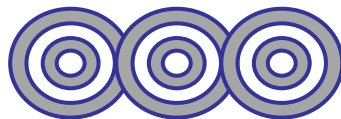




***Chemistry, The Central Science, 11th edition***  
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# **Chapter 15**

## **Chemical Equilibrium**

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**Chemical equilibrium** occurs when opposing reactions are proceeding at equal rates: The rate at which the products are formed from the reactants equals the rate at which the reactants are formed from the products. As a result, concentrations cease to change, making the reaction appear to be stopped.

How fast a reaction reaches equilibrium is a matter of kinetics. Chemical equilibrium are involved in a great many natural phenomena, and they play important roles in many industrial processes.

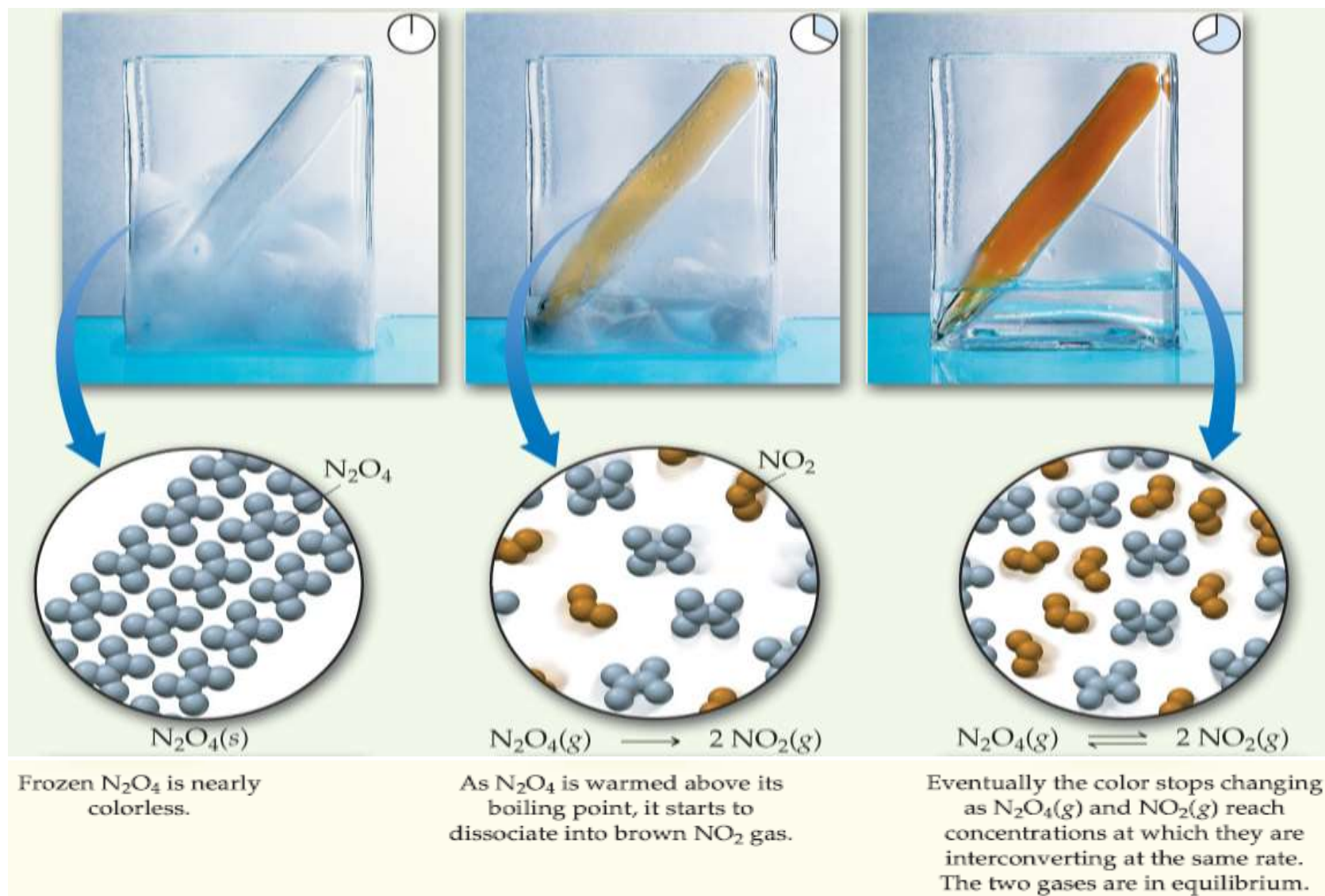
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# **15.1**

## **The Concept of Equilibrium**

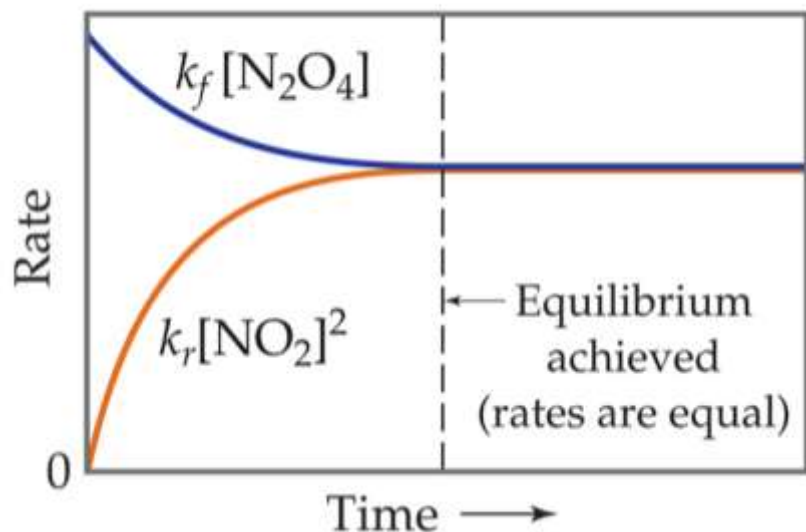
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Chemical equilibrium occurs when a reaction and its reverse reaction proceed at the same rate



### Establishing Equilibrium

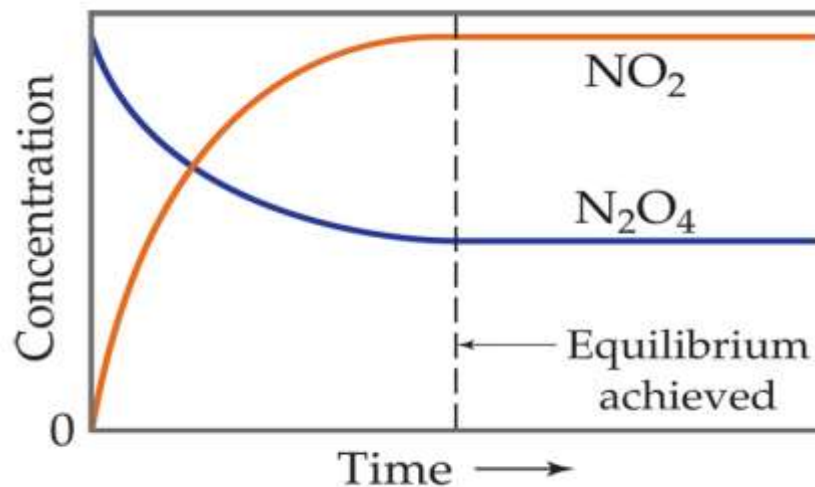
The condition in which the concentrations of all reactants and products in a closed system cease to change with time is called chemical equilibrium.



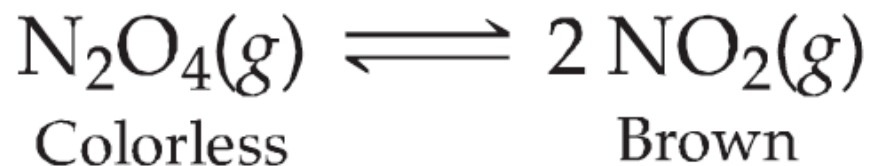
As a system approaches equilibrium, both the forward and reverse reactions are occurring.

At equilibrium, the forward and reverse reactions are proceeding at the same rate.

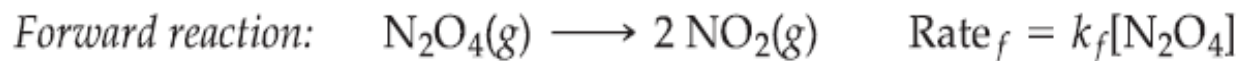
Once equilibrium is achieved, the amount of each reactant and product (concentrations) remains constant.



Since, in a system at equilibrium, both the forward and reverse reactions are being carried out, we write its equation with a double arrow.



The equilibrium mixture results because the reaction is **reversible**.  $\text{N}_2\text{O}_4$  can react to form  $\text{NO}_2$ , and  $\text{NO}_2$  can react to form  $\text{N}_2\text{O}_4$ . This situation is represented by writing the equation for the reaction with two half arrows pointing in both directions.



Where  $k_f$  and  $k_r$  are the rate constants for the forward and reverse reactions. At equilibrium, the rate at which products are produced from reactants equals the rate at which reactants are produced from products:

$$\begin{array}{ccc} k_f[\text{N}_2\text{O}_4] & = & k_r[\text{NO}_2]^2 \\ \text{Forward reaction} & & \text{Reverse reaction} \end{array}$$

$$\boxed{\frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{k_f}{k_r} = \text{a constant}}$$

At equilibrium the ratio of the concentration terms involving  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  equals a constant (called equilibrium constant). It makes no difference whether we start with  $\text{N}_2\text{O}_4$  or with  $\text{NO}_2$ , or even with some mixture of the two. At equilibrium the ratio equals a specific value.

- At equilibrium, the concentrations of reactants and products no longer change with time.
- For equilibrium to occur, neither reactants nor products can escape from the system.
- At equilibrium a particular ratio of concentration terms equals a constant.

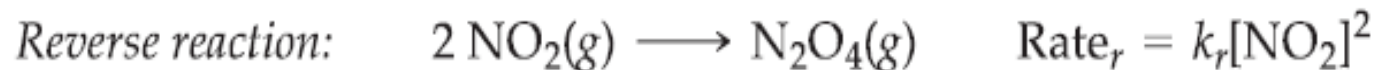
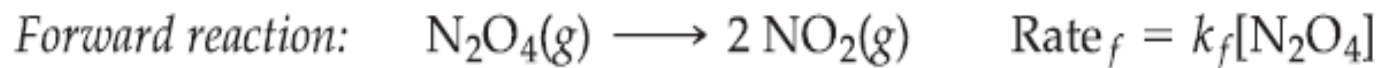
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# **15.2**

## **The Equilibrium Constant**

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- Therefore, at equilibrium
- $\text{Rate}_f = \text{Rate}_r$
- $k_f [\text{N}_2\text{O}_4] = k_r [\text{NO}_2]^2$
- Rewriting this, it becomes

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

The ratio of the rate constants is a constant at that temperature, and the expression becomes

$$K_{\text{eq}} = \frac{k_f}{k_r} = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$

Consider the generalized reaction



Note that once we know the balanced chemical equation for an equilibrium, we can write the equilibrium-constant expression even if we do not know the reaction mechanism. The equilibrium-constant expression depends only on the stoichiometry of the reaction, not on its mechanism.

The **equilibrium-constant expression (or equilibrium expression)** for this reaction would be

$$K_c = \frac{[D]^d[E]^e}{[A]^a[B]^b}$$

$$K_c = \frac{[D]^d[E]^e}{[A]^a[B]^b} \quad \begin{array}{l} \longleftarrow \text{products} \\ \longleftarrow \text{reactants} \end{array}$$

The value of the equilibrium constant at any given temperature does not depend on the initial amounts of reactants and products. It also does not matter whether other substances are present, as long as they do not react with a reactant or a product. The value of the equilibrium constant depends only on the particular reaction and on the temperature.

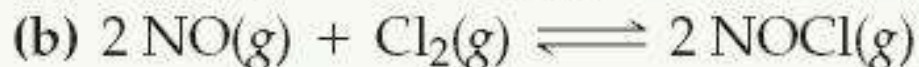
When the reactants and products in a chemical reaction are **gases**, we can formulate the equilibrium-constant expression in terms of partial pressures instead of molar concentrations since pressure is proportional to concentration for gases in a closed system.

When partial pressures in atmospheres are used in the equilibrium-constant expression, we can denote the equilibrium constant as  $K_p$  (where the subscript p stands for pressure).

$$K_p = \frac{(P_D^d) (P_E^e)}{(P_A^a) (P_B^b)}$$

## Sample Exercise 15.1 Writing Equilibrium-Constant Expressions

Write the equilibrium expression for  $K_c$  for the following reactions:



### Solution

$$\textbf{Solve:} \quad (a) \quad K_c = \frac{[\text{O}_2]^3}{[\text{O}_3]^2}, \quad (b) \quad K_c = \frac{[\text{NOCl}]^2}{[\text{NO}]^2[\text{Cl}_2]}, \quad (c) \quad K_c = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2}$$

# Relationship Between $K_c$ and $K_p$

- From the Ideal Gas Law we know that

$$PV = nRT$$

- Rearranging it, we get

$$P = \frac{n}{V} RT$$

Plugging this into the expression for  $K_p$  for each substance, the relationship between  $K_c$  and  $K_p$  becomes:

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

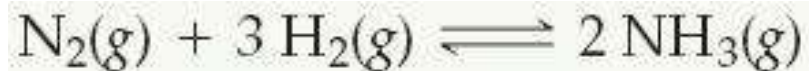
where

$$\Delta n = (\text{moles of gaseous product}) - (\text{moles of gaseous reactant})$$

For example, in the reaction  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ , there are two moles of the product  $\text{NO}_2$  (the coefficient in the balanced equation) and one mole of the reactant  $\text{N}_2\text{O}_4$ . Therefore,  $\Delta n = 2 - 1 = 1$ , and  $K_p = K_c(RT)$  for this reaction. From Equation, we see that  $K_p = K_c$  only when the same number of moles of gas appears on both sides of the balanced chemical equation, which means that  $\Delta n = 0$ .

## Sample Exercise 15.2 Converting between $K_c$ and $K_p$

In the synthesis of ammonia from nitrogen and hydrogen,



$K_c = 9.60$  at  $300\text{ }^\circ\text{C}$ . Calculate  $K_p$  for this reaction at this temperature.

