

Petrucci's General Chemistry

PRINCIPLES AND MODERN APPLICATIONS

Twelfth Edition

PETRUCCI

HERRING

MADURA

BISSONNETTE

Principles of Chemical Equilibrium

16

Solutions and their Physical Properties



CONTENTS

- 16-1 The Nature of the Equilibrium State
- 16-2 The Equilibrium Constant Expression
- 16-3 Relationships Involving Equilibrium Constants
- 16-4 The Magnitude of an Equilibrium Constant
- 16-5 Predicting the Direction of Net Chemical Change
- 16-6 Altering Equilibrium Conditions: Le Châtelier's Principle
- 16-7 Equilibrium Calculations: Some Illustrative Examples

16-1 The Nature of the Equilibrium State

In a closed reaction vessel at constant temperature, a reaction proceeds spontaneously toward equilibrium. At equilibrium, the reaction quotient Q attains the same constant value, K , irrespective of the starting amounts of reactants and products.

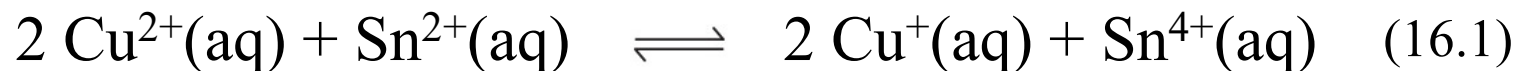


Table 16.1 Activities of Some Substances

Substance	Activity ^a	Comment
Ideal gas, X(g)	$a = P_X/P^\circ$	P_X is the partial pressure of the gas and $P^\circ = 1 \text{ bar} \approx 1 \text{ atm}$. When pressure is expressed in bar, the activity is equal to the numerical value of the pressure.
Pure solid or liquid, X(s) or X(l)	$a = 1$	For pressures normally encountered, ^b the activity of a pure solid (or a pure liquid) is equal to 1.
Solute in an ideal aqueous solution, X(aq)	$a = [X]/c^\circ$	[X] is the concentration in mol/L and $c^\circ = 1 \text{ mol/L}$. When concentration is expressed in mol/L, the activity of a dissolved solute is equal to the numerical value of [X].

^aTo incorporate deviations from ideal behavior, we would write $a = \gamma P_X/P^\circ$ for a gas and $a = \gamma[X]/c^\circ$ for a solute in aqueous solution, where γ is an experimentally determined correction factor called the *activity coefficient*. More advanced treatments of this topic show how γ is related to the composition of the system.

^bSee Exercise 97.



$$Q = \frac{a_{\text{Cu}^{+}}^2 \times a_{\text{Sn}^{4+}}}{a_{\text{Cu}^{2+}} \times a_{\text{Sn}^{2+}}} \quad (16.2)$$

