molar concentrations, for which the units are mol/L;  $K_p$  involves pressures expressed in atm. Thus the appropriate value of  $R$  to use for these conversions must include these units. We use  $0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}$ , rounded to the number of places appropriate to the problem.

For *gas-phase reactions*, we can calculate the amounts of substances present at equilibrium using either  $K_p$  or  $K_c$ . The results are the same by either method (when they are both expressed in the same terms). To illustrate, let's solve the following problem by both methods.

**EXAMPLE 17-14 Using  $K_c$  and  $K_p$**

We place 10.0 grams of  $\text{SbCl}_5$  in a 5.00-liter container at  $448^\circ\text{C}$  and allow the reaction to attain equilibrium. How many grams of  $\text{SbCl}_5$  are present at equilibrium? Solve this problem (a) using  $K_c$  and molar concentrations and (b) using  $K_p$  and partial pressures.



**(a) Plan (using  $K_c$ )**

We calculate the initial concentration of  $\text{SbCl}_5$ , write the reaction summary and represent the equilibrium concentrations; then we substitute into the  $K_c$  expression to obtain the equilibrium concentrations.

**(a) Solution (using  $K_c$ )**

Because we are given  $K_c$ , we use concentrations. The initial concentration of  $\text{SbCl}_5$  is

$$[\text{SbCl}_5] = \frac{10.0 \text{ g SbCl}_5}{5.00 \text{ L}} \times \frac{1 \text{ mol}}{299 \text{ g}} = 0.00669 \text{ M SbCl}_5$$

Let  $x = \text{mol/L}$  of  $\text{SbCl}_5$  that react. In terms of molar concentrations, the reaction summary is

	$\text{SbCl}_5$	$\rightleftharpoons$	$\text{SbCl}_3$	$+$	$\text{Cl}_2$
initial	0.00669 M		0		0
change due to rxn	$-x \text{ M}$		$+x \text{ M}$		$+x \text{ M}$
equilibrium	$(0.00669 - x) \text{ M}$		$x \text{ M}$		$x \text{ M}$

$$K_c = \frac{[\text{SbCl}_3][\text{Cl}_2]}{[\text{SbCl}_5]}$$

$$2.51 \times 10^{-2} = \frac{(x)(x)}{0.00669 - x}$$

$$x^2 = 1.68 \times 10^{-4} - 2.51 \times 10^{-2}x$$

$$x^2 + 2.51 \times 10^{-2}x - 1.68 \times 10^{-4} = 0$$

Solving by the quadratic formula gives

$$x = 5.49 \times 10^{-3} \quad \text{and} \quad -3.06 \times 10^{-2} \text{ (extraneous root)}$$

$$[\text{SbCl}_5] = (0.00669 - x) M = (0.00669 - 0.00549) M = 1.20 \times 10^{-3} M$$

$$\underline{?} \text{ g SbCl}_5 = 5.00 \text{ L} \times \frac{1.20 \times 10^{-3} \text{ mol}}{\text{L}} \times \frac{299 \text{ g}}{\text{mol}} = \boxed{1.79 \text{ g SbCl}_5}$$

Let us now solve the same problem *using*  $K_p$  and partial pressures.

**(b) Plan (using  $K_p$ )**

Calculate the initial partial pressure of  $\text{SbCl}_5$ , and write the reaction summary. Substitution of the representations of the equilibrium partial pressures into  $K_p$  gives their values.

**(b) Solution (using  $K_p$ )**

We calculate the initial *pressure* of  $\text{SbCl}_5$  in atmospheres, using  $PV = nRT$ .

$$P_{\text{SbCl}_5} = \frac{nRT}{V} = \frac{\left[ (10.0 \text{ g}) \left( \frac{1 \text{ mol}}{299 \text{ g}} \right) \right] \left( 0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (721 \text{ K})}{5.00 \text{ L}} = 0.396 \text{ atm}$$

The *partial pressure* of each substance is proportional to the *number of moles* of that substance.

Clearly,  $P_{\text{SbCl}_3} = 0$  and  $P_{\text{Cl}_2} = 0$  because only  $\text{SbCl}_5$  is present initially. We write the reaction summary in terms of partial pressures in atmospheres, because  $K_p$  refers to pressures in atmospheres.

Let  $y =$  decrease in pressure (atm) of  $\text{SbCl}_5$  due to reaction. In terms of partial pressures, the reaction summary is

	$\text{SbCl}_5$	$\rightleftharpoons$	$\text{SbCl}_3$	$+$	$\text{Cl}_2$
initial	0.396 atm		0		0
change due to rxn	$-y$ atm		$+y$ atm		$+y$ atm
equilibrium	$(0.396 - y)$ atm		$y$ atm		$y$ atm

If we did not know the value of  $K_p$ , we could calculate it from the known value of  $K_c$ , using the relationship  $K_p = K_c(RT)^{\Delta n}$ .

$$K_p = \frac{(P_{\text{SbCl}_3})(P_{\text{Cl}_2})}{P_{\text{SbCl}_5}} = 1.48 = \frac{(y)(y)}{0.396 - y}$$

$$0.586 - 1.48y = y^2 \quad y^2 + 1.48y - 0.586 = 0$$

Solving by the quadratic formula gives

$$y = 0.325 \quad \text{and} \quad -1.80 \text{ (extraneous root)}$$

$$P_{\text{SbCl}_5} = (0.396 - y) = (0.396 - 0.325) = 0.071 \text{ atm}$$

We use the ideal gas law,  $PV = nRT$ , to calculate the number of moles of  $\text{SbCl}_5$ .

$$n = \frac{PV}{RT} = \frac{(0.071 \text{ atm})(5.00 \text{ L})}{\left( 0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (721 \text{ K})} = 0.0060 \text{ mol SbCl}_5$$

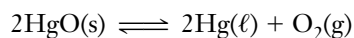
$$\underline{?} \text{ g SbCl}_5 = 0.0060 \text{ mol} \times \frac{299 \text{ g}}{\text{mol}} = \boxed{1.8 \text{ g SbCl}_5}$$

We see that within roundoff range the same result is obtained by both methods.

*You should now work Exercises 75 and 78.*

**17-11 HETEROGENEOUS EQUILIBRIA**

Thus far, we have considered only equilibria involving species in a single phase, that is, homogeneous equilibria. **Heterogeneous equilibria** involve species in more than one phase. Consider the following reversible reaction at 25°C.



When equilibrium is established for this system, a solid, a liquid, and a gas are present. Neither solids nor liquids are significantly affected by changes in pressure. The fundamental definition of the equilibrium constant in thermodynamics is in terms of the activities of the substances involved.

For any pure solid or pure liquid, the activity is taken as 1 (Section 17-2), so terms for pure liquids and pure solids *do not* appear in the  $K$  expressions for heterogeneous equilibria.

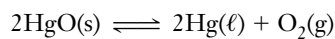
Thus, for the reaction



These equilibrium constant expressions indicate that equilibrium exists at a given temperature for *one and only one* concentration and one partial pressure of oxygen in contact with liquid mercury and solid mercury(II) oxide.



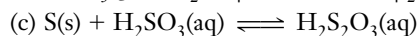
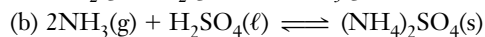
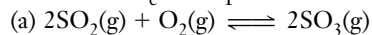
A photograph of the reaction



The reaction is not at equilibrium here, because  $\text{O}_2$  gas has been allowed to escape.

**EXAMPLE 17-15**  $K_c$  and  $K_p$  for Heterogeneous Equilibrium

Write both  $K_c$  and  $K_p$  for the following reversible reactions.

**Plan**

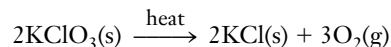
We apply the definitions of  $K_c$  and  $K_p$  to each reaction.

**Solution**

<p>(a) <math>K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]}</math></p>	<p><math>K_p = \frac{(P_{\text{SO}_3})^2}{(P_{\text{SO}_2})^2(P_{\text{O}_2})}</math></p>
<p>(b) <math>K_c = \frac{1}{[\text{NH}_3]^2} = [\text{NH}_3]^{-2}</math></p>	<p><math>K_p = \frac{1}{(P_{\text{NH}_3})^2} = (P_{\text{NH}_3})^{-2}</math></p>
<p>(c) <math>K_c = \frac{[\text{H}_2\text{S}_2\text{O}_3]}{[\text{H}_2\text{SO}_3]}</math></p>	<p><math>K_p</math> undefined; no gases involved</p>

**EXAMPLE 17-16** Heterogeneous Equilibria

The value of  $K_p$  is 27 for the thermal decomposition of potassium chlorate at a given high temperature. What is the partial pressure of oxygen in a closed container in which the following system is at equilibrium at the given temperature? (This can be a dangerous reaction.)

**Plan**

Because two solids,  $\text{KClO}_3$  and  $\text{KCl}$ , and only one gas,  $\text{O}_2$ , are involved, we see that  $K_p$  involves only the partial pressure of  $\text{O}_2$ , that is,  $K_p = (P_{\text{O}_2})^3$ .