### Solution

There are two moles of gaseous products ( $2 \text{NH}_3$ ) and four moles of gaseous reactants ( $1 \text{N}_2 + 3 \text{H}_2$ ). Therefore,  $\Delta n = 2 - 4 = -2$ . The temperature,  $T$ , is  $273 + 300 = 573 \text{ K}$ . The value for the ideal-gas constant,  $R$ , is  $0.0821 \text{ L-atm/mol-K}$ . Using  $K_c = 9.60$ , we therefore have

$$K_p = K_c(RT)^{\Delta n} = (9.60)(0.0821 \times 573)^{-2} = \frac{(9.60)}{(0.0821 \times 573)^2} = 4.34 \times 10^{-3}$$

## Equilibrium can be reached from either direction

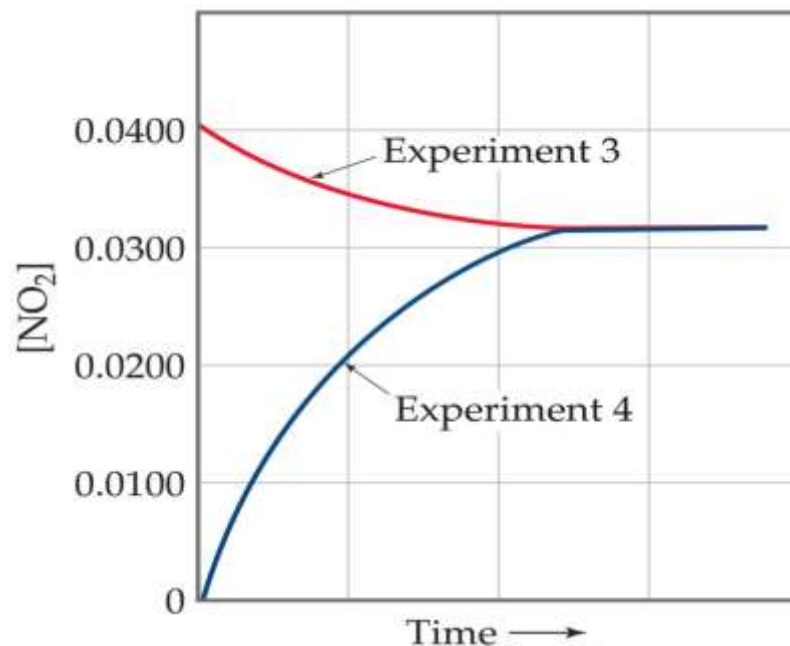
TABLE 15.1 ■ Initial and Equilibrium Concentrations of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  in the Gas Phase at  $100^\circ\text{C}$

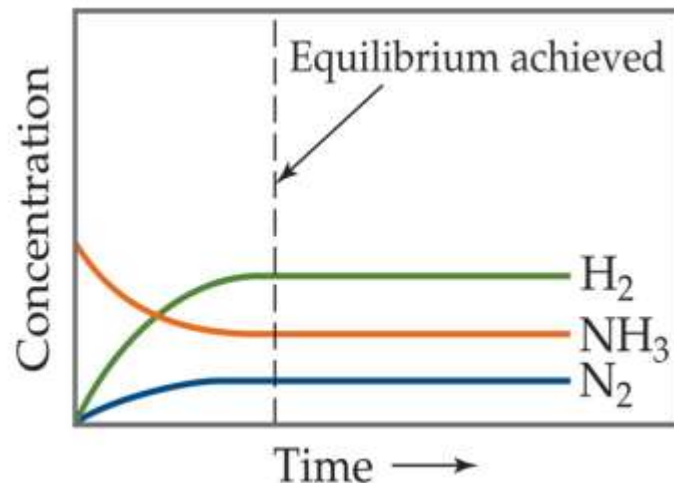
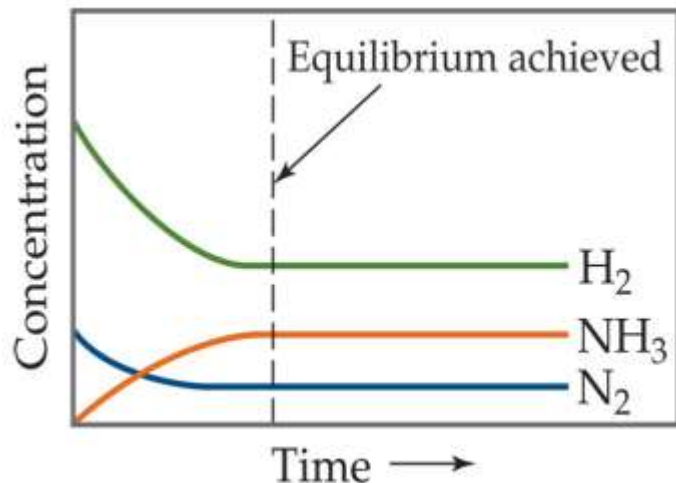
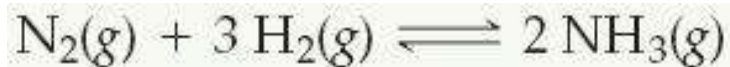
Experiment	Initial $[\text{N}_2\text{O}_4]$ (M)	Initial $[\text{NO}_2]$ (M)	Equilibrium $[\text{N}_2\text{O}_4]$ (M)	Equilibrium $[\text{NO}_2]$ (M)	$K_c$
1	0.0	0.0200	0.00140	0.0172	0.211
2	0.0	0.0300	0.00280	0.0243	0.211
3	0.0	0.0400	0.00452	0.0310	0.213
4	0.0200	0.0	0.00452	0.0310	0.213

The ratio of  $[\text{NO}_2]^2$  to  $[\text{N}_2\text{O}_4]$  remains constant at this temperature, no matter what the initial concentrations of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  are. This is the data from the last two trials from the table.

### Concentration changes approaching equilibrium

The same equilibrium mixture is produced starting with either 0.0400 M  $\text{NO}_2$  (Experiment 3) or 0.0200 M  $\text{N}_2\text{O}_4$  (Experiment 4).





### Concentration changes approaching equilibrium

- (a) Equilibrium for the reaction is approached beginning with  $\text{H}_2$  and  $\text{N}_2$  present in the ratio 3:1 and no  $\text{NH}_3$  present.
- (b) Equilibrium for the same reaction is approached beginning with only  $\text{NH}_3$  in the reaction vessel.

It doesn't matter whether we start with  $\text{N}_2$  and  $\text{H}_2$  or whether we start with  $\text{NH}_3$ : we will have the same proportions of all three substances at equilibrium.

Notice that an equilibrium mixture is obtained regardless of whether we begin with  $\text{N}_2$  and  $\text{H}_2$  or only with  $\text{NH}_3$ . The equilibrium condition can be reached from either direction.



# Equilibrium Constants and Units

Why equilibrium constants are reported without units. The equilibrium constant is related to the kinetics of a reaction as well as to the thermodynamics of the process. Equilibrium constants derived from thermodynamic measurements are defined in terms of **activities** rather than **concentrations** or **partial pressures**.

The activity of any substance in an ideal mixture is the ratio of the concentration or pressure of the substance to a reference concentration (1 M) or a reference pressure (1 atm).

For example, if the concentration of a substance in an equilibrium mixture is 0.010 M, its activity is  $0.010 \text{ M} / 1 \text{ M} = 0.010$ . The units of such ratios always cancel, and consequently, activities have no units. Furthermore, the numerical value of the activity equals the concentration. For pure solids and pure liquids, the situation is even simpler because the activities then merely equal 1 (again with no units).

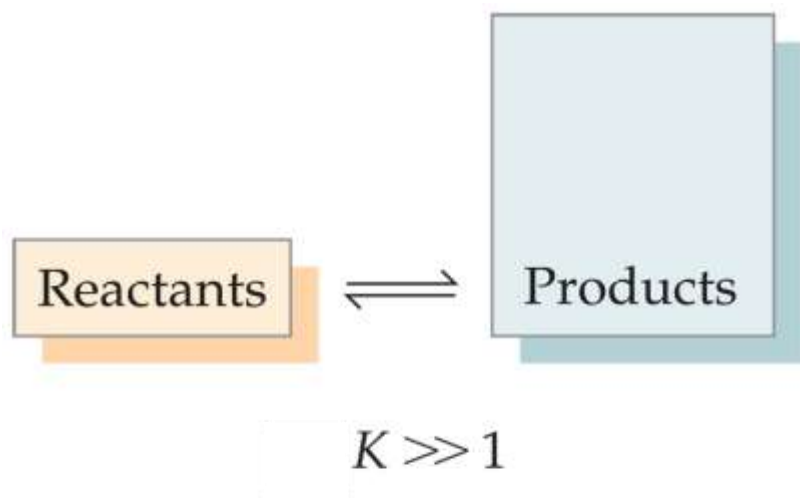
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## **15.3**

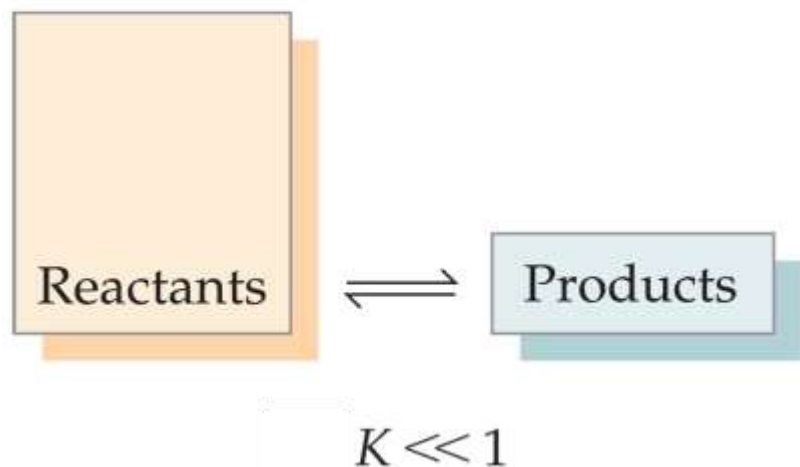
# **Interpreting and Working with Equilibrium Constants**

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What the magnitude of an equilibrium constant can tell us about the relative concentrations of reactants and products in an equilibrium mixture.



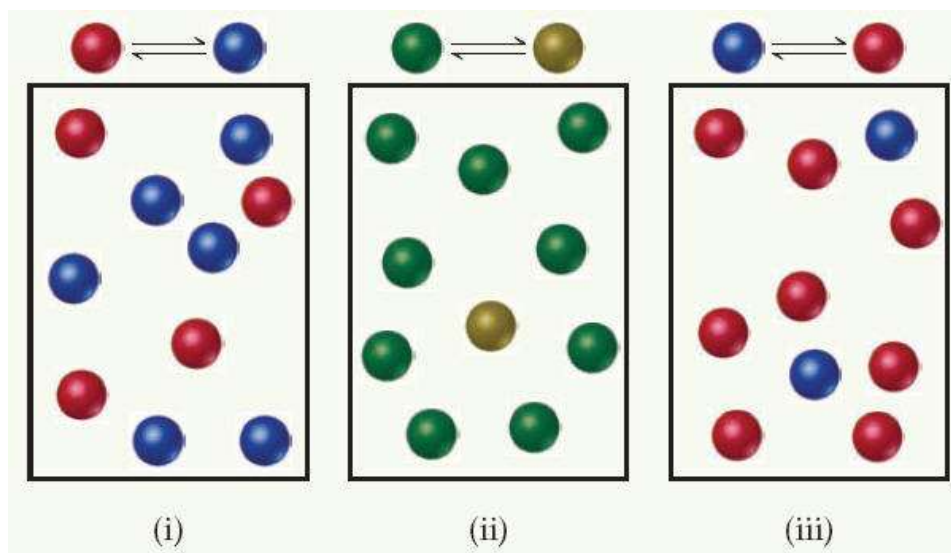
- If  $K \gg 1$ , the reaction is *product-favored*, product predominates at equilibrium.



- If  $K \ll 1$ , the reaction is *reactant-favored*, reactant predominates at equilibrium.

## Sample Exercise 15.3 Interpreting the Magnitude of an Equilibrium Constant

The following diagrams represent three different systems at equilibrium, all in the same size containers. **(a)** Without doing any calculations, rank the three systems in order of increasing equilibrium constant,  $K_c$ . **(b)** If the volume of the containers is 1.0 L and each sphere represents 0.10 mol, calculate  $K_c$  for each system.



### Solution

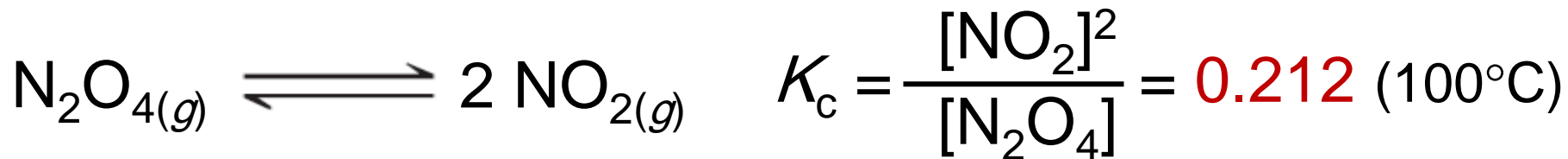
**(a)** Each box contains 10 spheres. The amount of product in each varies as follows: (i) 6, (ii) 1, (iii) 8. Thus, the equilibrium constant varies in the order (ii) < (i) < (iii).

**(b)** In (i) we have 0.60 mol/L product and 0.40 mol/L reactant, giving  $K_c = 0.60/0.40 = 1.5$ . (You will get the same result by merely dividing the number of spheres of each kind: 6 spheres/4 spheres = 1.5.) In (ii) we have 0.10 mol/L product and 0.90 mol/L reactant, giving  $K_c = 0.10/0.90 = 0.11$  (or 1 sphere/9 spheres = 0.11). In (iii) we have 0.80 mol/L product and 0.20 mol/L reactant, giving  $K_c = 0.80/0.20 = 4.0$  (or 8 spheres/2 spheres = 4.0). These calculations verify the order in (a).