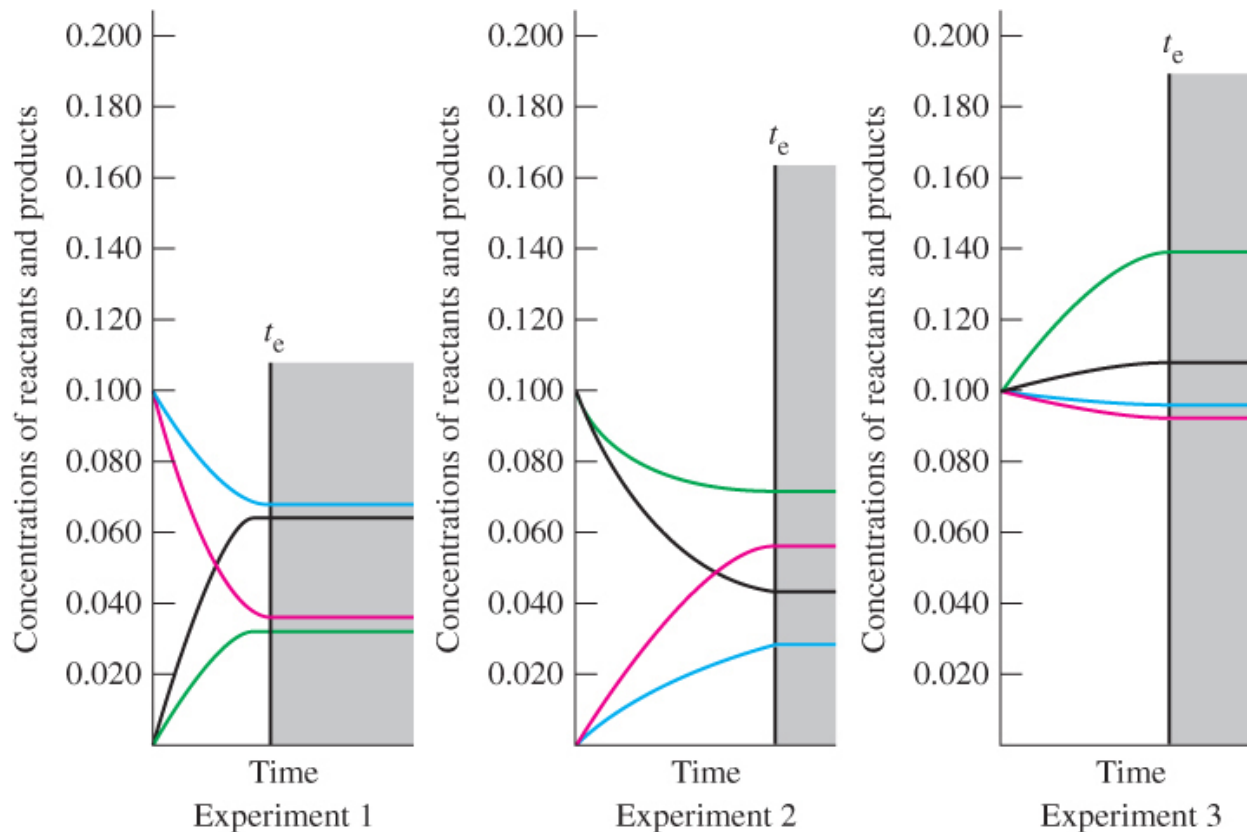
$$Q = \frac{a_{\text{Cu}^{+}}^2 \times a_{\text{Sn}^{4+}}}{a_{\text{Cu}^{2+}} \times a_{\text{Sn}^{2+}}} = \frac{([\text{Cu}^{+}]/c^{\circ})^2 \times ([\text{Sn}^{4+}]/c^{\circ})}{([\text{Cu}^{2+}]/c^{\circ}) \times ([\text{Sn}^{2+}]/c^{\circ})} = \frac{[\text{Cu}^{+}]^2 [\text{Sn}^{4+}]}{[\text{Cu}^{2+}] [\text{Sn}^{2+}]} \quad (16.3)$$

Table 16.2 Three Approaches to Equilibrium in the Reaction $2 \text{Cu}^{2+}(\text{aq}) + \text{Sn}^{2+}(\text{aq}) \rightleftharpoons 2 \text{Cu}^{+}(\text{aq}) + \text{Sn}^{4+}(\text{aq})$

	[Cu ²⁺]	[Sn ²⁺]	[Cu ⁺]	[Sn ⁴⁺]	Q
Experiment 1					
Initial:	0.100	0.100	0.000	0.000	$\frac{(0)^2 (0)}{(0.100)^2 (0.100)} = 0$
Equilibrium:	0.0360	0.0680	0.0640	0.0320	$\frac{(0.0640)^2 (0.0320)}{(0.0360)^2 (0.0680)} = 1.49$
Experiment 2					
Initial:	0.000	0.000	0.100	0.100	$\frac{(0.100)^2 (0.100)}{(0)^2 (0)} = \infty^a$
Equilibrium:	0.0567	0.0283	0.0433	0.0717	$\frac{(0.0433)^2 (0.0717)}{(0.0567)^2 (0.0283)} = 1.48$
Experiment 3					
Initial:	0.100	0.100	0.100	0.100	$\frac{(0.100)^2 (0.100)}{(0.100)^2 (0.100)} = 1$
Equilibrium:	0.0922	0.0961	0.1078	0.1039	$\frac{(0.1078)^2 (0.1039)}{(0.0922)^2 (0.0961)} = 1.48$

^aStrictly speaking, we cannot evaluate Q in this case. Any value divided by zero is undefined. By writing $Q = \infty$, we mean that as [Cu²⁺] and [Sn²⁺] approach zero, the value of Q approaches infinity.