**Solution**

We are given

$$K_p = (P_{\text{O}_2})^3 = 27$$

Let  $x$  atm =  $P_{\text{O}_2}$  at equilibrium. Then we have


$$(P_{\text{O}_2})^3 = 27 = x^3 \quad x = 3.0 \text{ atm}$$

This tells us that the partial pressure of oxygen at equilibrium is 3.0 atm.

*You should now work Exercises 80 and 91.*

## 17-12

 RELATIONSHIP BETWEEN  $\Delta G_{\text{rxn}}^0$  AND THE EQUILIBRIUM CONSTANT

 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 20.9, Thermodynamics and the Equilibrium Constant.

Let us consider in thermodynamic terms what may happen when two substances are mixed together at constant temperature and pressure. First, as a result of mixing, there is usually an increase in entropy due to the increase in disorder. If the two substances can react with



each other, the chemical reaction begins, heat is released or absorbed, and the concentrations of the substances in the mixture change. An additional change in entropy, which depends on changes in the nature of the reactants and products, also begins to occur. The evolution or absorption of heat energy, the changes in entropy, and the changes in concentrations all continue until equilibrium is established. Equilibrium may be reached with large amounts of products formed, with virtually all of the reactants remaining unchanged, or at *any* intermediate combination of concentrations.

The standard free energy change for a reaction is  $\Delta G_{\text{rxn}}^0$ . This is the free energy change that would accompany *complete* conversion of *all* reactants initially present at standard conditions to *all* products at standard conditions—the standard reaction (Section 15-15). The free energy change for any other concentrations or pressures is  $\Delta G_{\text{rxn}}$  (no superscript zero). The two quantities are related by the equation

$$\Delta G_{\text{rxn}} = \Delta G_{\text{rxn}}^0 + RT \ln Q$$

$R$  is the universal gas constant,  $T$  is the absolute temperature, and  $Q$  is the reaction quotient (Section 17-4). When a system is *at equilibrium*,  $\Delta G_{\text{rxn}} = 0$  (Section 15-15) and  $Q = K$  (Section 17-4). Recall that the reaction quotient may represent nonequilibrium concentrations (or partial pressures) of products and reactants. As reaction occurs, the free energy of the mixture and the concentrations change until at equilibrium  $\Delta G_{\text{rxn}} = 0$ , and the concentrations of reactants and products satisfy the equilibrium constant. At that point,  $Q$  becomes equal to  $K$  (Section 17-4). Then

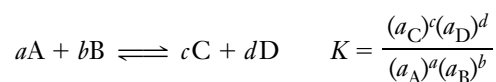
$$0 = \Delta G_{\text{rxn}}^0 + RT \ln K \quad (\text{at equilibrium})$$

Rearranging gives

$$\Delta G_{\text{rxn}}^0 = -RT \ln K$$

This equation shows the relationship between the standard free energy change and the **thermodynamic equilibrium constant**.

For the following generalized reaction, the thermodynamic equilibrium constant is defined in terms of the activities of the species involved.



where  $a_A$  is the activity of substance A, and so on. The mass action expression to which it is related involves concentration terms for species in solution and partial pressures for gases.

When the relationship  $\Delta G_{\text{rxn}}^0 = -RT \ln K$  is used with

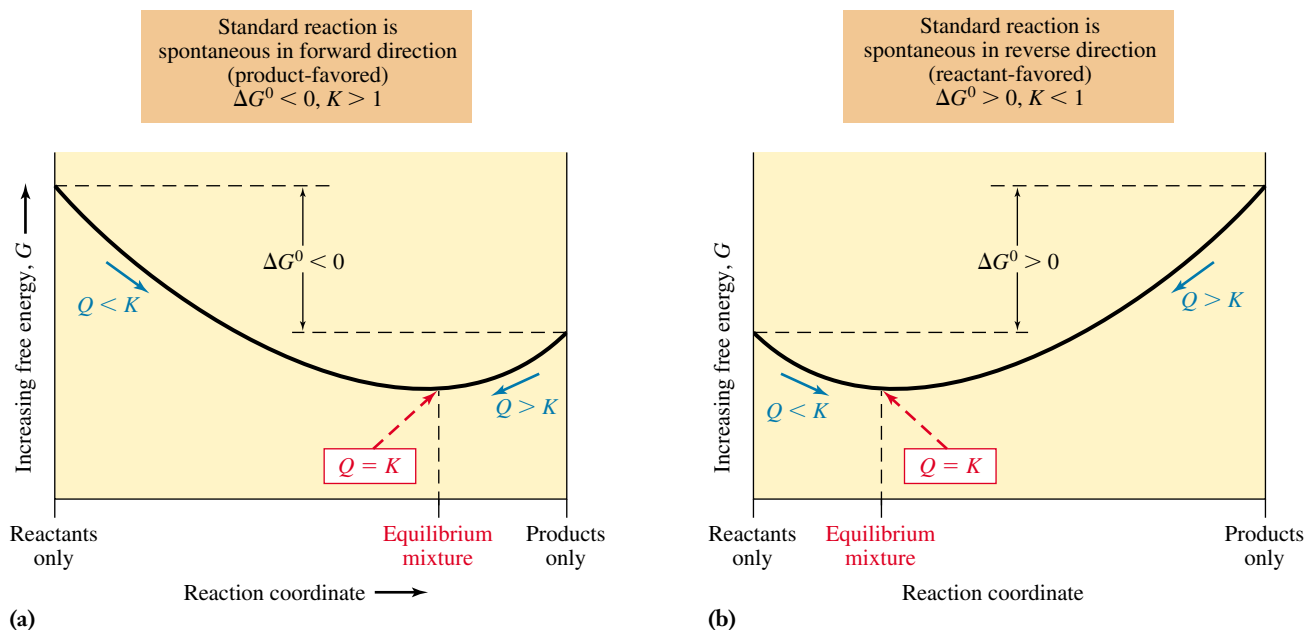
1. all gaseous reactants and products,  $K$  represents  $K_p$ ;
2. all solution reactants and products,  $K$  represents  $K_c$ ;
3. a mixture of solution and gaseous reactants,  $K$  represents the thermodynamic equilibrium constant, and we do not make the distinction between  $K_p$  and  $K_c$ .

Thermodynamic standard states are  
(1) pure solids or pure liquids at 1 atm,  
(2) solutions of one-molar concentrations, and (3) gases at partial pressures of 1 atm.

The energy units of  $R$  *must* match those of  $\Delta G^0$ . We usually use

$$R = 8.314 \text{ J/mol} \cdot \text{K}$$

We will encounter equilibrium calculations of solution and gaseous species in Chapter 21, “Electrochemistry.”



**Figure 17-4** Variation in total free energy for a reversible reaction carried out at constant  $T$ . The *standard* free energy change,  $\Delta G^0$ , represents the free energy change for the *standard reaction*—the *complete* conversion of reactants into products. In (a) this change is negative, indicating that the standard reaction is product-favored (spontaneous); the collection of just products would be more stable than the collection of just reactants. The mixture of reactants and products corresponding to the minimum of the curve is even more stable, however, and represents the equilibrium mixture. Because  $\Delta G^0$  is negative,  $K > 1$ , and the equilibrium mixture contains more products than reactants. At any point on the curve, comparing  $Q$  and  $K$  indicates the direction in which the reaction must proceed to approach equilibrium, that is, which way is “downhill” in free energy. The plot in (b) is for positive  $\Delta G^0$  (the standard reaction is reactant-favored). In this case  $K < 1$ , and the equilibrium mixture contains more reactants than products.

Figure 17-4 displays the relationships between free energy and equilibrium. The *left* end of each curve represents the total free energy of the reactants and the *right* end of each curve represents the total free energy of the products at standard state conditions. The difference between them is  $\Delta G_{\text{rxn}}^0$ ; like  $K$ ,  $\Delta G_{\text{rxn}}^0$  depends only on temperature and is a constant for any given reaction.

From the preceding equation that relates  $\Delta G_{\text{rxn}}^0$  and  $K$ , we see that when  $\Delta G_{\text{rxn}}^0$  is negative,  $\ln K$  *must* be positive, and  $K$  is greater than 1. This tells us that products are favored over reactants at equilibrium. This case is illustrated in Figure 17-4a. When  $\Delta G_{\text{rxn}}^0$  is positive,  $\ln K$  *must* be negative, and  $K$  is less than 1. This tells us that reactants are favored over products at equilibrium (Figure 17-4b). In the *rare* case of a chemical reaction for which  $\Delta G_{\text{rxn}}^0 = 0$ , then  $K = 1$  and the numerator and the denominator must be equal in the equilibrium constant expression, (i.e.,  $[C]^c[D]^d \dots = [A]^a[B]^b \dots$ ). These relationships are summarized as follows.