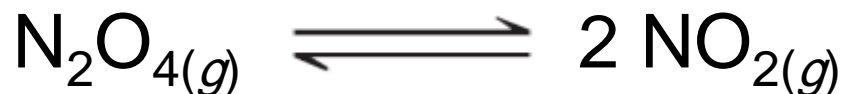
# Manipulating Equilibrium Constants

Because an equilibrium can be approached from either direction, the direction in which we write the chemical equation for an equilibrium is arbitrary.

The equilibrium constant of a reaction in the reverse reaction is the reciprocal of the equilibrium constant of the forward reaction.



The equilibrium constant of a reaction that has been multiplied by a number is the equilibrium constant raised to a power that is equal to that number.

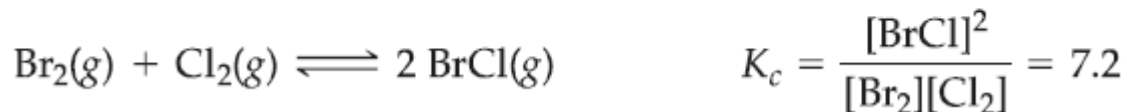
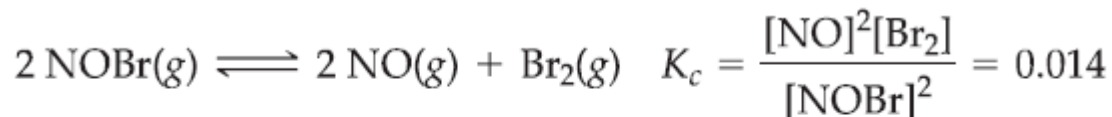


$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = 0.212 \text{ (100}^\circ\text{C)}$$



$$K_c = \frac{[\text{NO}_2]^4}{[\text{N}_2\text{O}_4]^2} = (0.212)^2 = 0.0449 \text{ (100}^\circ\text{C)}$$

The equilibrium constant for a net reaction made up of two or more steps is the product of the equilibrium constants for the individual steps.



The net sum of these two equations is:



The equilibrium-constant expression for the net equation is the product of the expressions for the individual steps:

$$K_c = \frac{[\text{NO}]^2[\text{BrCl}]^2}{[\text{NOBr}]^2[\text{Cl}_2]} = \frac{[\text{NO}]^2[\text{Br}_2]}{[\text{NOBr}]^2} \times \frac{[\text{BrCl}]^2}{[\text{Br}_2][\text{Cl}_2]}$$

Because the equilibrium-constant expression for the net equation is the product of two equilibrium-constant expressions, the equilibrium constant for the net equation is the product of the two individual equilibrium constants:

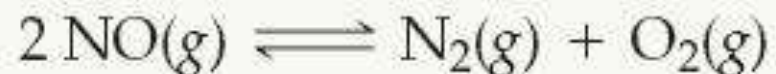
$$\mathbf{K_c = 0.014 \times 7.2 = 0.10}$$

## Sample Exercise 15.4 Evaluating an Equilibrium Constant When an Equation is Reversed

The equilibrium constant for the reaction of  $\text{N}_2$  with  $\text{O}_2$  to form  $\text{NO}$  equals  $K_c = 1 \times 10^{-30}$  at  $25^\circ\text{C}$ :



Using this information, write the equilibrium constant expression and calculate the equilibrium constant for the following reaction:



### Solution

Writing products over reactants, we have

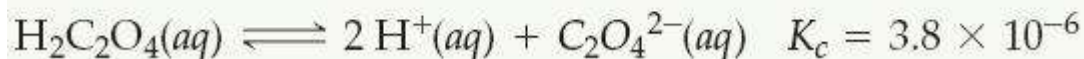
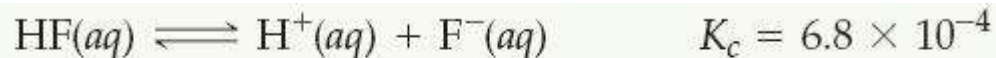
Both the equilibrium-constant expression and the numerical value of the equilibrium constant are the reciprocals of those for the formation of  $\text{NO}$  from  $\text{N}_2$  and  $\text{O}_2$ :

$$K_c = \frac{[\text{N}_2][\text{O}_2]}{[\text{NO}]^2}$$
$$K_c = \frac{[\text{N}_2][\text{O}_2]}{[\text{NO}]^2} = \frac{1}{1 \times 10^{-30}} = 1 \times 10^{30}$$



## Sample Exercise 15.5 Combining Equilibrium Expressions

Given the following information,

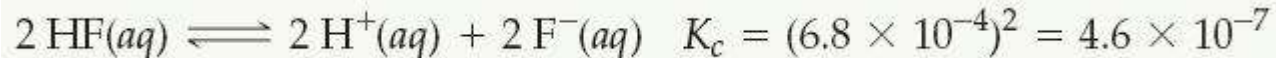


determine the value of  $K_c$  for the reaction

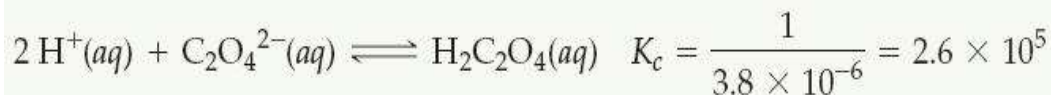


### Solution

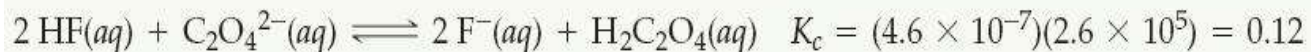
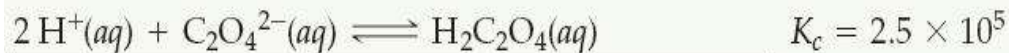
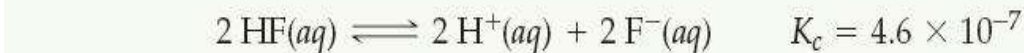
If we multiply the first equation by 2 and make the corresponding change to its equilibrium constant (raising to the power 2), we get



Reversing the second equation and again making the corresponding change to its equilibrium constant (taking the reciprocal) gives



Now we have two equations that sum to give the net equation, and we can multiply the individual  $K_c$  values to get the desired equilibrium constant.



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# **15.4**

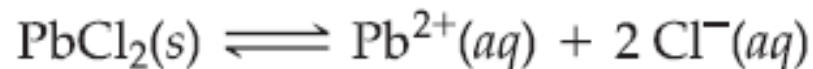
## **Heterogeneous Equilibria**

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Many equilibria, such as the hydrogen-nitrogen-ammonia system, involve substances all in the same phase. Such equilibria are called **homogeneous equilibria**. In other cases the substances in equilibrium are in different phases, giving rise to **heterogeneous equilibria**.

## The concentrations of **solids** and **liquids** are essentially **constant**

Both can be obtained by multiplying the density of the substance by its molar mass, and both of these are constants at constant temperature. Therefore, the concentrations of solids and liquids do not appear in the equilibrium expression.



$$K_c = [\text{Pb}^{2+}] [\text{Cl}^{-}]^2$$

The concentration of a pure solid or liquid has a constant value. If the mass of a solid is doubled, its volume also doubled. Thus, its concentration, which relates to the ratio of mass to volume, stays the same. Because equilibrium-constant expressions include terms only for reactants and products whose concentrations can change during a chemical reaction, the concentrations of pure solids and pure liquids are omitted.

The omission of pure solids and liquids from equilibrium-constant expressions can also be rationalized in a second way. Remember that what is substituted into a thermodynamic equilibrium expression is the activity of each substance, which is a ratio of the concentration to a reference value. For a pure substance, the reference value is the concentration of the pure substance itself, so that the activity of any pure solid or liquid is always simply 1.

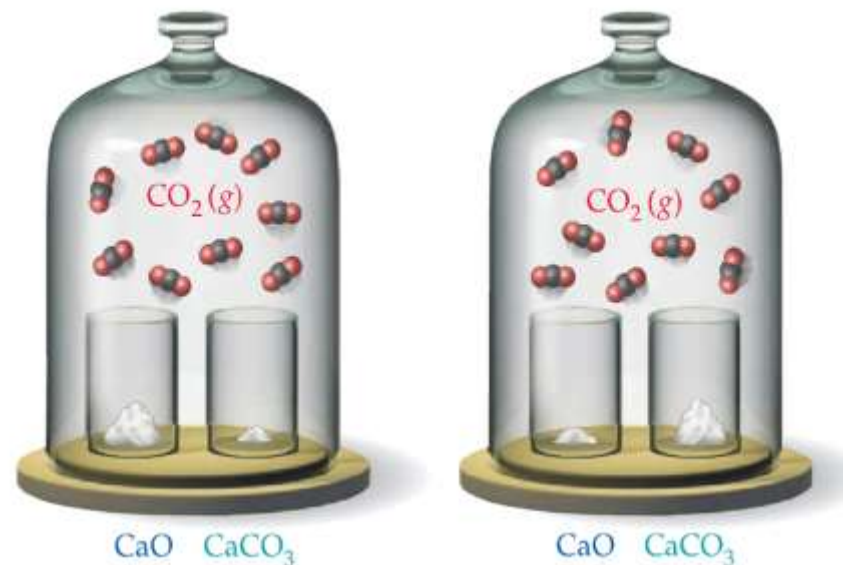
As a further example of a heterogeneous reaction, consider the decomposition of calcium carbonate:



As long as some  $\text{CaCO}_3$  or  $\text{CaO}$  remain in the system, the amount of  $\text{CO}_2$  above the solid will remain the same.

The equilibrium-constant expression for the reaction is

$$K_c = [\text{CO}_2] \quad \text{and} \quad K_p = P_{\text{CO}_2}$$



A heterogeneous equilibrium. The equilibrium involving  $\text{CaCO}_3$  or  $\text{CaO}$  and  $\text{CO}_2$  is a heterogeneous equilibrium. The equilibrium pressure of  $\text{CO}_2$  is the same in the two bell jars as long as the two systems are at the same temperature, even though the relative amounts of pure  $\text{CaCO}_3$  and  $\text{CaO}$  differ greatly.

When a solvent is involved as a reactant or product in an equilibrium, its concentration is also excluded from the equilibrium-constant expression, provided the concentrations of reactants and products are low, so that the solvent is essentially a pure substance.

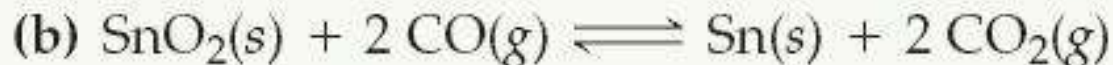


Gives an equilibrium-constant expression in which  $[\text{H}_2\text{O}]$  is excluded:

$$K_c = \frac{[\text{OH}^-][\text{HCO}_3^-]}{[\text{CO}_3^{2-}]}$$

## Sample Exercise 15.6 Writing Equilibrium-Constant Expressions for Heterogeneous Reactions

Write the equilibrium-constant expression for  $K_c$  for each of the following reactions:



### Solution

(a) The equilibrium-constant expression is

$$K_c = \frac{[\text{CO}]}{[\text{CO}_2][\text{H}_2]}$$

Because  $\text{H}_2\text{O}$  appears in the reaction as a pure liquid, its concentration does not appear in the equilibrium-constant expression.

(b) The equilibrium-constant expression is

$$K_c = \frac{[\text{CO}_2]^2}{[\text{CO}]^2}$$

Because  $\text{SnO}_2$  and  $\text{Sn}$  are both pure solids, their concentrations do not appear in the equilibrium-constant expression.

# **15.5**

## **Calculating Equilibrium Constants**



A closed system initially containing  $1.00 \times 10^{-3} \text{ M H}_2$  and  $2.00 \times 10^{-3} \text{ M I}_2$  at  $448^\circ\text{C}$  is allowed to reach equilibrium. Analysis of the equilibrium mixture shows that the concentration of HI is  $1.87 \times 10^{-3} \text{ M}$ . Calculate  $K_c$  at  $448^\circ\text{C}$  for the reaction taking place, which is :



What Do We Know?

	$[\text{H}_2], \text{ M}$	$[\text{I}_2], \text{ M}$	$[\text{HI}], \text{ M}$
Initially	$1.000 \times 10^{-3}$	$2.000 \times 10^{-3}$	0
Change			
At equilibrium			$1.87 \times 10^{-3}$

[HI] Increases by  $1.87 \times 10^{-3} M$

	$[H_2], M$	$[I_2], M$	$[HI], M$
Initially	$1.00 \times 10^{-3}$	$2.00 \times 10^{-3}$	0
Change			$+1.87 \times 10^{-3}$
At equilibrium			$1.87 \times 10^{-3}$

Stoichiometry tells us  $[H_2]$  and  $[I_2]$  decrease by half as much.

	$[H_2], M$	$[I_2], M$	$[HI], M$
Initially	$1.000 \times 10^{-3}$	$2.000 \times 10^{-3}$	0
Change	$-0.935 \times 10^{-3}$	$-0.935 \times 10^{-3}$	$+1.87 \times 10^{-3}$
At equilibrium			$1.87 \times 10^{-3}$

We can now calculate the equilibrium concentrations of all three compounds

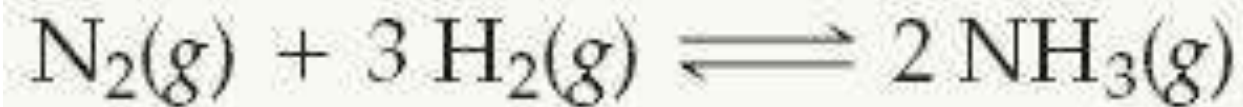
	$[\text{H}_2], M$	$[\text{I}_2], M$	$[\text{HI}], M$
Initially	$1.000 \times 10^{-3}$	$2.000 \times 10^{-3}$	0
Change	$-0.935 \times 10^{-3}$	$-0.935 \times 10^{-3}$	$+1.87 \times 10^{-3}$
At equilibrium	$0.065 \times 10^{-3}$	$1.065 \times 10^{-3}$	$1.87 \times 10^{-3}$

and, therefore, the equilibrium constant

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$
$$= \frac{(1.87 \times 10^{-3})^2}{(6.5 \times 10^{-5})(1.065 \times 10^{-3})} = 51$$

## Sample Exercise 15.8 Calculating $K$ When All Equilibrium Concentrations Are Known

A mixture of hydrogen and nitrogen in a reaction vessel is allowed to attain equilibrium at 472 °C. The equilibrium mixture of gases was analyzed and found to contain 7.38 atm  $\text{H}_2$ , 2.46 atm  $\text{N}_2$ , and 0.166 atm  $\text{NH}_3$ . From these data, calculate the equilibrium constant  $K_p$  for the reaction



### Solution

$$K_p = \frac{(P_{\text{NH}_3})^2}{P_{\text{N}_2}(P_{\text{H}_2})^3} = \frac{(0.166)^2}{(2.46)(7.38)^3} = 2.79 \times 10^{-5}$$

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# **15.6**

## **Applications of Equilibrium Constants**

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We have seen that the magnitude of  $K$  indicates the extent to which a reaction will proceed.