1. The reaction quotient Q has the same value at equilibrium no matter what the starting concentrations are.
2. The equilibrium value of Q is represented by the symbol K and is called the equilibrium constant



t_e = time for equilibrium to be reached

— mol Cu^{2+}
 — mol Sn^{2+}
 — mol Cu^+
 — mol Sn^{4+}

▲ FIGURE 16-1

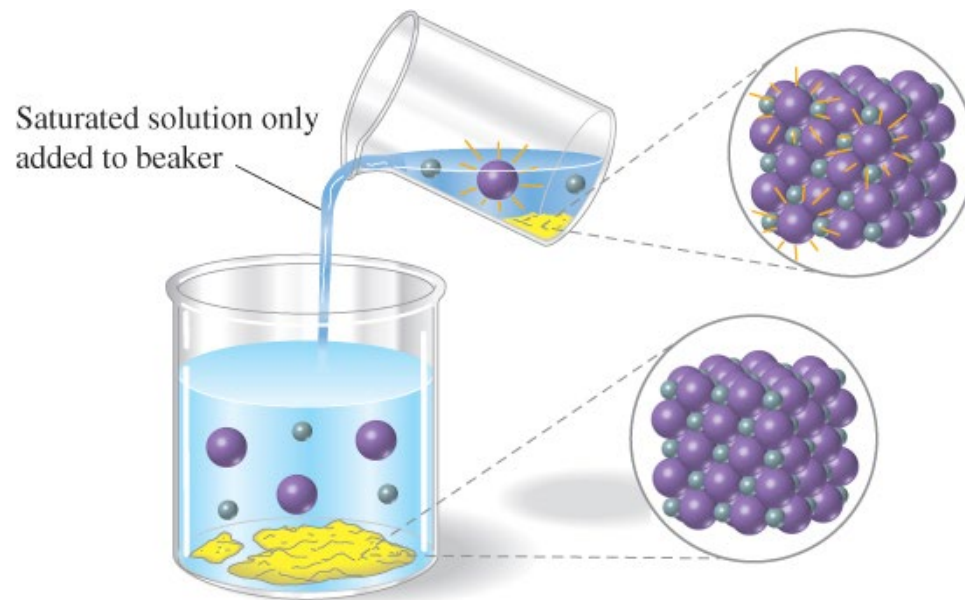
Three approaches to equilibrium in the reaction



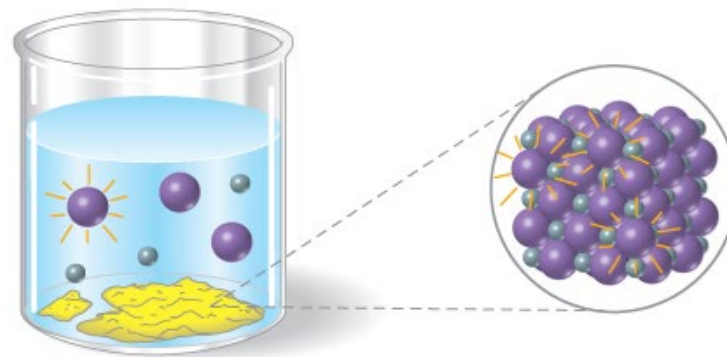
The Dynamic Nature of the Equilibrium Condition

The equilibrium condition is dynamic, with the forward and reverse reactions occurring not only indefinitely but also at exactly the same rate.