$\Delta G_{\text{rxn}}^0$	$K$	Product Formation
$\Delta G_{\text{rxn}}^0 < 0$	$K > 1$	Products favored over reactants at equilibrium
$\Delta G_{\text{rxn}}^0 = 0$	$K = 1$	At equilibrium when $[C]^c[D]^d \dots = [A]^a[B]^b \dots$ (very rare)
$\Delta G_{\text{rxn}}^0 > 0$	$K < 1$	Reactants favored over products at equilibrium

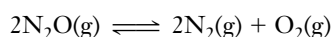
The direction of approach to equilibrium and the actual free energy change ( $\Delta G_{\text{rxn}}$ ) are *not* constants. They vary with the conditions and the initial concentrations. If the initial concentrations correspond to  $Q < K$ , equilibrium is approached from left to right on the curves in Figure 17-4, and the forward reaction predominates. If  $Q > K$ , equilibrium is approached from right to left, and the reverse reaction predominates.

The magnitude of  $\Delta G_{\text{rxn}}^0$  indicates the *extent* to which a chemical reaction occurs under standard state conditions, that is, how far the reaction goes toward the formation of products before equilibrium is reached. The more negative the  $\Delta G_{\text{rxn}}^0$  value, the larger is the

value of  $K$  and the more favorable is the formation of products. We think of some reactions as going to “completion.” These generally have very negative  $\Delta G_{\text{rxn}}^0$  values. The more positive the  $\Delta G_{\text{rxn}}^0$  value, the smaller is the value of  $K$  and the less favorable is the formation of products.

### EXAMPLE 17-17 $K$ versus $\Delta G_{\text{rxn}}^0$

Use the data in Appendix K to calculate  $K_{\text{p}}$  for the following reaction at 25°C.



#### Plan

The temperature is 25°C, so we evaluate  $\Delta G_{\text{rxn}}^0$  for the reaction from  $\Delta G_{\text{f}}^0$  values in Appendix K. The reaction involves only gases, so  $K$  is  $K_{\text{p}}$ . This means that  $\Delta G_{\text{rxn}}^0 = -RT \ln K_{\text{p}}$ . We solve for  $K_{\text{p}}$ .

#### Solution

$$\begin{aligned}\Delta G_{\text{rxn}}^0 &= [2 \Delta G_{\text{f}}^0(\text{N}_2(\text{g})) + \Delta G_{\text{f}}^0(\text{O}_2(\text{g}))] - [2 \Delta G_{\text{f}}^0(\text{N}_2\text{O}(\text{g}))] \\ &= [2(0) + 0] - [2(104.2)] = -208.4 \text{ kJ/mol, or } -2.084 \times 10^5 \text{ J/mol}\end{aligned}$$

This is a gas-phase reaction, so  $\Delta G_{\text{rxn}}^0$  is related to  $K_{\text{p}}$  by

$$\begin{aligned}\Delta G_{\text{rxn}}^0 &= -RT \ln K_{\text{p}} \\ \ln K_{\text{p}} &= \frac{\Delta G_{\text{rxn}}^0}{-RT} = \frac{-2.084 \times 10^5 \text{ J/mol}}{-(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})} = 84.1 \\ K_{\text{p}} &= e^{84.1} = 3.3 \times 10^{36}\end{aligned}$$

The very large value of  $K_{\text{p}}$  tells us that the equilibrium lies *very* far to the right. This reaction is so slow at 25°C, however, that very little  $\text{N}_2\text{O}$  decomposes to  $\text{N}_2$  and  $\text{O}_2$  at that temperature.

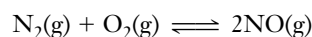
*You should now work Exercise 84.*

Units cancel when we express  $\Delta G^0$  in joules per mole. We interpret this as meaning “per mole of reaction”—that is, for the number of moles of each substance shown in the balanced equation.

On some calculators, we evaluate  $e^x$  as follows: Enter the value of  $x$ , then press  $\boxed{\text{INV}}$  followed by  $\boxed{\ln x}$ .

### EXAMPLE 17-18 $K$ versus $\Delta G_{\text{rxn}}^0$

In Examples 15-16 and 15-17 we evaluated  $\Delta G_{\text{rxn}}^0$  for the following reaction at 25°C and found it to be +173.1 kJ/mol. Calculate  $K_{\text{p}}$  at 25°C for this reaction.



#### Plan

In this example we use  $\Delta G_{\text{rxn}}^0 = -RT \ln K_{\text{p}}$ .

#### Solution

$$\begin{aligned}\Delta G_{\text{rxn}}^0 &= -RT \ln K_{\text{p}} \\ \ln K_{\text{p}} &= \frac{\Delta G_{\text{rxn}}^0}{-RT} = \frac{1.731 \times 10^5 \text{ J/mol}}{-(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K})} \\ &= -69.9 \\ K_{\text{p}} &= e^{-69.9} = 4.4 \times 10^{-31}\end{aligned}$$

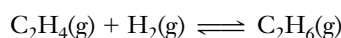
This very small number indicates that at equilibrium almost no  $\text{N}_2$  and  $\text{O}_2$  are converted to NO at  $25^\circ\text{C}$ . For all practical purposes, the reaction does not occur at  $25^\circ\text{C}$ .

*You should now work Exercise 86.*

A very important application of the relationships in this section is the use of measured  $K$  values to calculate  $\Delta G_{\text{rxn}}^0$ .

### EXAMPLE 17-19 $K$ versus $\Delta G_{\text{rxn}}^0$

The equilibrium constant,  $K_p$ , for the following reaction is  $5.04 \times 10^{17}$  at  $25^\circ\text{C}$ . Calculate  $\Delta G_{298}^0$  for the hydrogenation of ethylene to form ethane.



#### Plan

We use the relationship between  $\Delta G^0$  and  $K_p$ .

#### Solution

$$\begin{aligned}\Delta G_{298}^0 &= -RT \ln K_p \\ &= -(8.314 \text{ J/mol} \cdot \text{K})(298 \text{ K}) \ln (5.04 \times 10^{17}) \\ &= -1.01 \times 10^5 \text{ J/mol} \\ &= \mathbf{-101 \text{ kJ/mol}}\end{aligned}$$

*You should now work Exercise 88(a).*

## 17-13 EVALUATION OF EQUILIBRIUM CONSTANTS AT DIFFERENT TEMPERATURES

Chemists have determined equilibrium constants for thousands of reactions. It would be an impossibly huge task to catalog such constants at every temperature of interest for each reaction. Fortunately, there is no need to do this. If we determine the equilibrium constant,  $K_{T_1}$ , for a reaction at one temperature,  $T_1$ , and also its  $\Delta H^0$ , we can then *estimate* the equilibrium constant at a second temperature,  $T_2$ , using the **van't Hoff equation**.

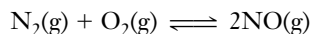
Compare the form of this equation to the Arrhenius equation (Section 16-8) and to the Clausius–Clapeyron equation (Section 13-9).

$$\ln \left( \frac{K_{T_2}}{K_{T_1}} \right) = \frac{\Delta H^0}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

Thus, if we know  $\Delta H^0$  for a reaction and  $K$  at a given temperature (say 298 K), we can use the van't Hoff equation to calculate the value of  $K$  at any other temperature.

### EXAMPLE 17-20 Evaluation of $K_p$ at Different Temperatures

We found in Example 17-18 that  $K_p = 4.4 \times 10^{-31}$  at  $25^\circ\text{C}$  (298 K) for the following reaction.  $\Delta H^0 = 180.5 \text{ kJ/mol}$  for this reaction. Evaluate  $K_p$  at 2400. K.

**Plan**

We are given  $K_p$  at one temperature, 25°C, and the value of  $\Delta H^0$ . We are given the second temperature, 2400. K. These data allow us to evaluate the right side of the van't Hoff equation, which gives us  $\ln(K_{T_2}/K_{T_1})$ . Because we know  $K_{T_1}$ , we can find the value for  $K_{T_2}$ .

**Solution**

Let  $T_1 = 298$  K and  $T_2 = 2400$ . K. Then

$$\ln\left(\frac{K_{T_2}}{K_{T_1}}\right) = \frac{\Delta H^0}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Let us first evaluate the right side of the equation.

$$\ln\left(\frac{K_{T_2}}{K_{T_1}}\right) = \frac{1.805 \times 10^5 \text{ J/mol}}{8.314 \text{ J/mol} \cdot \text{K}}\left(\frac{1}{298 \text{ K}} - \frac{1}{2400. \text{ K}}\right) = 63.8$$

Now take the inverse logarithm of both sides.

$$\frac{K_{T_2}}{K_{T_1}} = e^{63.8} = 5.1 \times 10^{27}$$

Solving for  $K_{T_2}$  and substituting the known value of  $K_{T_1}$ , we obtain

$$K_{T_2} = (5.1 \times 10^{27})(K_{T_1}) = (5.1 \times 10^{27})(4.4 \times 10^{-31}) = 2.2 \times 10^{-3} \text{ at } 2400. \text{ K}$$

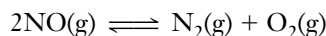
You should now work Exercise 88(b–f).