- If  $K$  is very large, the equilibrium mixture will contain mostly substances on the product side of the equation. (That is, the reaction will tend to proceed far to the right).
- If  $K$  is very small (that is, much less than 1), the equilibrium mixture will contain mainly reactants.

The equilibrium constant also allows us to

- (1) predict the direction in which a reaction mixture will proceed to achieve equilibrium, and
- (2) calculate the concentrations of reactants and products when equilibrium has been reached.

# Predicting the Direction of Reaction - Reaction Quotient

The reaction quotient,  $Q$ , is a number obtained by substituting reactant and product concentrations or partial pressures at any point during a reaction into an equilibrium-constant expression.



The reaction quotient is defined as:

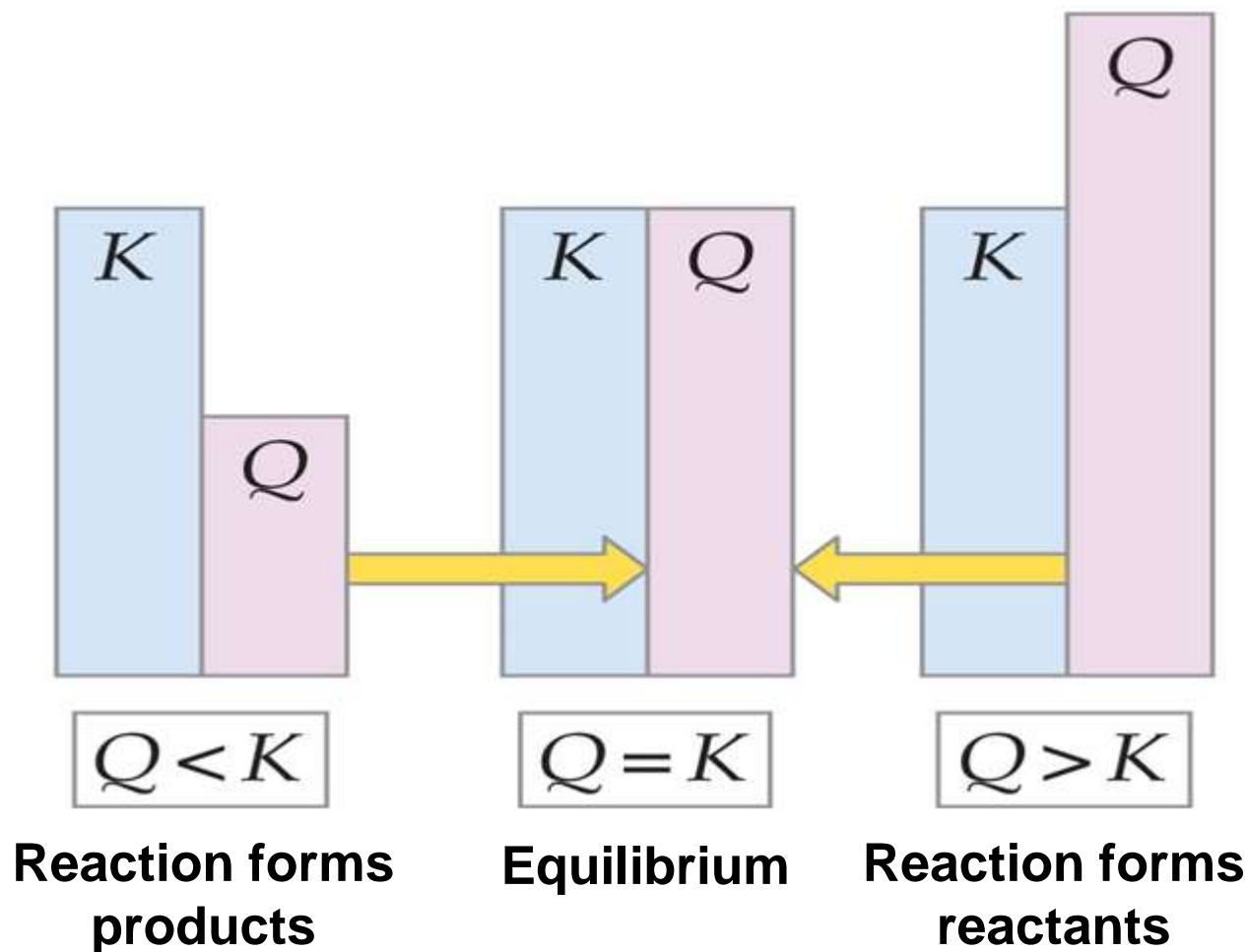
$$Q_c = \frac{[D]^d [E]^e}{[A]^a [B]^b}$$

- $Q$  gives the same ratio the equilibrium expression gives, but for a system that is *not* at equilibrium.
- To calculate  $Q$ , one substitutes the initial concentrations on reactants and products into the equilibrium expression.

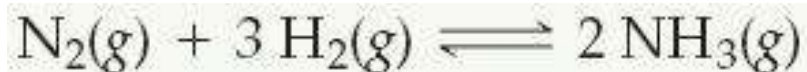
If  $Q = K$ , the system is at equilibrium (reaction quotient = equilibrium constant).

If  $Q > K$ , there is too much products, and the equilibrium shifts to the left.

If  $Q < K$ , there is too much reactants, and the equilibrium shifts to the right.







For the formation of  $\text{NH}_3$  from  $\text{N}_2$  and  $\text{H}_2$ ,  $K_c = 0.105$  at  $472^\circ\text{C}$ . Suppose we place a mixture of 2.00 mol of  $\text{H}_2$ , 1.00 mol of  $\text{N}_2$ , and 2.00 mol of  $\text{NH}_3$  in a 1.00-L container at  $472^\circ\text{C}$ . How will the mixture react to reach equilibrium? Will  $\text{N}_2$  and  $\text{H}_2$  react to form more  $\text{NH}_3$ , or will  $\text{NH}_3$  decompose to form  $\text{N}_2$  and  $\text{H}_2$ ?

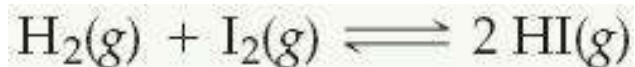
To answer this question, we can substitute the starting concentrations of  $\text{N}_2$ ,  $\text{H}_2$ , and  $\text{NH}_3$  into the equilibrium-constant expression and compare its value to the equilibrium constant:

$$\frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(2.00)^2}{(1.00)(2.00)^3} = 0.500 \quad \text{whereas} \quad K_c = 0.105$$

To reach equilibrium, the quotient will need to decrease. This change can happen only if the concentration of  $\text{NH}_3$  decreases and the concentrations of  $\text{N}_2$  and  $\text{H}_2$  increase. Thus, the reaction proceeds toward equilibrium by forming  $\text{N}_2$  and  $\text{H}_2$  from  $\text{NH}_3$ ; that is, the reaction proceeds from right to left.

## Sample Exercise 15.10 Predicting the Direction of Approach to Equilibrium

At 448 °C the equilibrium constant  $K_c$  for the reaction



is 50.5. Predict in which direction the reaction will proceed to reach equilibrium at 448 °C if we start with  $2.0 \times 10^{-2}$  mol of HI,  $1.0 \times 10^{-2}$  mol of  $\text{H}_2$ , and  $3.0 \times 10^{-2}$  mol of  $\text{I}_2$  in a 2.00-L container.

### Solution

The initial concentrations are

$$[\text{HI}] = 2.0 \times 10^{-2} \text{ mol}/2.00 \text{ L} = 1.0 \times 10^{-2} \text{ M}$$

$$[\text{H}_2] = 1.0 \times 10^{-2} \text{ mol}/2.00 \text{ L} = 5.0 \times 10^{-3} \text{ M}$$

$$[\text{I}_2] = 3.0 \times 10^{-2} \text{ mol}/2.00 \text{ L} = 1.5 \times 10^{-2} \text{ M}$$

The reaction quotient is therefore

$$Q_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(1.0 \times 10^{-2})^2}{(5.0 \times 10^{-3})(1.5 \times 10^{-2})} = 1.3$$

Because  $Q_c < K_c$  the concentration of HI must increase and the concentrations of  $\text{H}_2$  and  $\text{I}_2$  must decrease to reach equilibrium; the reaction will proceed from left to right as it moves toward equilibrium.

# Calculating Equilibrium Concentrations

## Sample Exercise 15.11 Calculating Equilibrium Concentrations

For the Haber process,  $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$ ,  $K_p = 1.45 \times 10^{-5}$  at  $500^\circ\text{C}$ . In an equilibrium mixture of the three gases at  $500^\circ\text{C}$ , the partial pressure of  $\text{H}_2$  is 0.928 atm and that of  $\text{N}_2$  is 0.432 atm. What is the partial pressure of  $\text{NH}_3$  in this equilibrium mixture?

### Solution

We tabulate the equilibrium pressures as follows:

	$\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$		
Equilibrium pressure (atm)	0.432	0.928	$x$

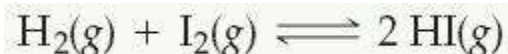
Because we do not know the equilibrium pressure of  $\text{NH}_3$ , we represent it with a variable,  $x$ . At equilibrium the pressures must satisfy the equilibrium-constant expression:

We now rearrange the equation to solve for  $x$ .

$$K_p = \frac{(P_{\text{NH}_3})^2}{P_{\text{N}_2}(P_{\text{H}_2})^3} = \frac{x^2}{(0.432)(0.928)^3} = 1.45 \times 10^{-5}$$
$$x^2 = (1.45 \times 10^{-5})(0.432)(0.928)^3 = 5.01 \times 10^{-6}$$
$$x = \sqrt{5.01 \times 10^{-6}} = 2.24 \times 10^{-3} \text{ atm} = P_{\text{NH}_3}$$
$$K_p = \frac{(2.24 \times 10^{-3})^2}{(0.432)(0.928)^3} = 1.45 \times 10^{-5}$$

## Sample Exercise 15.12 Calculating Equilibrium Concentrations from Initial Concentrations

A 1.000-L flask is filled with 1.000 mol of  $\text{H}_2$  and 2.000 mol of  $\text{I}_2$  at 448 °C. The value of the equilibrium constant  $K_c$  for the reaction



at 448 °C is 50.5. What are the equilibrium concentrations of  $\text{H}_2$ ,  $\text{I}_2$ , and  $\text{HI}$  in moles per liter?

### Solution

First, we note the initial concentrations of  $\text{H}_2$  and  $\text{I}_2$  in the 1.000-L flask:

Second, we construct a table in which we tabulate the initial concentrations:

Third, we use the stoichiometry of the reaction to determine the changes in concentration that occur as the reaction proceeds to equilibrium. The concentrations of  $\text{H}_2$  and  $\text{I}_2$  will decrease as equilibrium is established and that of  $\text{HI}$  will increase. Let's represent the change in concentration of  $\text{H}_2$  by the variable  $x$ . The balanced chemical equation tells us the relationship between the changes in the concentrations of the three gases:

Fourth, we use the initial concentrations and the changes in concentrations, as dictated by stoichiometry, to express the equilibrium concentrations. With all our entries, our table now looks like this:

$[\text{H}_2] = 1.000 \text{ M}$  and  $[\text{I}_2] = 2.000 \text{ M}$

	$\text{H}_2(\text{g})$	+	$\text{I}_2(\text{g})$	$\rightleftharpoons$	$2 \text{HI}(\text{g})$
Initial	1.000 M		2.000 M		0 M
Change					
Equilibrium					

For each  $x$  mol of  $\text{H}_2$  that reacts,  $x$  mol of  $\text{I}_2$  are consumed and  $2x$  mol of  $\text{HI}$  are produced:

	$\text{H}_2(\text{g})$	+	$\text{I}_2(\text{g})$	$\rightleftharpoons$	$2 \text{HI}(\text{g})$
Initial	1.000 M		2.000 M		0 M
Change	$-x$		$-x$		$+2x$
Equilibrium					

	$\text{H}_2(\text{g})$	+	$\text{I}_2(\text{g})$	$\rightleftharpoons$	$2 \text{HI}(\text{g})$
Initial	1.000 M		2.000 M		0 M
Change	$-x$		$-x$		$+2x$
Equilibrium	$(1.000 - x) \text{ M}$		$(2.000 - x) \text{ M}$		$2x \text{ M}$

## Solution (continued)

Fifth, we substitute the equilibrium concentrations into the equilibrium-constant expression and solve for the unknown,  $x$ :

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(2x)^2}{(1.000 - x)(2.000 - x)} = 50.5$$

If you have an equation-solving calculator, you can solve this equation directly for  $x$ . If not, expand this expression to obtain a quadratic equation in  $x$ :

$$\begin{aligned} 4x^2 &= 50.5(x^2 - 3.000x + 2.000) \\ 46.5x^2 - 151.5x + 101.0 &= 0 \end{aligned}$$

Solving the quadratic equation (Appendix A.3) leads to two solutions for  $x$ :

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

When we substitute  $x = 2.323$  into the expressions for the equilibrium concentrations, we find *negative* concentrations of  $\text{H}_2$  and  $\text{I}_2$ . Because a negative concentration is not chemically meaningful, we reject this solution. We then use  $x = \mathbf{0.935}$  to find the equilibrium concentrations:

$$x = \frac{-(-151.5) \pm \sqrt{1(-151.5)^2 - 4(46.5)(101.0)}}{2(46.5)} = 2.323 \text{ or } 0.935$$

$$[\text{H}_2] = 1.000 - x = 0.065 \text{ M}$$

$$[\text{I}_2] = 2.000 - x = 1.065 \text{ M}$$

$$[\text{HI}] = 2x = 1.87 \text{ M}$$

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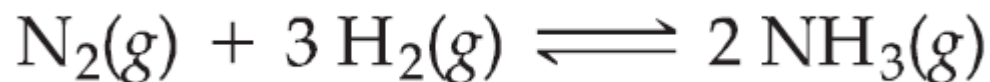
# **15.7**

## **Le Chatelier's Principle**

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# The Haber Process

The transformation of nitrogen and hydrogen into ammonia (NH<sub>3</sub>) is of tremendous significance in agriculture, where ammonia-based fertilizers are of utmost importance.