(a)



(b)

▲ FIGURE 16-2
Dynamic equilibrium illustrated



$$Q = \frac{a_C^c \times a_D^d \times \dots}{a_A^a \times a_B^b \times \dots} \quad (16.5)$$

$$K = \frac{a_{C,eq}^c \times a_{D,eq}^d \times \dots}{a_{A,eq}^a \times a_{B,eq}^b \times \dots} \quad (16.6)$$

$$K = \frac{a_C^c \times a_D^d \dots}{a_A^a \times a_B^b \dots} \quad (16.7)$$

in 16.7, equilibrium values of a are implied

Equilibria Involving Gases

$$K = \frac{(P_C / P^\circ)^c (P_D / P^\circ)^d \dots}{(P_A / P^\circ)^a (P_B / P^\circ)^b \dots} = \frac{P_C^c \times P_D^d \dots}{P_A^a \times P_B^b \dots} \times \left(\frac{1}{P^\circ} \right)^{\Delta \nu} \quad (16.8)$$

$$\Delta \nu = \underbrace{(c + d + \dots)}_{\text{The sum of coefficients for the products}} - \underbrace{(a + b + \dots)}_{\text{The sum of coefficients for the reactants}}$$

The sum of coefficients
for the products

The sum of coefficients
for the reactants

$$K_P = \frac{P_C^c \times P_D^d \dots}{P_A^a \times P_B^b \dots} \quad (16.9)$$

$$K = K_P \times \left(\frac{1}{P^\circ} \right)^{\Delta \nu} \quad (16.10)$$

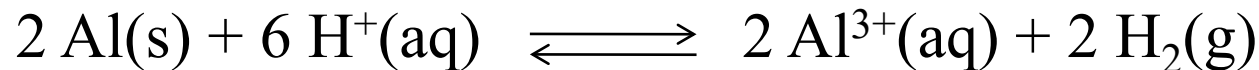
Equilibria in Aqueous Solution

$$K = \frac{([C]/c^\circ)^c ([D]/c^\circ)^d \dots}{([A]/c^\circ)^a ([B]/c^\circ)^b \dots} = \frac{[C]^c \times [D]^d \dots}{[A]^a \times [B]^b \dots} \times \left(\frac{1}{c^\circ}\right)^{\Delta\nu} \quad (16.11)$$

$$K_c = \frac{[C]^c \times [D]^d \dots}{[A]^a \times [B]^b \dots} \quad (16.12)$$