2400 K is a typical temperature inside the combustion chambers of automobile engines. Large quantities of  $\text{N}_2$  and  $\text{O}_2$  are present during gasoline combustion, because the gasoline is mixed with air.

 **Problem-Solving Tip: Use the Correct  $K$** 

The  $K$  values that appear in the van't Hoff equation represent the *thermodynamic equilibrium constant* (see Section 17-12). For a gas-phase reaction (such as that in Example 17-20),  $K$  represents  $K_p$ ; if the value of  $K_c$  were given, we would have to convert it to  $K_p$  (see Section 17-10) before using the van't Hoff equation.

In Example 17-20 we see that  $K_{T_2}$  ( $K_p$  at 2400. K) is quite small, which tells us that the equilibrium favors  $\text{N}_2$  and  $\text{O}_2$  rather than  $\text{NO}$ . Nevertheless,  $K_{T_2}$  is very much larger than  $K_{T_1}$ , which is  $4.4 \times 10^{-31}$ . At 2400. K, significantly more  $\text{NO}$  is present at equilibrium, relative to  $\text{N}_2$  and  $\text{O}_2$ , than at 298 K. So automobiles emit small amounts of  $\text{NO}$  into the atmosphere, sufficient to cause severe air pollution problems. Catalytic converters (Section 16-9) are designed to catalyze the breakdown of  $\text{NO}$  into  $\text{N}_2$  and  $\text{O}_2$ .



This reaction is spontaneous. Catalysts do not shift the position of equilibrium. They favor neither consumption nor production of  $\text{NO}$ . They merely allow the system to reach equilibrium more rapidly. The time factor is very important because the  $\text{NO}$  stays in the automobile exhaust system for only a very short time.

The  $K_p$  value could be converted to  $K_c$  using the relationship  $K_c = K_p(RT)^{-\Delta n}$  (Section 17-10).

## Key Terms

**Activity (of a component of an ideal mixture)** A dimensionless quantity whose magnitude is equal to molar concentration in an ideal solution, equal to partial pressure (in atmospheres) in an ideal gas mixture, and defined as 1 for pure solids or liquids.

**Chemical equilibrium** A state of dynamic balance in which the rates of forward and reverse reactions are equal; there is no net change in concentrations of reactants or products while a system is at equilibrium.

**Dynamic equilibrium** An equilibrium in which processes occur continuously, with no *net* change.

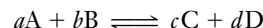
**Equilibrium constant, ( $K_c$ )** A quantity that indicates the extent to which a reversible reaction occurs.  $K_c$  varies with temperature.

**Heterogeneous equilibria** Equilibria involving species in more than one phase.

**Homogeneous equilibria** Equilibria involving only species in a single phase, that is, all gases, all liquids, or all solids.

**LeChatelier's Principle** If a stress (change of conditions) is applied to a system at equilibrium, the system shifts in the direction that reduces the stress, to move toward a new state of equilibrium.

**Mass action expression** For a reversible reaction,



the product of the molar concentrations of the products (species on the right), each raised to the power that corresponds to its coefficient in the balanced chemical equation, divided by the product of the concentrations of the reactants (species on the left), each raised to the power that corresponds to its coefficient in the balanced chemical equation. At equilibrium the mass action expression is equal to  $K_c$ ; at other conditions, it is  $Q$ .

$$\frac{[C]^c[D]^d}{[A]^a[B]^b} = Q \text{ or, at equilibrium, } K_c$$

**Reaction quotient,  $Q$**  The mass action expression under any set of conditions (not necessarily equilibrium); its magnitude relative to  $K_c$  determines the direction in which reaction must occur to establish equilibrium.

**Reversible reactions** Reactions that do not go to completion and occur in both the forward and reverse directions.

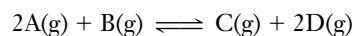
**van't Hoff equation** The relationship between  $\Delta H^0$  for a reaction and its equilibrium constants at two different temperatures.

## Exercises

### Basic Concepts

- Define and illustrate the following terms: (a) reversible reaction, (b) chemical equilibrium, (c) equilibrium constant.
- Equilibrium constants do not have units. Explain.
- Distinguish between the terms "static equilibrium" and "dynamic equilibrium." Which kind does chemical equilibrium represent?
- (a) Describe three examples of static equilibrium. (b) Describe three examples of dynamic equilibrium (besides chemical equilibrium).
- Explain the significance of (a) a very large value of  $K$ , (b) a very small value of  $K$ , and (c) a value of  $K$  of about 1.
- What can be said about the magnitude of the equilibrium constant in a reaction whose equilibrium lies far to the right? To the left?
- What is the relationship between equilibrium and the rates of opposing processes?
- What does the value of an equilibrium constant tell us about the time required for the reaction to reach equilibrium?
- When giving the value of an equilibrium constant, it is necessary also to write the balanced chemical equation. Why? Give examples to illustrate your explanation.

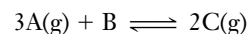
- (a) How is the equilibrium constant related to the forward and reverse rate constants? (b) Can the rate expressions for forward and reverse reactions be written from the balanced chemical equation? Explain. (c) Can the equilibrium constant expression be written from the balanced chemical equation? Explain.
- (a) Sketch a set of curves similar to Figure 17-2 for concentration changes with time for a reaction



assuming that  $K$  is much greater than 1. In each case, assume that A and B start at the same concentration and that no C or D are present.

(b) Repeat part (a) for the case that  $K$  is much less than 1.

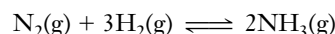
- (a) Sketch a set of curves similar to Figure 17-2 for concentration changes with time for a reaction



assuming that  $K$  is much greater than 1. In each case, assume that A and B start at the same concentration and that no C is present.

(b) Repeat part (a) for the case that  $K$  is much less than 1.

- At some temperature, the reaction



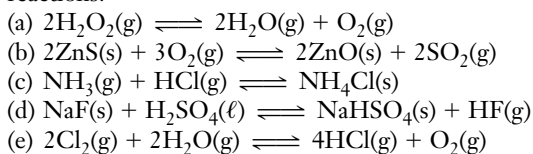
has an equilibrium constant  $K_c$  numerically equal to 1. State whether each of the following is true or false, and explain why.

- (a) An equilibrium mixture must have the  $H_2$  concentration three times that of  $N_2$  and the  $NH_3$  concentration twice that of  $H_2$ .
- (b) An equilibrium mixture must have the  $H_2$  concentration three times that of  $N_2$ .
- (c) A mixture in which the  $H_2$  concentration is three times that of  $N_2$  and the  $NH_3$  concentration is twice that of  $N_2$  could be an equilibrium mixture.
- (d) A mixture in which the concentration of each reactant and each product is 1 M is an equilibrium mixture.
- (e) Any mixture in which the concentrations of all reactants and products are equal is an equilibrium mixture.
- (f) An equilibrium mixture must have equal concentrations of all reactants and products.
14. Why do we omit concentrations of pure solids and pure liquids from equilibrium constant expressions?
15. Consider the following compounds, in the states indicated, as possible reactants or products in a chemical reaction. Which of these compounds would be omitted from the equilibrium constant expression?  $H_2O(s)$ ,  $H_2O(l)$ ,  $H_2O(g)$ ,  $HCl(g)$ ,  $HCl(aq)$ ,  $NaHCO_3(s)$ ,  $N_2(g)$ ,  $NH_3(l)$ ,  $CO(g)$ , and  $Fe_2O_3(s)$ .
16. Consider the following compounds, in the states indicated, as possible reactants or products in a chemical reaction. Which of these compounds would be omitted from the equilibrium constant expression? Explain.  $CaCO_3(s)$ ,  $H_2SO_4(l)$ ,  $NaOH(s)$ ,  $NaOH(aq)$ ,  $O_2(g)$ ,  $CH_3COOH(l)$ ,  $HI(g)$ ,  $I_2(s)$ ,  $C(\text{graphite})$ , and  $SO_3(g)$ .