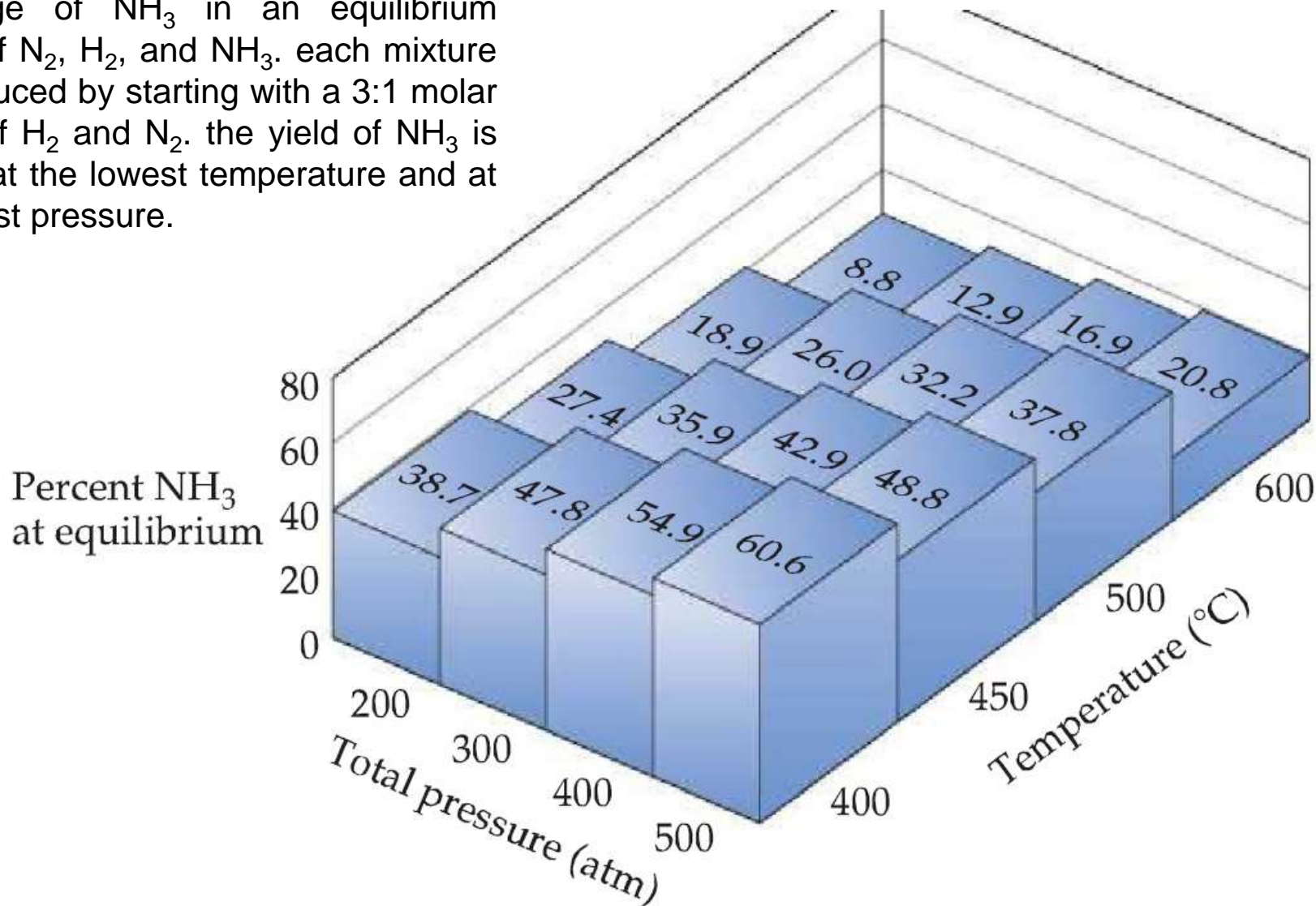


When Haber developed his process for making ammonia from N<sub>2</sub> and H<sub>2</sub>, he sought the factors that might be varied to increase the yield of NH<sub>3</sub>. Using the values of the equilibrium constant at various temperatures, he calculated the equilibrium amounts of NH<sub>3</sub> formed under a variety of conditions.

Notice that the percent of NH<sub>3</sub> present at equilibrium decreases with increasing temperature and increases with increasing pressure. We can understand these effects in terms of a principle first put forward by Henri-Louis Le Chatelier.



Effect of temperature and pressure on the percentage of  $\text{NH}_3$  in an equilibrium mixture of  $\text{N}_2$ ,  $\text{H}_2$ , and  $\text{NH}_3$ . each mixture was produced by starting with a 3:1 molar mixture of  $\text{H}_2$  and  $\text{N}_2$ . the yield of  $\text{NH}_3$  is greatest at the lowest temperature and at the highest pressure.





# Le Chatelier's Principle

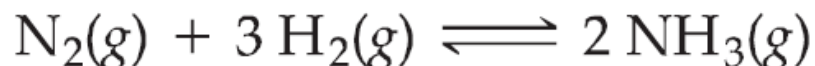
“If a system at equilibrium is disturbed by a change in **temperature**, **pressure**, or the **concentration** of one of the components, the system will shift its equilibrium position so as to counteract the effect of the disturbance.”

We will consider three ways that a chemical equilibrium can be disturbed:

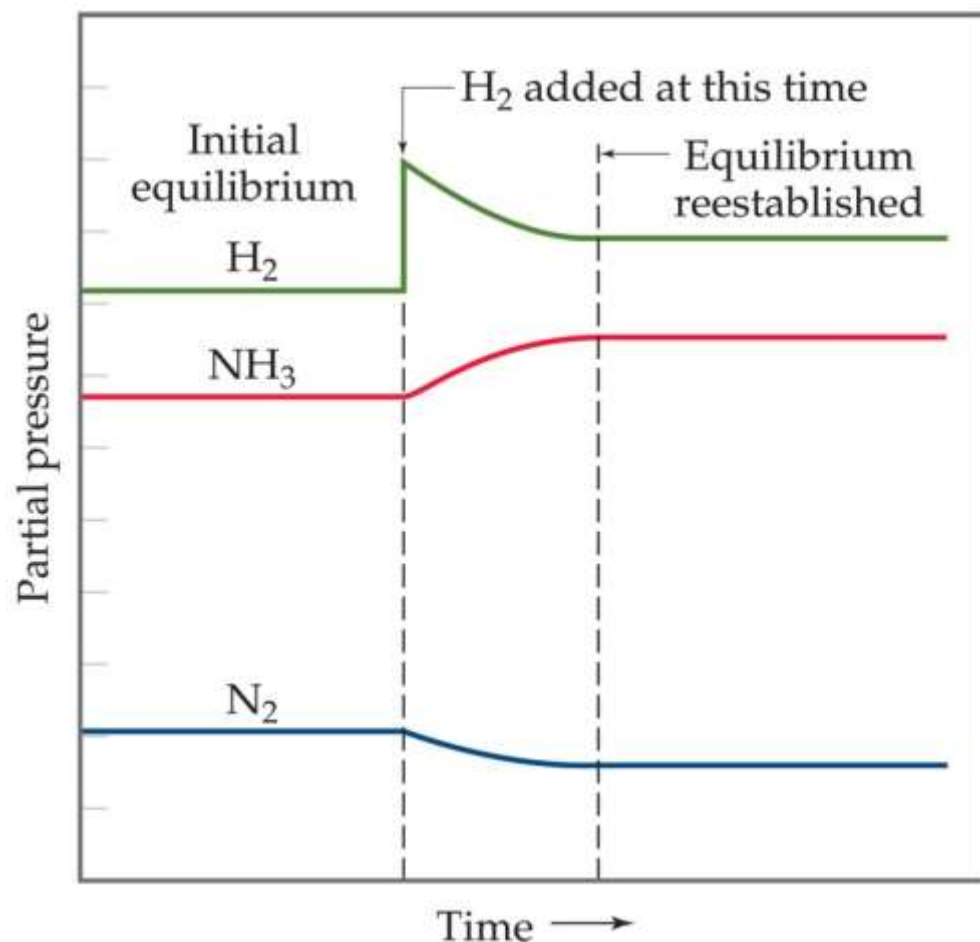
- (1) Adding or removing a reactant or product.
- (2) Changing the pressure by changing the volume.
- (3) Changing the temperature.

# Change in Reactant or Product Concentrations

If  $\text{H}_2$  is added to the system,  $\text{N}_2$  will be consumed and the two reagents will form more  $\text{NH}_3$ .



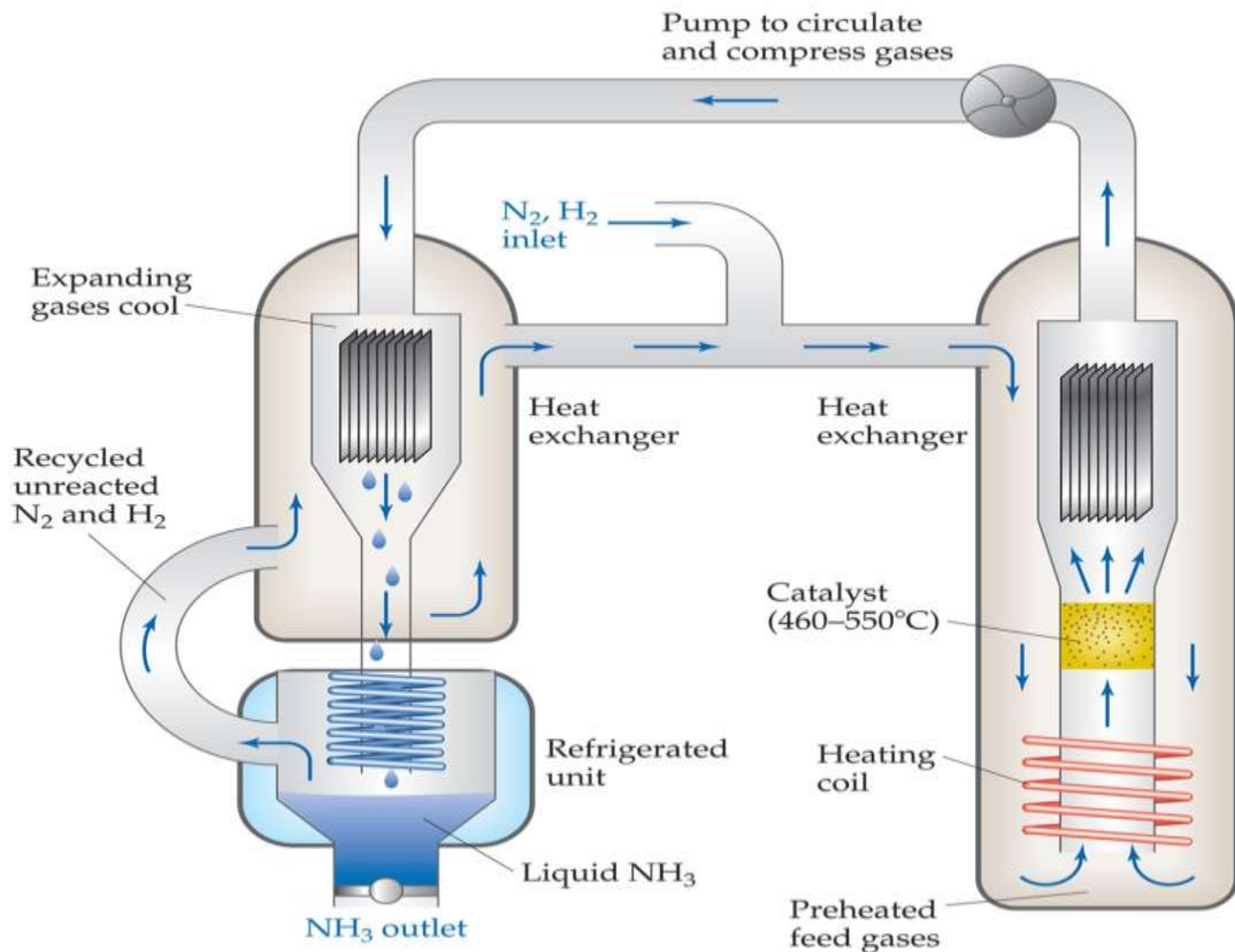
If a chemical system is at equilibrium and we increase or decrease the concentration of a substance (either a reactant or a product), the system reacts to consume or produce some of the substance.



In the **Haber reaction**, some of the added ammonia would decompose to form  $\text{N}_2$  and  $\text{H}_2$ . Therefore, removing  $\text{NH}_3$  from an equilibrium mixture causes the reaction to shift from left to right to form more  $\text{NH}_3$ .

Schematic diagram of the industrial production of ammonia.

This apparatus helps push the equilibrium to the right by removing the ammonia from the system as a liquid.



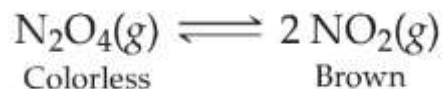
In the industrial production of ammonia, the NH<sub>3</sub> is continuously removed by selectively liquefying it; the boiling point of NH<sub>3</sub> (-33 °C) is much higher than that of N<sub>2</sub> (-196 °C) and H<sub>2</sub> (-253 °C). The liquid NH<sub>3</sub> is removed, and the N<sub>2</sub> and H<sub>2</sub> are recycled to form more NH<sub>3</sub>. By continuously removing the product, the reaction is driven essentially to completion.