$$K = K_c \times \left(\frac{1}{c^\circ}\right)^{\Delta\nu} \quad (16.13)$$

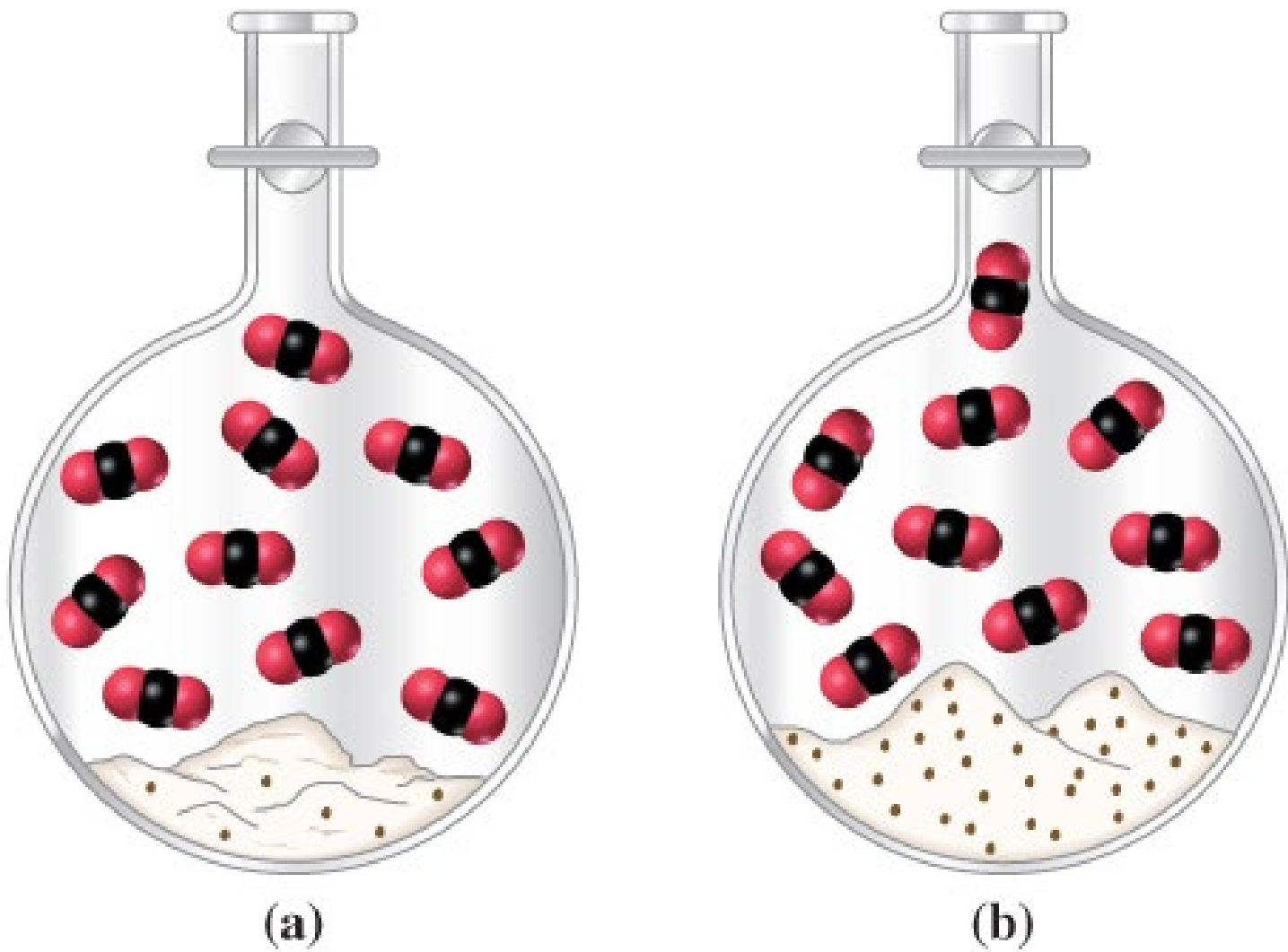
Equilibria Involving Pure Liquids and Solids



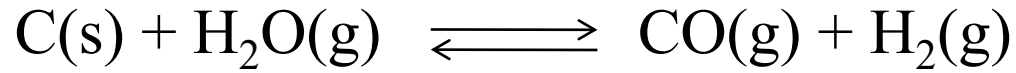
Pure solids and liquids are not included in equilibrium constant expressions

Recall from Chapter 13

$$\begin{aligned} K &= \frac{(a_{\text{Al}^{3+}, \text{eq}})^2 (a_{\text{H}_2, \text{eq}})^3}{(a_{\text{Al}, \text{eq}})^2 (a_{\text{H}^+, \text{eq}})^6} \approx \frac{([\text{Al}^{3+}]_{\text{eq}} / c^\circ)^2 (P_{\text{H}_2, \text{eq}} / P^\circ)^3}{(1)^2 ([\text{H}^+]_{\text{eq}} / c^\circ)^6} \\ &= \frac{[\text{Al}^{3+}]_{\text{eq}}^2 (P_{\text{H}_2})^3}{[\text{H}^+]_{\text{eq}}^6} \times (c^\circ)^4 \times \left(\frac{1}{P^\circ}\right)^3 \end{aligned}$$