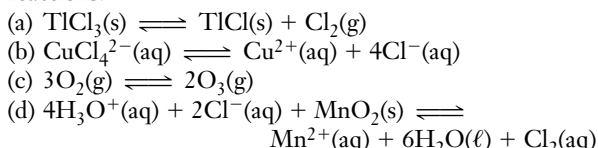
### Equilibrium Constant Expression and Value of $K$

17. Write the expression for  $K_c$  for each of the following reactions:
- (a)  $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$
- (b)  $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$
- (c)  $2CHCl_3(g) + 3H_2(g) \rightleftharpoons 2CH_4(g) + 3Cl_2(g)$
- (d)  $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
- (e)  $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$
18. Write the expression for  $K_c$  for each of the following reactions:
- (a)  $2H_2O(g) + 2SO_2(g) \rightleftharpoons 2H_2S(g) + 3O_2(g)$
- (b)  $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$
- (c)  $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$
- (d)  $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
- (e)  $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
19. Write the expression for  $K_c$  for each of the following reactions:
- (a)  $2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$
- (b)  $SrCO_3(s) \rightleftharpoons SrO(s) + CO_2(g)$
- (c)  $2HBr(g) \rightleftharpoons H_2(g) + Br_2(l)$
- (d)  $P_4(g) + 3O_2(g) \rightleftharpoons P_4O_6(s)$
- (e)  $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

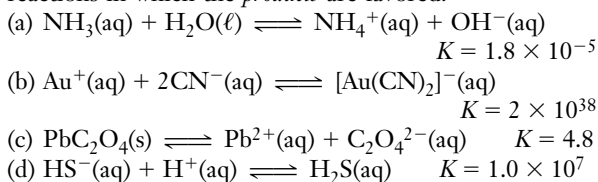
20. Write the expression for  $K_c$  for each of the following reactions:



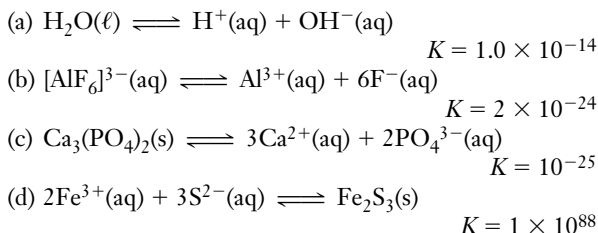
21. Write the expression for  $K_c$  for each of the following reactions:



22. On the basis of the equilibrium constant values, choose the reactions in which the *products* are favored.

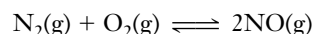


23. On the basis of the equilibrium constant values, choose the reactions in which the *reactants* are favored.



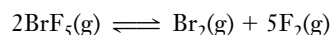
### Calculation of $K$

24. The reaction between nitrogen and oxygen to form  $NO(g)$  is represented by the chemical equation



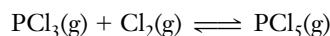
Equilibrium concentrations of the gases at 1500 K are  $1.7 \times 10^{-3}$  mol/L for  $O_2$ ,  $6.4 \times 10^{-3}$  mol/L for  $N_2$ , and  $1.1 \times 10^{-5}$  mol/L for  $NO$ . Calculate the value of  $K_c$  at 1500 K from these data.

25. At elevated temperatures,  $BrF_5$  establishes the following equilibrium.



The equilibrium concentrations of the gases at 1500 K are 0.0064 mol/L for  $BrF_5$ , 0.0018 mol/L for  $Br_2$ , and 0.0090 mol/L for  $F_2$ . Calculate the value of  $K_c$ .

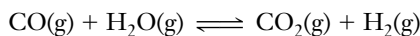
26. At some temperature the reaction



is at equilibrium when the concentrations of  $PCl_3$ ,  $Cl_2$ , and  $PCl_5$  are 10, 9, and 12 mol/L, respectively. Calculate the value of  $K_c$  for this reaction at that temperature.

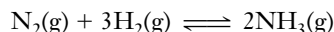


27. For the reaction



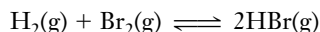
the value of the equilibrium constant,  $K_c$ , is 1.845 at a given temperature. We place 0.500 mole CO and 0.500 mole  $\text{H}_2\text{O}$  in a 1.00-L container at this temperature, and allow the reaction to reach equilibrium. What will be the equilibrium concentrations of all substances present?

28. Given:  $\text{A(g)} + \text{B(g)} \rightleftharpoons \text{C(g)} + 2\text{D(g)}$   
One mole of A and one mole of B are placed in a 0.400-liter container. After equilibrium has been established, 0.20 mole of C is present in the container. Calculate the equilibrium constant,  $K_c$ , for the reaction.
29. Nitrogen reacts with hydrogen to form ammonia.



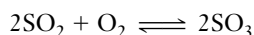
An equilibrium mixture at a given temperature is found to contain 0.31 mol/L  $\text{N}_2$ , 0.50 mol/L  $\text{H}_2$ , and 0.14 mol/L  $\text{NH}_3$ . Calculate the value of  $K_c$  at the given temperature.

30. For the following equation,
- $K_c = 7.9 \times 10^{11}$
- at 500 K.



- (a)  $\frac{1}{2}\text{H}_2\text{(g)} + \frac{1}{2}\text{Br}_2\text{(g)} \rightleftharpoons \text{HBr(g)}$        $K_c = ?$   
 (b)  $2\text{HBr(g)} \rightleftharpoons \text{H}_2\text{(g)} + \text{Br}_2\text{(g)}$        $K_c = ?$   
 (c)  $4\text{HBr(g)} \rightleftharpoons 2\text{H}_2\text{(g)} + 2\text{Br}_2\text{(g)}$        $K_c = ?$

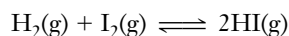
31. The equilibrium constant for the reaction



is  $K_c = 279$  at a given high temperature. What is the value of the equilibrium constant for each of the following reactions at this temperature?

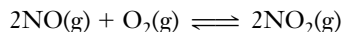
- (a)  $2\text{SO}_3 \rightleftharpoons 2\text{SO}_2 + \text{O}_2$   
 (b)  $\text{SO}_2 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{SO}_3$

32. A sealed tube initially contains
- $9.84 \times 10^{-4}$
- mol
- $\text{H}_2$
- and
- $1.38 \times 10^{-3}$
- mol
- $\text{I}_2$
- . It is kept at
- $350^\circ\text{C}$
- until the reaction



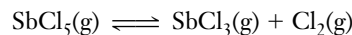
comes to equilibrium. At equilibrium,  $4.73 \times 10^{-4}$  mol  $\text{I}_2$  is present. Calculate (a) the numbers of moles of  $\text{H}_2$  and HI present at equilibrium; (b) the equilibrium constant,  $K_c$ , for the reaction.

33. NO and
- $\text{O}_2$
- are mixed in a container of fixed volume kept at 1000 K. Their initial concentrations are 0.0200 mol/L and 0.0300 mol/L, respectively. When the reaction



has come to equilibrium, the concentration of  $\text{NO}_2$  is  $2.2 \times 10^{-3}$  mol/L. Calculate (a) the concentration of NO at equilibrium, (b) the concentration of  $\text{O}_2$  at equilibrium, and (c) the equilibrium constant,  $K_c$ , for the reaction.

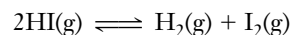
34. Antimony pentachloride decomposes in a gas-phase reaction at high temperatures.



(a) At some temperature, an equilibrium mixture in a 5.00-L container is found to contain 6.91 g of  $\text{SbCl}_5$ , 16.45 g of  $\text{SbCl}_3$ , and 5.11 g of  $\text{Cl}_2$ . Evaluate  $K_c$ .

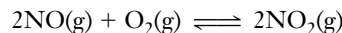
(b) If 10.0 grams of  $\text{SbCl}_5$  is placed in the 5.00-liter container and allowed to establish equilibrium at the temperature in part (a), what will be the equilibrium concentrations of all species?

35. At standard temperature and pressure, the reaction indicated by the following equation has an equilibrium constant,
- $K_c$
- , equal to 0.021



Calculate the equilibrium constant,  $K_c$ , for the reverse equation.

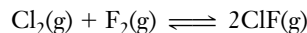
36. The following reaction has an equilibrium constant,
- $K_c$
- , equal to 1538 at
- $1800^\circ\text{C}$



Calculate the equilibrium constant,  $K_c$ , for the reverse equation.

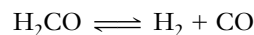
### The Reaction Quotient, $Q$

37. Define the reaction quotient,  $Q$ . Distinguish between  $Q$  and  $K$ .
38. Why is it useful to compare  $Q$  with  $K$ ? What is the situation when (a)  $Q = K$ ? (b)  $Q < K$ ? (c)  $Q > K$ ?
39. How does the form of the reaction quotient compare with that of the equilibrium constant? What is the difference between these two expressions?
40. If the reaction quotient is larger than the equilibrium constant, what will happen to the reaction? What will happen if  $Q < K$ ?
41.  $K_c = 19.9$  for the reaction



What will happen in a reaction mixture originally containing  $[\text{Cl}_2] = 0.4$  mol/L,  $[\text{F}_2] = 0.2$  mol/L, and  $[\text{ClF}] = 7.3$  mol/L?

42. The concentration equilibrium constant for the gas-phase reaction

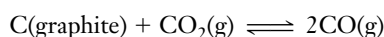


has the numerical value 0.50 at a given temperature. A mixture of  $\text{H}_2\text{CO}$ ,  $\text{H}_2$ , and CO is introduced into a flask at this temperature. After a short time, analysis of a small sample of the reaction mixture shows the concentrations to be  $[\text{H}_2\text{CO}] = 0.50$  M,  $[\text{H}_2] = 1.50$  M, and  $[\text{CO}] =$

0.25 M. Classify each of the following statements about this reaction mixture as true or false.

- The reaction mixture is at equilibrium.
- The reaction mixture is not at equilibrium, but no further reaction will occur.
- The reaction mixture is not at equilibrium, but will move toward equilibrium by using up more  $\text{H}_2\text{CO}$ .
- The forward rate of this reaction is the same as the reverse rate.