# Effects of Volume and Pressure Changes

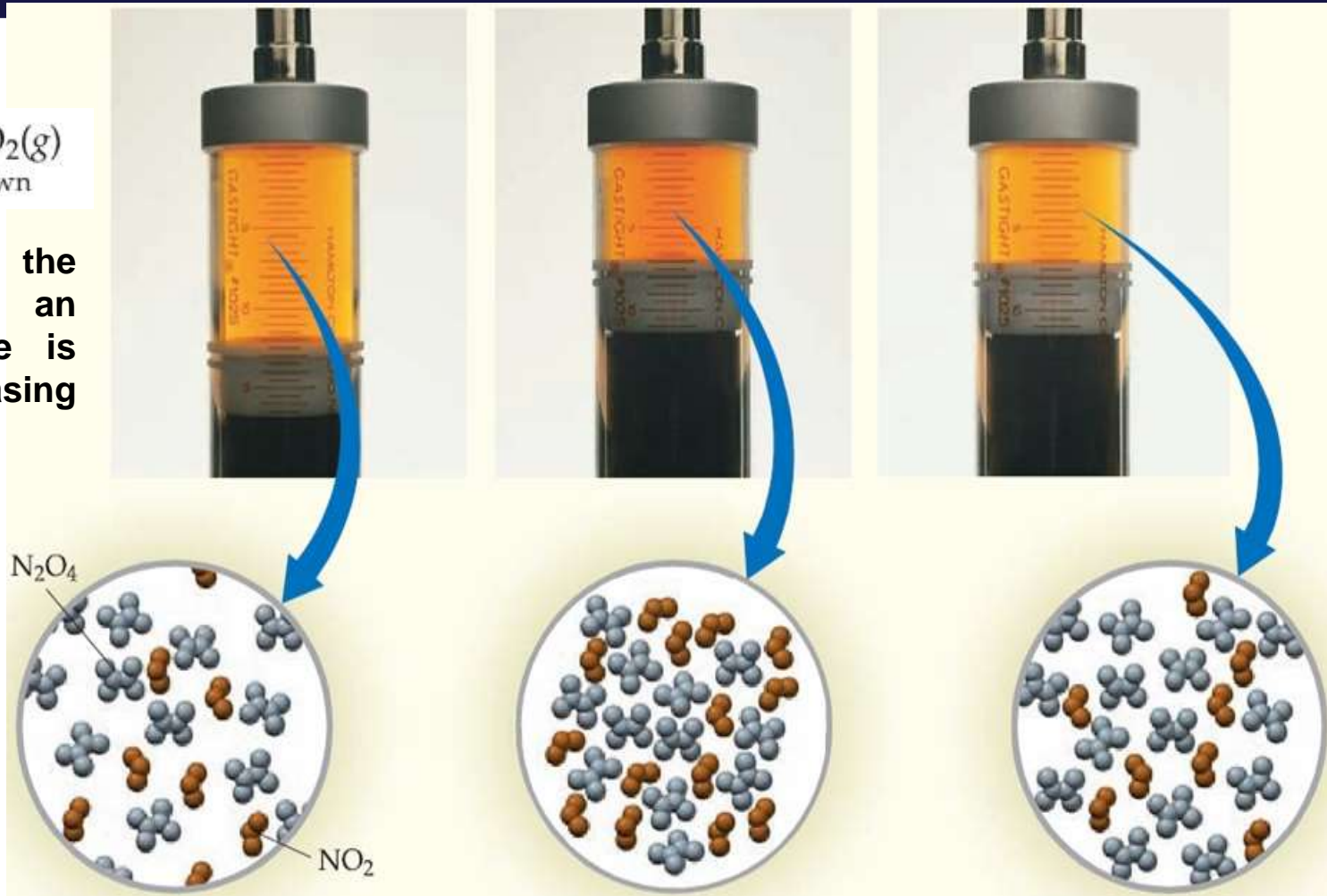
If a system is at equilibrium and its volume is decreases thereby increasing its total pressure, Le Chatelier's principle indicates that the system will respond by shifting its equilibrium position to reduce the pressure.

A system can reduce its pressure by reducing the total number of gas molecules (fewer molecules of gas exert a lower pressure).

Thus, at constant temperature, reducing the volume of a gaseous equilibrium mixture causes the system to shift in the direction that reduces the number of moles of gas. Conversely, increasing the volume causes a shift in the direction that produces more gas molecules.

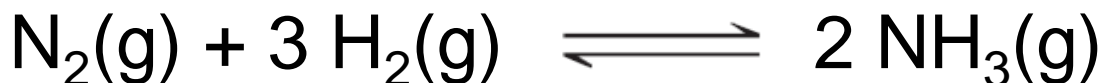


**What happens if the total pressure of an equilibrium mixture is increased by decreasing the volume ?**



According to Le Chatelier's principle, we expect the equilibrium to shift to the side that reduces the total number of moles of gas, which is the reactant side in this case. We therefore expect the equilibrium to shift to the left, so that  $\text{NO}_2$  is converted into  $\text{N}_2\text{O}_4$  as equilibrium is reestablished. In the Figure, compressing the gas mixture initially causes the color to darken as the concentration of  $\text{NO}_2$  increases. The color then fades as equilibrium is reestablished. The color fades because the pressure increase causes the equilibrium to shift in favor of colorless  $\text{N}_2\text{O}_4$ .

For the reaction



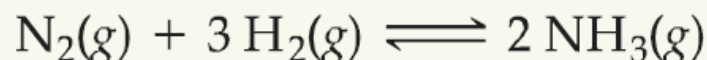
four molecules of reactant are consumed for every two molecules of product produced. Consequently, an increase in pressure (decrease in volume) causes a shift toward the side with fewer gas molecules, which leads to the formation of more  $\text{NH}_3$ .

In the case of the reaction  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$ , the number of molecules of gaseous products (two) equals the number of molecules of gaseous reactants; therefore, changing the pressure will not influence the position of the equilibrium.

Changes in concentrations or partial pressures cause shifts in equilibrium without changing the value of the equilibrium constant.

## Example

A mixture of hydrogen and nitrogen in a reaction vessel is allowed to attain equilibrium at 472 °C. The equilibrium mixture of gases was analyzed and found to contain 7.38 atm H<sub>2</sub>, 2.46 atm N<sub>2</sub>, and 0.166 atm NH<sub>3</sub>. From these data, calculate the equilibrium constant  $K_p$  for the reaction



$$K_p = \frac{(P_{\text{NH}_3})^2}{P_{\text{N}_2}(P_{\text{H}_2})^3} = \frac{(0.166)^2}{(2.46)(7.38)^3} = 2.79 \times 10^{-5}$$

What happens when we suddenly reduce the volume of the system by one-half. This volume change would cause the partial pressures of all substances to double, giving  $P_{\text{H}_2} = 14.76$  atm,  $P_{\text{N}_2} = 4.92$  atm, and  $P_{\text{NH}_3} = 0.332$  atm. The reaction  $Q$  would then no longer equal the equilibrium constant.

$$Q_p = \frac{(P_{\text{NH}_3})^2}{P_{\text{N}_2}(P_{\text{H}_2})^3} = \frac{(0.332)^2}{(4.92)(14.76)^3} = 6.97 \times 10^{-6} \neq K_p$$

Because  $Q_p < K_p$ , the system is no longer at equilibrium. Equilibrium will be reestablished by increasing  $P_{\text{NH}_3}$  and decreasing  $P_{\text{N}_2}$  and  $P_{\text{H}_2}$  until  $Q_p = K_p = 2.79 \times 10^{-5}$ . Therefore, the equilibrium shifts to the right as Le Châtelier's principle predicts.



It is possible to change the total pressure of the system without changing its volume. For example, pressure increases if additional amounts of any of the reacting components are added to the system.

The total pressure within the reaction vessel might also be increased by adding a gas that is not involved in the equilibrium. For example, argon might be added to the ammonia equilibrium system. The argon would not alter the partial pressures of any of the reacting components and therefore would not cause a shift in equilibrium.

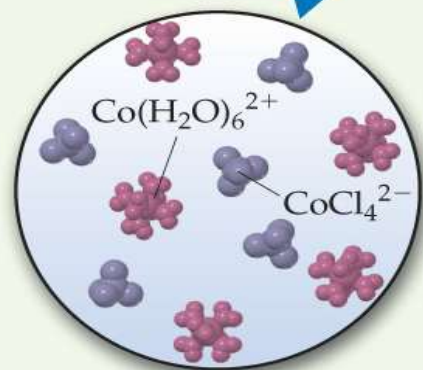
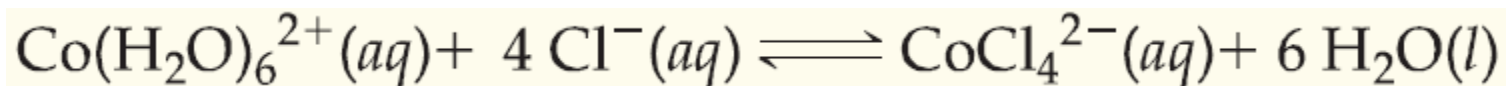


# Effect of Temperature Changes

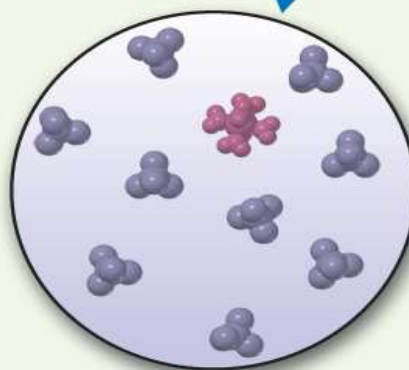
Changes in concentrations or partial pressures cause shifts in equilibrium without changing the value of the equilibrium constant. In contrast, almost every equilibrium constant changes in value as the temperature changes.

In an endothermic reactions, heat is absorbed as reactants are converted to products. Increasing the temperature causes the equilibrium to shift to the right and  $K$  to increase. Lowering the temperature shifts the equilibrium in the direction that produces heat, to the left, decreasing  $K$ .

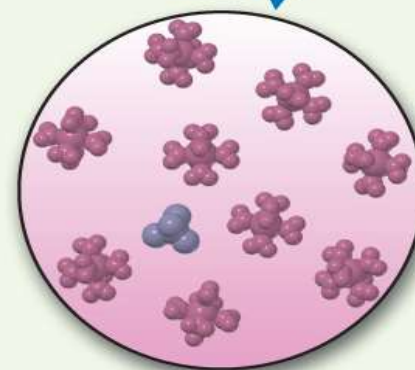
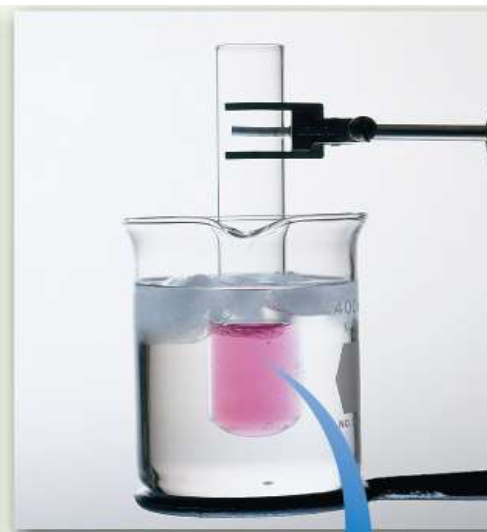
The reverse is correct for an exothermic reactions.



At room temperature both the pink  $\text{Co}(\text{H}_2\text{O})_6^{2+}$  and blue  $\text{CoCl}_4^{2-}$  ions are present in significant amounts, giving a violet color to the solution.



Heating the solution shifts the equilibrium to the right, forming more blue  $\text{CoCl}_4^{2-}$ .



Cooling the solution shifts the equilibrium to the left, toward pink  $\text{Co}(\text{H}_2\text{O})_6^{2+}$ .

We can deduce the rules for the temperature dependence of the equilibrium constant by applying Le Chateliers principle. A simple way to do this is to treat heat as if it were a chemical reagent.

In an endothermic (heat-absorbing) reaction we can consider heat as a reactant, whereas in an exothermic (heat-releasing) reaction we can consider heat as a product.

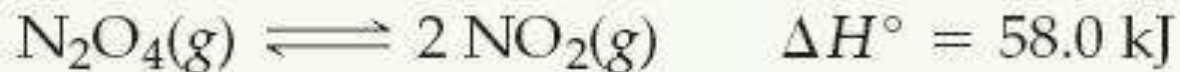
*Endothermic:*                      Reactants + *heat*  $\rightleftharpoons$  products

*Exothermic:*                      Reactants  $\rightleftharpoons$  products + *heat*

- Endothermic: Increasing T results in an increase in K.
- Exothermic: Increasing T result in a decrease in K.

## Sample Exercise 15.13 Using Le Châtelier's Principal to Predict shifts in Equilibrium

Consider the equilibrium



In which direction will the equilibrium shift when **(a)**  $\text{N}_2\text{O}_4$  is added, **(b)**  $\text{NO}_2$  is removed, **(c)** the total pressure is increased by addition of  $\text{N}_2(\text{g})$ , **(d)** the volume is increased, **(e)** the temperature is decreased?

### Solution

- (a)** The system will adjust to decrease the concentration of the added  $\text{N}_2\text{O}_4$ , so the equilibrium shifts to the right, in the direction of products.
- (b)** The system will adjust to the removal of  $\text{NO}_2$  by shifting to the side that produces more  $\text{NO}_2$ ; thus, the equilibrium shifts to the right.
- (c)** Adding  $\text{N}_2$  will increase the total pressure of the system, but  $\text{N}_2$  is not involved in the reaction. The partial pressures of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  are therefore unchanged, and there is no shift in the position of the equilibrium.
- (d)** If the volume is increased, the system will shift in the direction that occupies a larger volume (more gas molecules); thus, the equilibrium shifts to the right.
- (e)** The reaction is endothermic, so we can imagine heat as a reagent on the reactant side of the equation. Decreasing the temperature will shift the equilibrium in the direction that produces heat, so the equilibrium shifts to the left, toward the formation of more  $\text{N}_2\text{O}_4$ . Note that only this last change also affects the value of the equilibrium constant,  $K$ .

## Sample Exercise 15.14 Predicting the Effect of Temperature on $K$

(a) Using the standard heat of formation data in Appendix C, determine the standard enthalpy change for the reaction



(b) Determine how the equilibrium constant for this reaction should change with temperature.