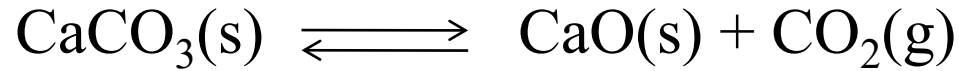


▲ FIGURE 16-3
Equilibrium in the reaction $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$



$$K = \frac{a_{\text{CO(g)}} a_{\text{H}_2\text{(g)}}}{a_{\text{C(s)}} a_{\text{H}_2\text{O(g)}} = \frac{(P_{\text{CO(g)}} / P^\circ)(P_{\text{H}_2\text{(g)}} / P^\circ)}{(1)(P_{\text{H}_2\text{O(g)}} / P^\circ)}$$

$$= \frac{P_{\text{CO(g)}} P_{\text{H}_2\text{(g)}}}{P_{\text{H}_2\text{O(g)}}} \times \frac{1}{P^\circ} = K_P \times \left(\frac{1}{P^\circ} \right)$$



$$K = \frac{a_{\text{CO}_2(\text{g})} a_{\text{CaO}(\text{s})}}{a_{\text{CaCO}_3(\text{s})}} = \frac{(P_{\text{CO}_2(\text{g})} / P^\circ)(1)}{(1)}$$

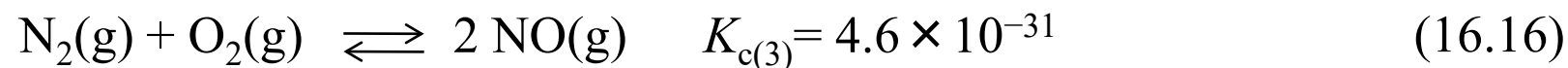
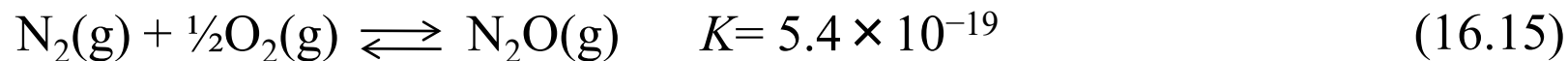
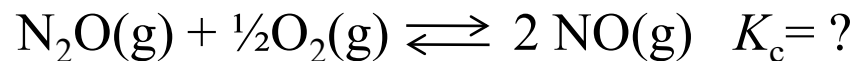
$$= P_{\text{CO}_2(\text{g})} \times \left(\frac{1}{P^\circ} \right) = K_P \times \left(\frac{1}{P^\circ} \right)$$

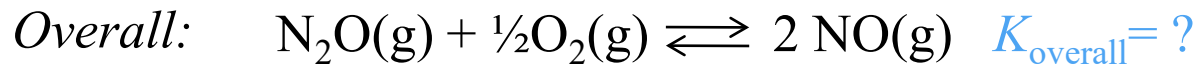
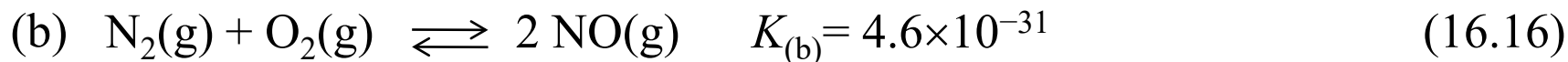
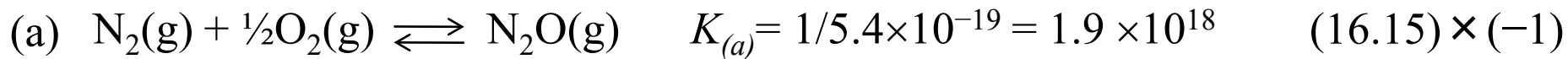
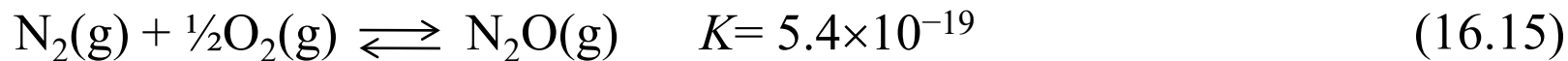
16-3 Relationships Involving the Equilibrium Constant

Relationship of K to the Balanced Chemical Equation

- When we *reverse* an equation, we *invert* the value of K .
- When we *multiply* the coefficients in a balanced equation by a common factor we raise the equilibrium constant to the *corresponding power*.
- When we *divide* the coefficients in a balanced equation by a common factor we take the *corresponding root* of the equilibrium constant.