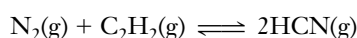
43. The value of  $K_c$  at  $25^\circ\text{C}$  for



is  $3.7 \times 10^{-23}$ . Describe what will happen if 2.0 mol of CO and 2.0 mol of  $\text{CO}_2$  are mixed in a 1.0-L container with a suitable catalyst to make the reaction “go” at this temperature.

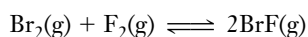
### Uses of the Equilibrium Constant, $K_c$

44. For the reaction described by the equation



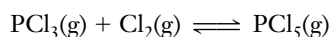
$K_c = 2.3 \times 10^{-4}$  at  $300^\circ\text{C}$ . What is the equilibrium concentration of hydrogen cyanide if the initial concentrations of  $\text{N}_2$  and acetylene ( $\text{C}_2\text{H}_2$ ) were 2.2 mol/L and 1.0 mol/L, respectively?

45. The equilibrium constant,  $K_c$ , for the reaction



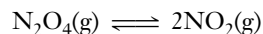
is 55.3. What are the equilibrium concentrations of all these gases if the initial concentrations of bromine and fluorine were both 0.250 mol/L?

46.  $K_c = 96.2$  at 400 K for the reaction



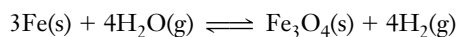
What is the concentration of  $\text{Cl}_2$  at equilibrium if the initial concentrations were 0.20 mol/L for  $\text{PCl}_3$  and 7.0 mol/L for  $\text{Cl}_2$ ?

47.  $K_c = 5.85 \times 10^{-3}$  at  $25^\circ\text{C}$  for the reaction



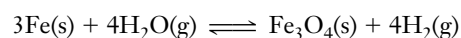
Fifteen (15.0) grams of  $\text{N}_2\text{O}_4$  is confined in a 5.00-L flask at  $25^\circ\text{C}$ . Calculate (a) the number of moles of  $\text{NO}_2$  present at equilibrium and (b) the percentage of the original  $\text{N}_2\text{O}_4$  that is dissociated.

48. The reaction of iron and water vapor results in an equilibrium



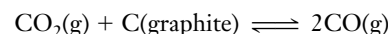
and an equilibrium constant,  $K_c$ , of 4.6 at  $850^\circ\text{C}$ . What is the concentration of hydrogen present at equilibrium if the reaction is initiated with 33 g of  $\text{H}_2\text{O}$  and excess Fe in a 16.0-liter container?

49. The reaction of iron and water vapor results in an equilibrium



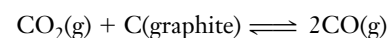
and an equilibrium constant,  $K_c$ , of 4.6 at  $850^\circ\text{C}$ . What is the concentration of water present at equilibrium if the reaction is initiated with 10. g of  $\text{H}_2$  and excess iron oxide,  $\text{Fe}_3\text{O}_4$ , in a 16.0-liter container?

50. Carbon dioxide reacts with hot carbon in the form of graphite. The equilibrium constant,  $K_c$ , for the reaction is 10.0 at  $850^\circ\text{C}$ .



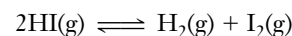
If 22 g of carbon monoxide is placed in a 2.5-L reaction vessel and heated to  $850^\circ\text{C}$ , what is the mass of carbon dioxide at equilibrium?

51. Carbon dioxide reacts with hot carbon in the form of graphite. The equilibrium constant,  $K_c$ , for the reaction is 10.0 at  $850^\circ\text{C}$ .



If 22 g of carbon dioxide and 50. grams of graphite are placed in a 2.5-L reaction vessel and heated to  $850^\circ\text{C}$ , what is the mass of carbon monoxide at equilibrium?

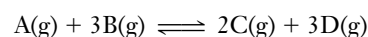
52. A 62.5-gram sample of HI was placed in a 1.50-L reaction vessel and allowed to come to equilibrium as illustrated in the following equation



The equilibrium constant,  $K_c$ , is 0.830. Calculate the concentration of each species present at equilibrium.

### Factors That Influence Equilibrium

53. State LeChatelier's Principle. Which factors have an effect on a system at equilibrium? How does the presence of a catalyst affect a system at chemical equilibrium? Explain your answer.
54. What will be the effect of increasing the total pressure on the equilibrium conditions for (a) a chemical equation that has more moles of gaseous products than gaseous reactants, (b) a chemical equation that has more moles of gaseous reactants than gaseous products, (c) a chemical equation that has the same number of moles of gaseous reactants and gaseous products, and (d) a chemical equation in which all reactants and products are pure solids, pure liquids, or in aqueous solution?
55. Suppose the following exothermic reaction is allowed to reach equilibrium.

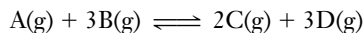


Then we make each of the following changes, and allow the reaction to reestablish equilibrium. Tell whether the

amount of B present at the new equilibrium will be (i) greater than, (ii) less than, or (iii) the same as the amount of B before the change was imposed.

(a) The temperature is increased while the volume is kept constant; (b) more A is added; (c) more C is added; (d) a small amount of D is removed; (e) the pressure is increased by decreasing the volume.

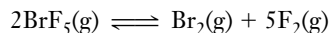
56. Suppose the following exothermic reaction is allowed to reach equilibrium.



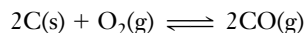
Then we make each of the following changes and allow the reaction to reestablish equilibrium. Tell whether the value of the equilibrium constant will be (i) greater than, (ii) less than, or (iii) the same as before the change was imposed.

(a) The temperature is increased while the volume is kept constant; (b) more A is added; (c) more C is added; (d) a small amount of D is removed; (e) the pressure is increased by decreasing the volume.

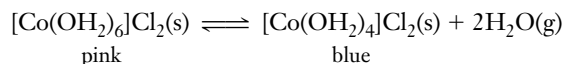
57. What would be the effect on the equilibrium position of an equilibrium mixture of  $Br_2$ ,  $F_2$ , and  $BrF_3$  if the total pressure of the system were increased?



58. What would be the effect on the equilibrium position of an equilibrium mixture of carbon, oxygen, and carbon monoxide if the total pressure of the system were increased?

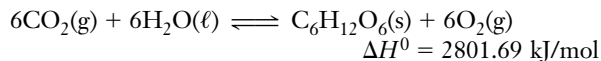


59. A weather indicator can be made with a hydrate of cobalt(II) chloride, which changes color as a result of the following reaction.



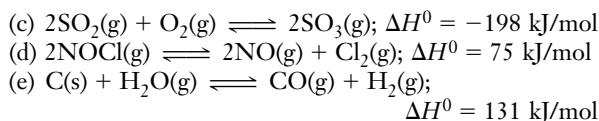
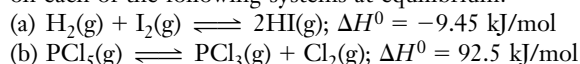
Does a blue color indicate “moist” or “dry” air? Explain.

60. Predict whether the equilibrium for the photosynthesis reaction described by the equation

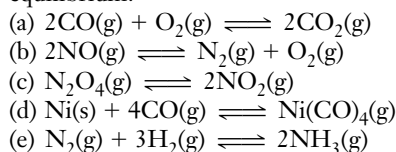


would (i) shift to the right, (ii) shift to the left, or (iii) remain unchanged if (a)  $[CO_2]$  were increased; (b)  $P_{O_2}$  were increased; (c) one half of the  $C_6H_{12}O_6$  were removed; (d) the total pressure were decreased; (e) the temperature were increased; (f) a catalyst were added.

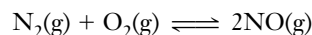
61. What would be the effect of decreasing the temperature on each of the following systems at equilibrium?



62. What would be the effect of decreasing the pressure by increasing the volume on each of the following systems at equilibrium?



63. The value of  $K_c$  is 0.020 at  $2870^\circ\text{C}$  for the reaction



There are 0.800 mole of  $N_2$ , 0.500 mole of  $O_2$ , and 0.400 mole of  $NO$  in a 1.00-liter container at  $2870^\circ\text{C}$ . Is the system at equilibrium or must the forward or reverse reaction occur to a greater extent to bring the system to equilibrium?

64. Given:  $A(g) + B(g) \rightleftharpoons C(g) + D(g)$   
 (a) At equilibrium a 1.00-liter container was found to contain 1.60 moles of C, 1.60 moles of D, 0.40 mole of A, and 0.40 mole of B. Calculate the equilibrium constant for this reaction.

(b) If 0.20 mole of B and 0.20 mole of C are added to this system, what will the new *equilibrium* concentration of A be?

65. Given:  $A(g) + B(g) \rightleftharpoons C(g) + D(g)$   
 When one mole of A and one mole of B are mixed and allowed to reach equilibrium at room temperature, the mixture is found to contain  $\frac{2}{3}$  mole of C.

(a) Calculate the equilibrium constant.  
 (b) If two moles of A were mixed with two moles of B and allowed to reach equilibrium, how many moles of C would be present at equilibrium?