### Solution

(a) Recall that the standard enthalpy change for a reaction is given by the sum of the standard molar enthalpies of formation of the products, each multiplied by its coefficient in the balanced chemical equation, less the same quantities for the reactants. At 25 °C,  $\Delta H_f^\circ$  for  $\text{NH}_3(\text{g})$  is  $-46.19 \text{ kJ/mol}$ . The  $\Delta H_f^\circ$  values for  $\text{H}_2(\text{g})$  and  $\text{N}_2(\text{g})$  are zero by definition because the enthalpies of formation of the elements in their normal states at 25 °C are defined as zero (Section 5.7). Because 2 mol of  $\text{NH}_3$  is formed, the total enthalpy change is

$$(2 \text{ mol})(-46.19 \text{ kJ/mol}) - 0 = -92.38 \text{ kJ}$$

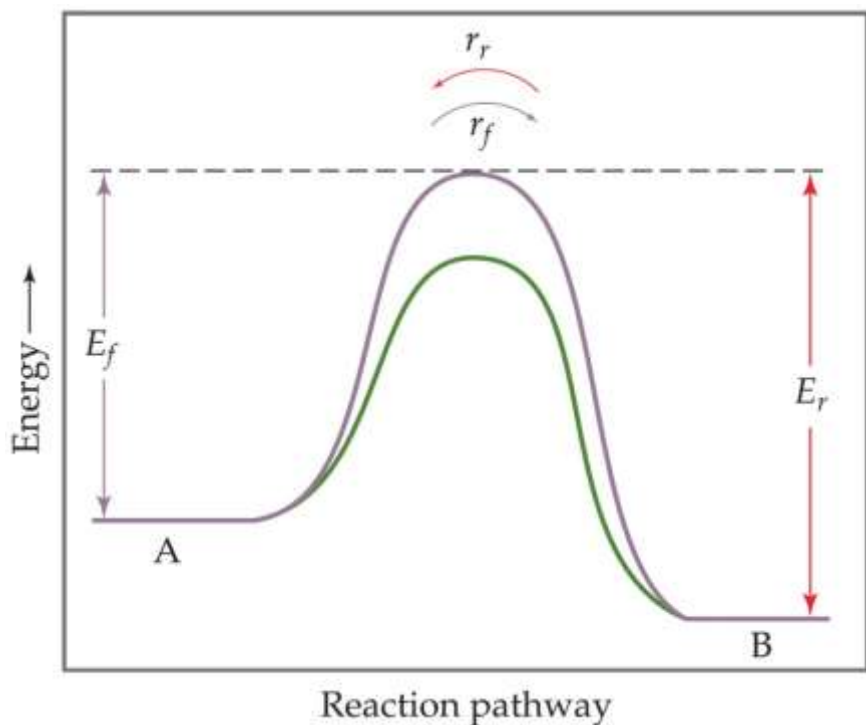
(b) Because the reaction in the forward direction is exothermic, we can consider heat a product of the reaction. An increase in temperature causes the reaction to shift in the direction of less  $\text{NH}_3$  and more  $\text{N}_2$  and  $\text{H}_2$ . This effect is seen in the values for  $K_p$  presented in **Table 15.2**. Notice that  $K_p$  changes markedly with changes in temperature and that it is larger at lower temperatures.

**TABLE 15.2** ■ Variation in  $K_p$  for the Equilibrium  $\text{N}_2 + 3 \text{H}_2 \rightleftharpoons 2 \text{NH}_3$  as a Function of Temperature

Temperature (°C)	$K_p$
300	$4.34 \times 10^{-3}$
400	$1.64 \times 10^{-4}$
450	$4.51 \times 10^{-5}$
500	$1.45 \times 10^{-5}$
550	$5.38 \times 10^{-6}$
600	$2.25 \times 10^{-6}$

# The Effect of Catalysts

Catalysts increase the rate of both the forward and reverse reactions. When one uses a catalyst, equilibrium is achieved faster, but the equilibrium composition remains unaltered.



A catalyst lowers the activation barrier between the reactants and products. The activation energy of the forward reaction is lowered to the same extent as that for the reverse reaction. The catalyst thereby increases the rates of both the forward and reverse reactions. As a result, a catalyst increases the rate at which equilibrium is achieved, but it does not change the composition of the equilibrium mixture and the value of the equilibrium constant.

The violet curve represents the path over the transition state in the absence of a catalyst. A catalyst lowers the energy of the transition state, as shown by the green curve.



Q & A



When a reaction is at a state of equilibrium, the rate of the forward reaction \_\_\_\_\_ the rate of the reverse reaction.

- a. is equal to
- b. is slower than
- c. is faster than
- d. is the reverse of



At equilibrium, the equilibrium constant is equal to:

- a.  $[\text{reactants}] / [\text{products}]$
- b.  $[\text{products}] / [\text{reactants}]$
- c.  $[\text{reactants}] \times [\text{products}]$
- d.  $[\text{reactants}] + [\text{products}]$

A large value of the equilibrium constant indicates that when the reaction reaches equilibrium, mostly \_\_\_\_\_ will be present.

- a. reactants
- b. products
- c. catalysts
- d. shrapnel

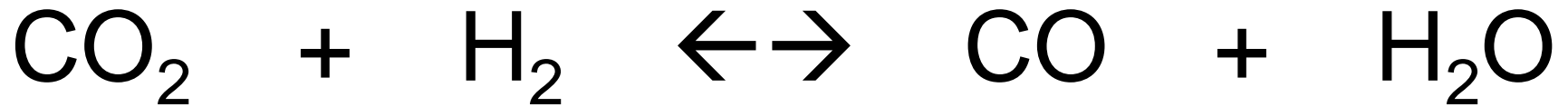
# When equilibrium is achieved:

a.  $Q > K$

b.  $Q < K$

c.  $Q = K$

d.  $Q^2 = K$



If all species are gases and  $\text{H}_2$  is added, the amount of CO present at equilibrium will:

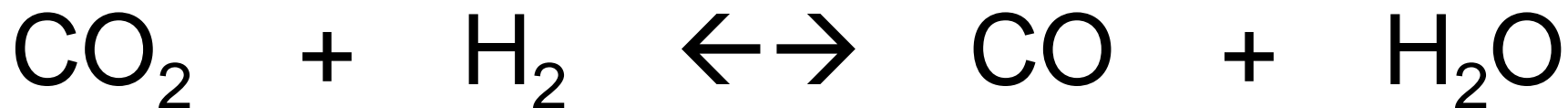
- a. increase
- b. decrease
- c. remain unchanged
- d. disappear

For the reaction:



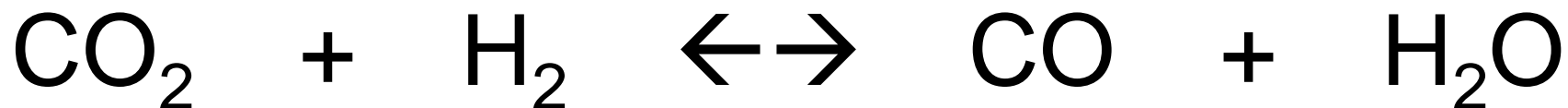
The equilibrium constant  $K_p = 794$  at 298 K and  $K_p = 54$  at 700 K. Is the formation of HI favored more at the higher or lower temperature?

**Answer:** the formation of product, HI, is favored at the lower temperature because  $K_p$  is larger at the lower temperature



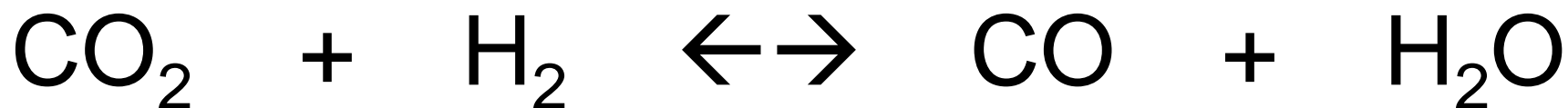
If all species are gases and  $\text{H}_2\text{O}$  is added, the amount of  $\text{CO}$  present at equilibrium will:

- a. increase
- b. decrease
- c. remain unchanged
- d. disappear



If all species are gases and  $\text{CO}_2$  is removed, the amount of CO present at equilibrium will:

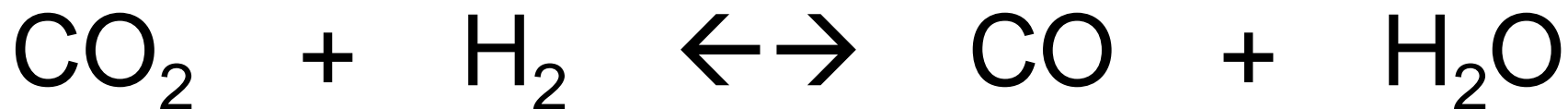
- a. increase
- b. decrease**
- c. remain unchanged
- d. disappear



If the reaction is endothermic and the temperature is raised, the amount of CO present will:

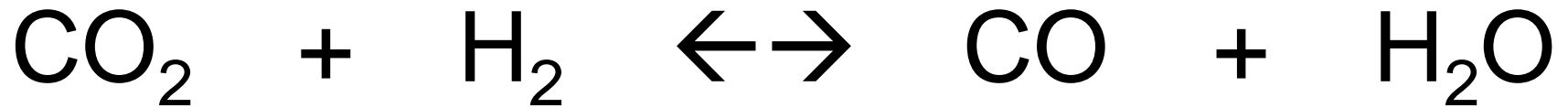
- a. increase
- b. decrease
- c. remain unchanged
- d. disappear





If all species are gases and the container is compressed, the amount of CO present will:

- a. increase
- b. decrease
- c. remain unchanged
- d. disappear



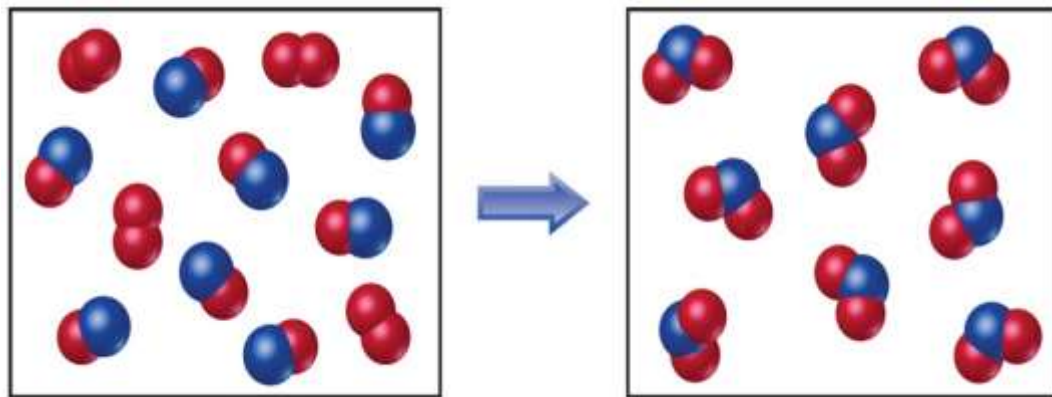
If a catalyst is added to the equilibrium, the amount of CO present will:

- a. increase
- b. decrease
- c. remain unchanged
- d. disappear

What is  $K_p$  in terms of  $K_c$  for the following reaction ?



- $K_p = K_c RT$
- $K_p = K_c / RT$
- $K_p = K_c R/T$
- $K_p = K_c$
- $K_p = K_c / (RT)^2$



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What is the correct equilibrium constant expression for the reaction:



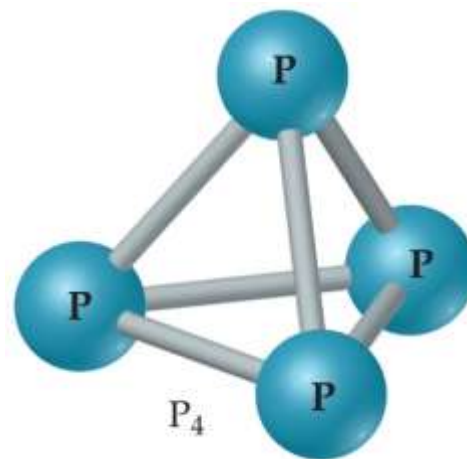
1.  $\frac{[\text{PCl}_3]^4}{[\text{P}_4][\text{Cl}_2]^6}$

2.  $\frac{[\text{PCl}_3]^4}{[\text{Cl}_2]^6}$

3.  $\frac{1}{[\text{Cl}_2]^6}$

4.  $\frac{[\text{Cl}_2]^6}{[\text{PCl}_3]^4}$

5.  $\frac{[4 \text{PCl}_3]^4}{[\text{P}_4][6 \text{Cl}_2]^6}$



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Which accurately reflects the changes in concentration that will occur if  $\text{O}_2$  is added to disturb the equilibrium?



	[NO]	[O <sub>2</sub> ]	[NO]
1.	Increase	Increase	Increase
2.	Increase	Increase	Decrease
3.	Decrease	Decrease	Decrease
4.	Decrease	Decrease	Increase
5.	Decrease	Increase	Increase

# Which of the following will result in an equilibrium shift to the right?



- Increase temperature/increase volume
- Increase temperature/decrease volume
- Decrease temperature/increase volume
- **Decrease temperature/decrease volume**
- None of the above



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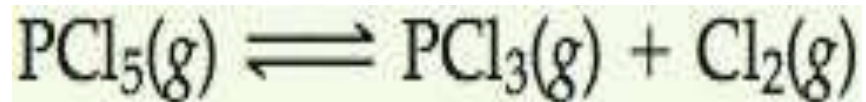


What is the value of  $K_c$  for the reaction?



- $K_c = 1/(5.0 \times 10^{18})^{1/2}$
- $K_c = 1/(2.5 \times 10^{18})$
- $K_c = -(5.0 \times 10^{18})/2$
- $K_c = -(5.0 \times 10^{18})^{1/2}$
- $K_c = 2/(5.0 \times 10^{18})^{1/2}$

At 500 K, the reaction

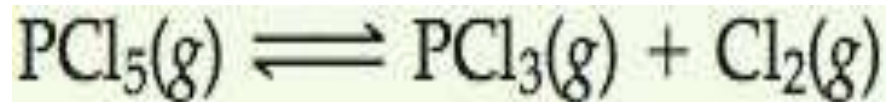


has  $K_p = 0.497$ . In an equilibrium mixture at 500 K, the partial pressure of  $\text{PCl}_5$  is 0.860 atm and that of  $\text{PCl}_3$  is 0.350 atm. What is the partial pressure of  $\text{Cl}_2$  in the equilibrium mixture?