Combining Equilibrium Constant Expressions





$$K(\text{overall}) = \frac{a_{\text{NO}(\text{g})}^2}{a_{\text{N}_2\text{O}(\text{g})}^2 a_{\text{O}_2(\text{g})}^{\frac{1}{2}}} = \frac{a_{\text{N}_2(\text{g})}^2 a_{\text{O}_2(\text{g})}^{\frac{1}{2}}}{a_{\text{N}_2\text{O}(\text{g})}^2} \times \frac{a_{\text{NO}(\text{g})}^2}{a_{\text{N}_2(\text{g})}^2 a_{\text{O}_2(\text{g})}} = K_{(a)} \times K_{(b)}$$

$$= 1.9 \times 10^{18} \times 4.6 \times 10^{-31} = 8.5 \times 10^{-13}$$

Relationship Between K_p and K_c for Reactions Involving Gases

$$P_A = \frac{n_A RT}{V} = [A]RT$$

$$K_p = \frac{P_C^c \times P_D^d \dots}{P_A^a \times P_B^b \dots} = \frac{([C]RT)^c ([D]RT)^d \dots}{([A]RT)^a ([B]RT)^b \dots} = \frac{[C]^c \times [D]^d \dots}{[A]^a \times [B]^b \dots} \times (RT)^{\Delta \nu_{\text{gas}}}$$

$$K_p = K_c \times (RT)^{\Delta \nu_{\text{gas}}} \quad (16.17)$$

16-4 The Magnitude of the Equilibrium Constant.

A very large value of K signifies that the reaction, as written, exhibits a strong tendency to go to completion. An equilibrium mixture contains about as much product as can be formed from the given initial amounts of reactants.

A very small value of K signifies that the reaction, as written, exhibits very little tendency to occur. An equilibrium mixture contains reactants, in essentially their initial amounts, and very small amounts of products.

Table 16.3 Equilibrium Constants of Some Common Reactions

Reaction	Equilibrium Constant, K
$2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{H}_2\text{O}(\text{l})$	1.4×10^{83} at 298 K
$\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$	1.9×10^{-23} at 298 K 1.0 at about 1200 K
$2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{SO}_3(\text{g})$	3.4 at 1000 K
$\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2(\text{g})$	1.6×10^{-21} at 298 K 10.0 at about 1100 K

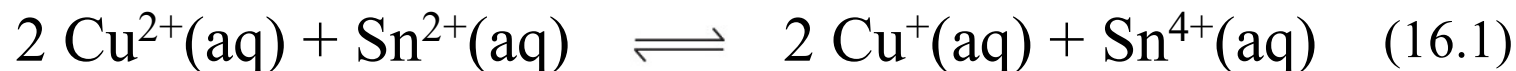


A reaction goes essentially to completion if $K = 10^{10}$ and not at all if $K = 10^{-10}$.