66. Given:  $A(g) \rightleftharpoons B(g) + C(g)$   
 (a) When the system is at equilibrium at  $200^\circ\text{C}$ , the concentrations are found to be:  $[A] = 0.30 \text{ M}$ ,  $[B] = [C] = 0.25 \text{ M}$ . Calculate  $K_c$ .

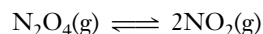
(b) If the volume of the container in which the system is at equilibrium is suddenly doubled at  $200^\circ\text{C}$ , what will the new equilibrium concentrations be?

(c) Refer back to part (a). If the volume of the container is suddenly halved at  $200^\circ\text{C}$ , what will the new equilibrium concentrations be?

- \*67. The equilibrium constant,  $K_c$  for the dissociation of phosphorus pentachloride is  $9.3 \times 10^{-2}$  at  $252^\circ\text{C}$ . How many moles and grams of  $PCl_5$  must be added to a 2.0-liter flask to obtain a  $Cl_2$  concentration of  $0.15 \text{ M}$ ?



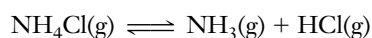
68. At  $25^\circ\text{C}$ ,  $K_c$  is  $5.84 \times 10^{-3}$  for the dissociation of dinitrogen tetroxide to nitrogen dioxide.



- (a) Calculate the equilibrium concentrations of both gases when 3.50 grams of  $\text{N}_2\text{O}_4$  is placed in a 2.00-liter flask at  $25^\circ\text{C}$ .
- (b) What will be the new equilibrium concentrations if the volume of the system is suddenly increased to 4.00 liters at  $25^\circ\text{C}$ ?
- (c) What will be the new equilibrium concentrations if the volume is decreased to 1.00 liter at  $25^\circ\text{C}$ ?

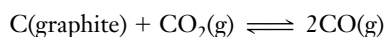
### K in Terms of Partial Pressures

69. Write the  $K_p$  expression for each reaction in Exercise 17.
70. Under what conditions are  $K_c$  and  $K_p$  for a reaction numerically equal? Are  $K_c$  and  $K_p$  numerically equal for any of the reactions in Exercises 17 and 18? Which ones?
71. 0.0100 mol of  $\text{NH}_4\text{Cl}$  and 0.0100 mol of  $\text{NH}_3$  are placed in a closed 2.00-L container and heated to 603 K. At this temperature, all the  $\text{NH}_4\text{Cl}$  vaporizes. When the reaction

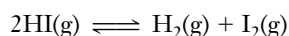


has come to equilibrium,  $5.8 \times 10^{-3}$  mol of  $\text{HCl}$  is present. Calculate (a)  $K_c$  and (b)  $K_p$  for this reaction at 603 K.

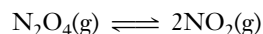
72.  $\text{CO}_2$  is passed over graphite at 500 K. The emerging gas stream contains  $4.0 \times 10^{-3}$  mol percent  $\text{CO}$ . The total pressure is 1.00 atm. Assume that equilibrium is attained. Find  $K_p$  for the reaction



73. At  $425^\circ\text{C}$ , the equilibrium partial pressures of  $\text{H}_2$ ,  $\text{I}_2$ , and  $\text{HI}$  are 0.06443 atm, 0.06540 atm, and 0.4821 atm, respectively. Calculate  $K_p$  for the following reaction at this temperature.



74. The equilibrium constant,  $K_p$ , for the reaction indicated by the following equation is 0.715 at  $47^\circ\text{C}$ .



Calculate the partial pressures of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  in an experiment in which 3.0 moles of  $\text{N}_2\text{O}_4$  is placed in a 5.0-L flask and allowed to establish equilibrium at  $47^\circ\text{C}$ .

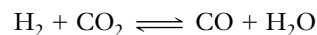
75. The equilibrium constant,  $K_p$ , is 1.92 at  $252^\circ\text{C}$  for the decomposition reaction of phosphorus pentachloride indicated in the following equation.



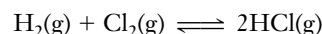
Calculate the partial pressures of all species present after 6.0 moles of  $\text{PCl}_5$  is placed in an evacuated 3.0-liter container and equilibrium is reached at  $252^\circ\text{C}$ .

76. The following equilibrium partial pressures were measured at  $750^\circ\text{C}$ :  $P_{\text{H}_2} = 0.387$  atm,  $P_{\text{CO}_2} = 0.152$  atm,  $P_{\text{CO}} =$

0.180 atm, and  $P_{\text{H}_2\text{O}} = 0.252$  atm. What is the value of the equilibrium constant,  $K_p$ , for the reaction?

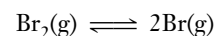


77. For the reaction



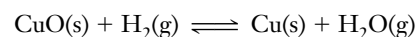
$K_c = 193$  at 2500 K. What is the value of  $K_p$ ?

78. For the reaction



$K_p = 2550$  at 4000 K. What is the value of  $K_c$ ?

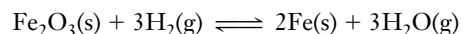
79. A stream of gas containing  $\text{H}_2$  at an initial partial pressure of 0.200 atm is passed through a tube in which  $\text{CuO}$  is kept at 500 K. The reaction



comes to equilibrium. For this reaction,  $K_p = 1.6 \times 10^9$ . What is the partial pressure of  $\text{H}_2$  in the gas leaving the tube? Assume that the total pressure of the stream is unchanged.

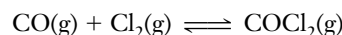
### Relationships Among $K$ , $\Delta G^0$ , $\Delta H^0$ , and $T$

80. In the distant future, when hydrogen may be cheaper than coal, steel mills may make iron by the reaction

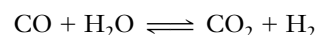


For this reaction,  $\Delta H = 96$  kJ/mol and  $K_c = 8.11$  at 1000 K. (a) What percentage of the  $\text{H}_2$  remains unreacted after the reaction has come to equilibrium at 1000 K? (b) Is this percentage greater or less if the temperature is decreased to below 1000 K?

81. What kind of equilibrium constant can be calculated from a  $\Delta G^0$  value for a reaction involving only gases?
82. What must be true of the value of  $\Delta G^0$  for a reaction if (a)  $K \gg 1$ ; (b)  $K = 1$ ; (c)  $K \ll 1$ ?
83. A mixture of 3.00 mol of  $\text{Cl}_2$  and 3.00 mol of  $\text{CO}$  is enclosed in a 5.00-L flask at  $600^\circ\text{C}$ . At equilibrium, 3.3% of the  $\text{Cl}_2$  has been consumed.



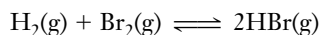
- (a) Calculate  $K_c$  for the reaction at  $600^\circ\text{C}$ .
- (b) Calculate  $\Delta G^0$  for the reaction at this temperature.
84. (a) Use the tabulated thermodynamic values of  $\Delta H_f^0$  and  $S^0$  to calculate the value of  $K_p$  at  $25^\circ\text{C}$  for the gas-phase reaction



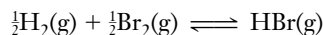
(b) Calculate the value of  $K_p$  for this reaction at  $200^\circ\text{C}$ , by the same method as in part (a).

(c) Repeat the calculation of part (a), using tabulated values of  $\Delta G_f^0$ .

85. The equilibrium constant  $K_c$  of the reaction

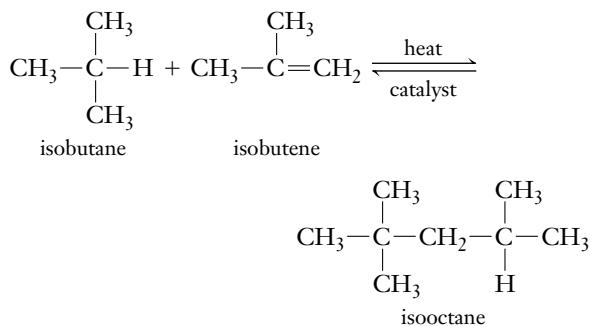


is  $1.6 \times 10^5$  at 1297 K and  $3.5 \times 10^4$  at 1495 K. (a) Is  $\Delta H^0$  for this reaction positive or negative? (b) Find  $K_c$  for the reaction



at 1297 K. (c) Pure HBr is placed in a container of constant volume and heated to 1297 K. What percentage of the HBr is decomposed to  $\text{H}_2$  and  $\text{Br}_2$  at equilibrium?

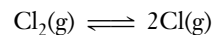
86. The air pollutant sulfur dioxide can be partially removed from stack gases in industrial processes and converted to sulfur trioxide, the acid anhydride of commercially important sulfuric acid. Write the equation for the reaction, using the smallest whole-number coefficients. Calculate the value of the equilibrium constant for this reaction at 25°C, from values of  $\Delta G_f^0$  in Appendix K.
87. The value of  $\Delta H^0$  for the reaction in Exercise 86 is  $-197.6$  kJ/mol. (a) Predict qualitatively (i.e., without calculation) whether the value of  $K_p$  for this reaction at 500°C would be greater than, the same as, or less than the value at room temperature (25°C). (b) Now calculate the value of  $K_p$  at 500°C.
- \*88. The following is an example of an alkylation reaction that is important in the production of isooctane (2,2,4-trimethylpentane) from two components of crude oil: isobutane and isobutene. Isooctane is an antiknock additive for gasoline.