**Answer:** 1.22 atm



For the reaction:



The equilibrium constant  $K_p$  has the value 0.497 at 500 K. A gas cylinder at 500 K is charged with  $\text{PCl}_5(\text{g})$  at an initial pressure of 1.66 atm. What are the equilibrium pressures of  $\text{PCl}_5$ ,  $\text{PCl}_3$ , and  $\text{Cl}_2$  at this temperature?

**Answer:**  $P_{\text{PCl}_5} = 0.967 \text{ atm};$   
 $P_{\text{PCl}_3} = P_{\text{Cl}_2} = 0.693 \text{ atm}$

Write the equilibrium-constant expression  $K_c$ , for (a)  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$ ,  
(b)  $\text{Cd}^{2+}(\text{aq}) + 4 \text{Br}^{-}(\text{aq}) \rightleftharpoons \text{CdBr}_4^{2-}(\text{aq})$

*Answers:* (a)  $K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$ ; (b)  $K_c = \frac{[\text{CdBr}_4^{2-}]}{[\text{Cd}^{2+}][\text{Br}^{-}]^4}$

For the equilibrium  $2 \text{SO}_3(g) \rightleftharpoons 2 \text{SO}_2(g) + \text{O}_2(g)$ ,  $K_c$  is  $4.08 \times 10^{-3}$  at 1000 K. Calculate the value for  $K_p$ .

*Answer:* 0.335

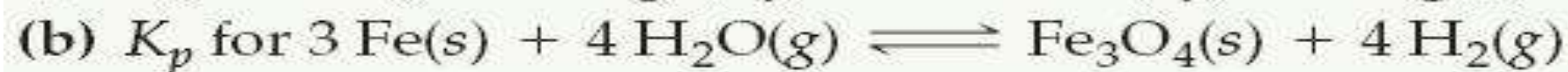
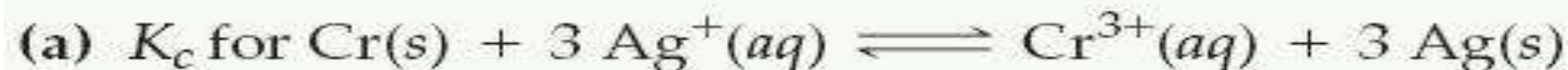
For the formation of  $\text{NH}_3$  from  $\text{N}_2$  and  $\text{H}_2$ ,  $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$ ,  $K_p = 4.34 \times 10^{-3}$  at  $300^\circ\text{C}$ . What is the value of  $K_p$  for the reverse reaction?

*Answer:*  $2.30 \times 10^2$

Given that, at 700 K,  $K_p = 54.0$  for the reaction  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$  and  $K_p = 1.04 \times 10^{-4}$  for the reaction  $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$ , determine the value of  $K_p$  for the reaction  $2 \text{NH}_3(\text{g}) + 3 \text{I}_2(\text{g}) \rightleftharpoons 6 \text{HI}(\text{g}) + \text{N}_2(\text{g})$  at 700 K.

*Answer:*  $\frac{(54.0)^3}{1.04 \times 10^{-4}} = 1.51 \times 10^9$

Write the following equilibrium-constant expressions:



*Answers:* (a)  $K_c = \frac{[\text{Cr}^{3+}]}{[\text{Ag}^+]^3}$ , (b)  $K_p = \frac{(P_{\text{H}_2})^4}{(P_{\text{H}_2\text{O}})^4}$

## Sample Exercise Analyzing a Heterogeneous Equilibrium

Each of the following mixtures was placed in a closed container and allowed to stand. Which is capable of attaining the equilibrium  $\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$ : (a) pure  $\text{CaCO}_3$ , (b)  $\text{CaO}$  and a  $\text{CO}_2$  pressure greater than the value of  $K_p$ , (c) some  $\text{CaCO}_3$  and a  $\text{CO}_2$  pressure greater than the value of  $K_p$ , (d)  $\text{CaCO}_3$  and  $\text{CaO}$ ?

### Solution

Equilibrium can be reached in all cases except (c) as long as sufficient quantities of solids are present.

(a)  $\text{CaCO}_3$  simply decomposes, forming  $\text{CaO}(s)$  and  $\text{CO}_2(g)$  until the equilibrium pressure of  $\text{CO}_2$  is attained. There must be enough  $\text{CaCO}_3$ , however, to allow the  $\text{CO}_2$  pressure to reach equilibrium.

(b)  $\text{CO}_2$  continues to combine with  $\text{CaO}$  until the partial pressure of the  $\text{CO}_2$  decreases to the equilibrium value.

(c) There is no  $\text{CaO}$  present, so equilibrium cannot be attained because there is no way the  $\text{CO}_2$  pressure can decrease to its equilibrium value (which would require some of the  $\text{CO}_2$  to react with  $\text{CaO}$ ).

(d) The situation is essentially the same as in (a):  $\text{CaCO}_3$  decomposes until equilibrium is attained. The presence of  $\text{CaO}$  initially makes no difference.

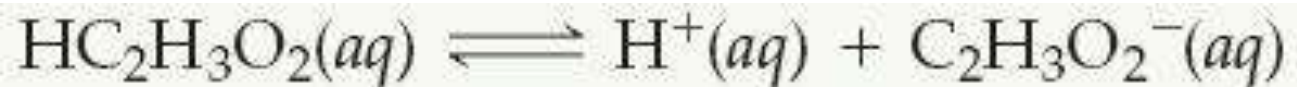
When added to  $\text{Fe}_3\text{O}_4(\text{s})$  in a closed container, which one of the following substances— $\text{H}_2(\text{g})$ ,  $\text{H}_2\text{O}(\text{g})$ ,  $\text{O}_2(\text{g})$ —will allow equilibrium to be established in the reaction

$$3 \text{Fe}(\text{s}) + 4 \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{Fe}_3\text{O}_4(\text{s}) + 4 \text{H}_2(\text{g})?$$

*Answer:* only  $\text{H}_2(\text{g})$



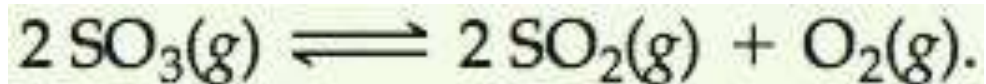
An aqueous solution of acetic acid is found to have the following equilibrium concentrations at 25 °C:  $[\text{HC}_2\text{H}_3\text{O}_2] = 1.65 \times 10^{-2} \text{ M}$ ;  $[\text{H}^+] = 5.44 \times 10^{-4} \text{ M}$ ; and  $[\text{C}_2\text{H}_3\text{O}_2^-] = 5.44 \times 10^{-4} \text{ M}$ . Calculate the equilibrium constant  $K_c$  for the ionization of acetic acid at 25 °C. The reaction is



***Answer:***  $1.79 \times 10^{-5}$

Sulfur trioxide decomposes at high temperature in a sealed container:

Initially, the vessel is charged at 1000 K with  $\text{SO}_3(g)$  at a partial pressure of 0.500 atm. At equilibrium the  $\text{SO}_3$  partial pressure is 0.200 atm. Calculate the value of  $K_p$  at 1000 K.

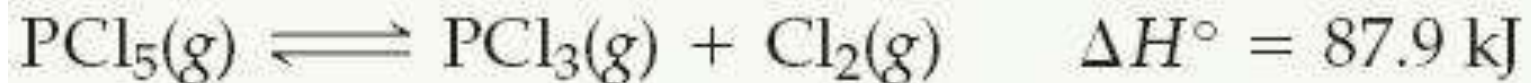


***Answer: 0.338***

At 1000 K the value of  $K_p$  for the reaction  $2 \text{SO}_3(g) \rightleftharpoons 2 \text{SO}_2(g) + \text{O}_2(g)$  is 0.338. Calculate the value for  $Q_p$ , and predict the direction in which the reaction will proceed toward equilibrium if the initial partial pressures are  $P_{\text{SO}_3} = 0.16 \text{ atm}$ ;  $P_{\text{SO}_2} = 0.41 \text{ atm}$ ;  $P_{\text{O}_2} = 2.5 \text{ atm}$ .

*Answer:*  $Q_p = 16$ ;  $Q_p > K_p$ , and so the reaction will proceed from right to left, forming more  $\text{SO}_3$ .

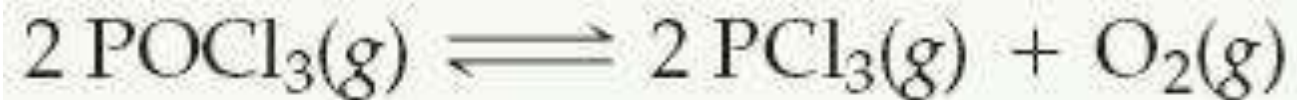
For the reaction



in which direction will the equilibrium shift when (a)  $\text{Cl}_2(g)$  is removed, (b) the temperature is decreased, (c) the volume of the reaction system is increased, (d)  $\text{PCl}_3(g)$  is added?

**Answer:** (a) right, (b) left, (c) right, (d) left

Using the thermodynamic data in Appendix C, determine the enthalpy change for the reaction



Use this result to determine how the equilibrium constant for the reaction should change with temperature.

**Answer:**  $\Delta H^\circ = 508.3 \text{ kJ}$ ; the equilibrium constant will increase with increasing temperature

## Sample Integrative Exercise Putting Concepts Together

At temperatures near 800 °C, steam passed over hot coke (a form of carbon obtained from coal) reacts to form CO and H<sub>2</sub>:



The mixture of gases that results is an important industrial fuel called *water gas*. **(a)** At 800 °C the equilibrium constant for this reaction is  $K_p = 14.1$ . What are the equilibrium partial pressures of H<sub>2</sub>O, CO, and H<sub>2</sub> in the equilibrium mixture at this temperature if we start with solid carbon and 0.100 mol of H<sub>2</sub>O in a 1.00-L vessel? **(b)** What is the minimum amount of carbon required to achieve equilibrium under these conditions? **(c)** What is the total pressure in the vessel at equilibrium? **(d)** At 25 °C the value of  $K_p$  for this reaction is  $1.7 \times 10^{-21}$ . Is the reaction exothermic or endothermic? **(e)** To produce the maximum amount of CO and H<sub>2</sub> at equilibrium, should the pressure of the system be increased or decreased?

### Solution

**(a)** To determine the equilibrium partial pressures, we use the ideal gas equation, first determining the starting partial pressure of hydrogen.

$$P_{\text{H}_2\text{O}} = \frac{n_{\text{H}_2\text{O}}RT}{V} = \frac{(0.100 \text{ mol})(0.0821 \text{ L-atm/mol-K})(1073 \text{ K})}{1.00 \text{ L}} = 8.81 \text{ atm}$$

We then construct a table of starting partial pressures and their changes as equilibrium is achieved:

	C(s)	+	H <sub>2</sub> O(g)	$\rightleftharpoons$	CO(g)	+	H <sub>2</sub> (g)
Initial			8.81 atm		0 atm		0 atm
Change			-x		+x		+x
Equilibrium			8.81 - x atm		x atm		x atm

There are no entries in the table under  $C(s)$  because the reactant, being a solid, does not appear in the equilibrium-constant expression. Substituting the equilibrium partial pressures of the other species into the equilibrium-constant expression for the reaction gives

$$K_p = \frac{P_{\text{CO}}P_{\text{H}_2}}{P_{\text{H}_2\text{O}}} = \frac{(x)(x)}{(8.81 - x)} = 14.1$$

$$x^2 = (14.1)(8.81 - x)$$

Multiplying through by the denominator gives a quadratic equation in  $x$ :  $x^2 + 14.1x - 124.22 = 0$

Solving this equation for  $x$  using the quadratic formula yields  $x = 6.14$  atm. Hence, the equilibrium partial pressures are  $P_{\text{CO}} = x = 6.14$  atm,  $P_{\text{H}_2} = x = 6.14$  atm, and  $P_{\text{H}_2\text{O}} = (8.81 - x) = 2.67$  atm.

(b) Part (a) shows that  $x = 6.14$  atm of  $\text{H}_2\text{O}$  must react for the system to achieve equilibrium. We can use the ideal-gas equation to convert this partial pressure into a mole amount.

$$n = \frac{PV}{RT} = \frac{(6.14 \text{ atm})(1.00 \text{ L})}{(0.0821 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K})(1073 \text{ K})} = 0.0697 \text{ mol}$$

Thus, 0.0697 mol of  $\text{H}_2\text{O}$  and the same amount of  $C$  must react to achieve equilibrium. As a result, there must be at least 0.0697 mol of  $C$  (0.836 g  $C$ ) present among the reactants at the start of the reaction.

(c) The total pressure in the vessel at equilibrium is simply the sum of the equilibrium partial pressures:

$$P_{\text{total}} = P_{\text{H}_2\text{O}} + P_{\text{CO}} + P_{\text{H}_2} = 2.67 \text{ atm} + 6.14 \text{ atm} + 6.14 \text{ atm} = 14.95 \text{ atm}$$

(d) In discussing Le Châtelier's principle, we saw that endothermic reactions exhibit an increase in  $K_p$  with increasing temperature. Because the equilibrium constant for this reaction increases as temperature increases, the reaction must be endothermic. From the enthalpies of formation given in Appendix C, we can verify our prediction by calculating the enthalpy change for the reaction,

$\Delta H^\circ = \Delta H_f^\circ(\text{CO}) + \Delta H_f^\circ(\text{H}_2) - \Delta H_f^\circ(C) - \Delta H_f^\circ(\text{H}_2\text{O}) = +131.3 \text{ kJ}$ . The positive sign for  $\Delta H^\circ$  indicates that the reaction is endothermic.

(e) According to Le Châtelier's principle, a decrease in the pressure causes a gaseous equilibrium to shift toward the side of the equation with the greater number of moles of gas. In this case there are two moles of gas on the product side and only one on the reactant side. Therefore, the pressure should be reduced to maximize the yield of the  $\text{CO}$  and  $\text{H}_2$ .