The thermodynamic equilibrium constant,  $K$ , for this reaction at 25°C is  $4.3 \times 10^6$ , and  $\Delta H^0$  is  $-78.58$  kJ/mol.

- Calculate  $\Delta G^0$  at 25°C.
- Calculate  $K$  at 800°C.
- Calculate  $\Delta G^0$  at 800°C.
- How does the spontaneity of the forward reaction at 800°C compare with that at 25°C?
- Why do you think the reaction mixture is heated in the industrial preparation of isooctane?
- What is the purpose of the catalyst? Does it affect the forward reaction more than the reverse reaction?

89. At sufficiently high temperatures, chlorine gas dissociates, according to



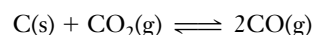
At 800°C,  $K_p$  for this reaction is  $5.63 \times 10^{-7}$ .

(a) A sample originally contained  $\text{Cl}_2$  at 1 atm and 800°C. Calculate the percentage dissociation of  $\text{Cl}_2$  when this reaction has reached equilibrium.

(b) At what temperature would  $\text{Cl}_2$  (originally at 1 atm pressure) be 1% dissociated into Cl atoms?

### Mixed Exercises

90. At 700°C,  $K_p$  is 1.50 for the reaction



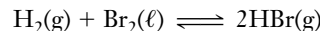
Suppose the total gas pressure at equilibrium is 1.00 atm. What are the partial pressures of CO and  $\text{CO}_2$ ?

91. At  $-10^\circ\text{C}$ , the solid compound  $\text{Cl}_2(\text{H}_2\text{O})_8$  is in equilibrium with gaseous chlorine, water vapor, and ice. The partial pressures of the two gases in equilibrium with a mixture of  $\text{Cl}_2(\text{H}_2\text{O})_8$  and ice are 0.20 atm for  $\text{Cl}_2$  and 0.00262 atm for water vapor. Find the equilibrium constant  $K_p$  for each of these reactions.
- $\text{Cl}_2(\text{H}_2\text{O})_8(\text{s}) \rightleftharpoons \text{Cl}_2(\text{g}) + 8\text{H}_2\text{O}(\text{g})$
  - $\text{Cl}_2(\text{H}_2\text{O})_8(\text{s}) \rightleftharpoons \text{Cl}_2(\text{g}) + 8\text{H}_2\text{O}(\text{s})$
- Why are your two answers so different?
92. A flask contains  $\text{NH}_4\text{Cl}(\text{s})$  in equilibrium with its decomposition products.

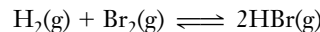


For this reaction,  $\Delta H = 176$  kJ/mol. How is the mass of  $\text{NH}_3$  in the flask affected by each of the following disturbances? (a) The temperature is decreased. (b)  $\text{NH}_3$  is added. (c) HCl is added. (d)  $\text{NH}_4\text{Cl}$  is added, with no appreciable change in the gas volume. (e) A large amount of  $\text{NH}_4\text{Cl}$  is added, decreasing the volume available to the gases.

93. The equilibrium constant for the reaction



is  $K_p = 4.5 \times 10^{18}$  at 25°C. The vapor pressure of liquid  $\text{Br}_2$  at this temperature is 0.28 atm. (a) Find  $K_p$  at 25°C for the reaction



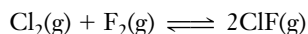
(b) How will the equilibrium in part (a) be shifted by an increase in the volume of the container if (1) liquid  $\text{Br}_2$  is absent; (2) liquid  $\text{Br}_2$  is present? Explain why the effect is different in these two cases.

94. Given that  $K_p$  is  $4.6 \times 10^{-14}$  at 25°C for the reaction



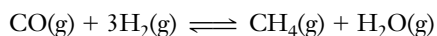
Calculate  $K_p$  and  $K_c$  for the reaction at  $400^\circ\text{C}$  and at  $800^\circ\text{C}$ .

95.  $K_c = 19.9$  for the reaction



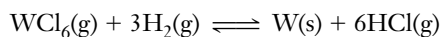
What will happen in a reaction mixture originally containing  $[\text{Cl}_2] = 0.200 \text{ mol/L}$ ,  $[\text{F}_2] = 0.300 \text{ mol/L}$ , and  $[\text{ClF}] = 0.950 \text{ mol/L}$ ?

96. A mixture of  $\text{CO}$ ,  $\text{H}_2$ ,  $\text{CH}_4$ , and  $\text{H}_2\text{O}$  is kept at  $1133 \text{ K}$  until the reaction



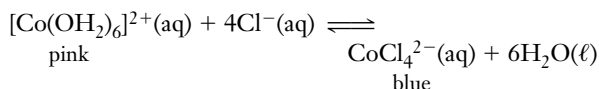
has come to equilibrium. The volume of the container is  $0.100 \text{ L}$ . The equilibrium mixture contains  $1.21 \times 10^{-4} \text{ mol CO}$ ,  $2.47 \times 10^{-4} \text{ mol H}_2$ ,  $1.21 \times 10^{-4} \text{ mol CH}_4$ , and  $5.63 \times 10^{-8} \text{ mol H}_2\text{O}$ . Calculate  $K_p$  for this reaction at  $1133 \text{ K}$ .

97. What would the pressure of hydrogen be at equilibrium when  $P_{\text{WCl}_6} = 0.012 \text{ atm}$  and  $P_{\text{HCl}} = 0.10 \text{ atm}$ ?  $K_p = 1.37 \times 10^{21}$  at  $900 \text{ K}$ .



### CONCEPTUAL EXERCISES

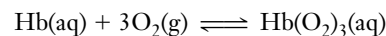
98. What is the relationship between the forward and reverse reactions in an equilibrium?
99. The term “equilibrium” brings to mind the word “equal.” What is the relationship between the two terms?
100. The masses of participants in a chemical equilibrium are not the same on both sides of the reaction. Does the equilibrium concept violate the Law of Conservation of Matter? Explain.
101. A sample of benzoic acid, a solid carbon-containing acid, is in equilibrium with an aqueous solution of benzoic acid. A tiny quantity of  $\text{D}_2\text{O}$ , water containing the isotope  $^2\text{H}$ , deuterium, is added to the solution. The solution is allowed to stand at constant temperature for several hours, after which some of the solid benzoic acid is removed and analyzed. The benzoic acid is found to contain a tiny quantity of deuterium,  $\text{D}$ , and the formula of the deuterium-containing molecules is  $\text{C}_6\text{H}_5\text{COOD}$ . Explain how this can happen.
102. Imagine yourself the size of atoms and molecules inside a beaker containing the following equilibrium mixture with a  $K$  greater than 1.



Write a brief description of what you observe around you before and after additional water is added to the mixture.

### BUILDING YOUR KNOWLEDGE

103. Hemoglobin,  $\text{Hb}$ , has four  $\text{Fe}$  atoms per molecule that, on the average, pick up roughly three molecules of  $\text{O}_2$ .

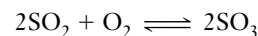


Discuss mountain or space sickness in terms of this equilibrium.



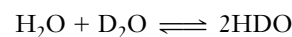
Astronauts incur the risk of space sickness.

104. At room temperature, the equilibrium constant for the reaction



is  $6.98 \times 10^{24}$ . Calculate  $\Delta G_{\text{rxn}}^0$  and  $\Delta G_{\text{f}}^0(\text{SO}_3)$ , given the additional information that  $\Delta G_{\text{f}}^0(\text{SO}_2) = -300.194 \text{ kJ/mol}$ . Check your answer by looking up  $\Delta G_{\text{f}}^0(\text{SO}_3)$  in Appendix K.

105. At  $25^\circ\text{C}$ ,  $550.0 \text{ g}$  of deuterium oxide,  $\text{D}_2\text{O}$  ( $20.0 \text{ g/mol}$ ; density  $1.10 \text{ g/mL}$ ), and  $498.5 \text{ g}$  of  $\text{H}_2\text{O}$  ( $18.0 \text{ g/mol}$ ; density  $0.997 \text{ g/mL}$ ) are mixed. The volumes are additive.  $47.0\%$  of the  $\text{H}_2\text{O}$  reacts to form  $\text{HDO}$ . Calculate  $K_c$  at  $25^\circ\text{C}$  for the reaction



106. At its normal boiling point of  $100^\circ\text{C}$ , the heat of vaporization of water is  $40.66 \text{ kJ/mol}$ . What is the equilibrium vapor pressure of water at  $50^\circ\text{C}$ ? (You may wish to review Example 15-20.)
107. Use the data in the preceding exercise to calculate the temperature at which the vapor pressure of water is  $1.50 \text{ atm}$ .