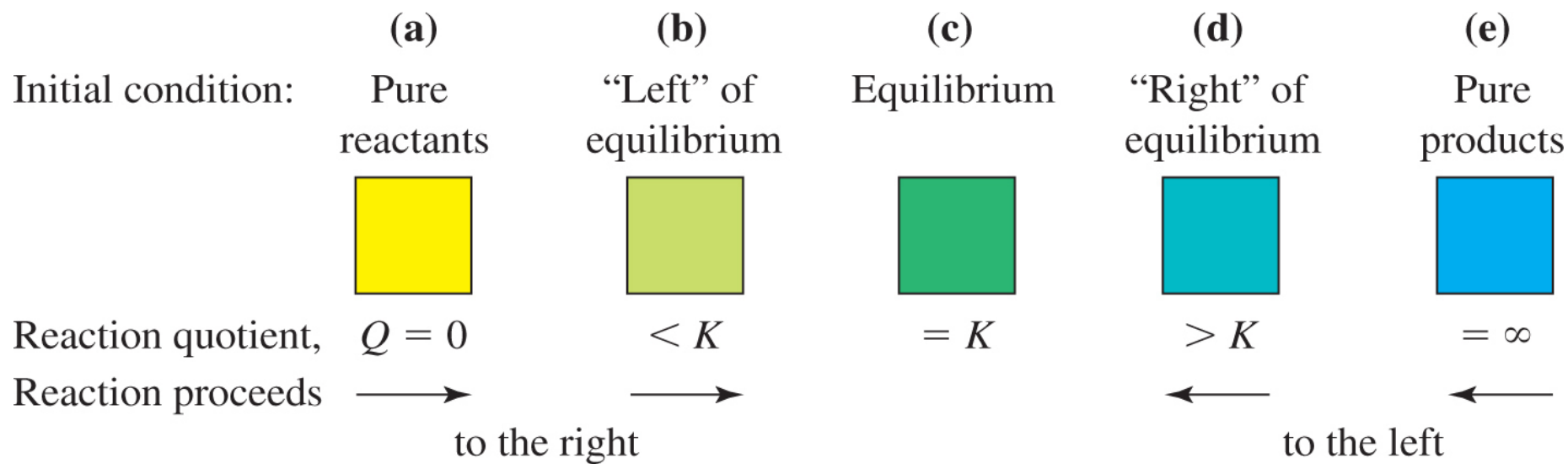
16-5 Predicting the Direction of Net Change.

Table 16.4 Using Q and K to Predict the Direction of Net Chemical Change

Condition	Direction of Net Chemical Change
$Q < K$	To the right (\longrightarrow)
$Q > K$	To the left (\longleftarrow)
$Q = K$	Equilibrium; no net change (\rightleftharpoons)



$$Q = \frac{[\text{Cu}^{+}]^2 [\text{Sn}^{4+}]}{[\text{Cu}^{2+}]^2 [\text{Sn}^{2+}]} \quad K = 1.48$$



▲ FIGURE 16-4
Predicting the direction of net change

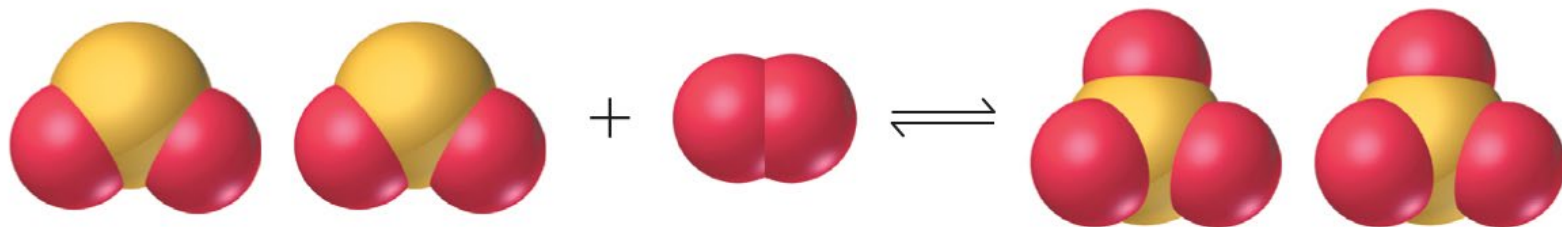
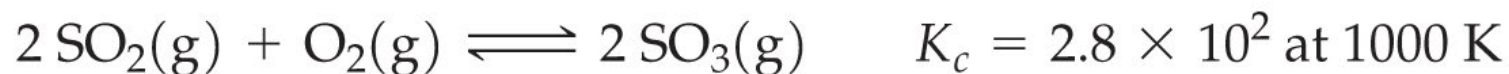
16-6 Altering Equilibrium Conditions: Le Châtelier's Principle

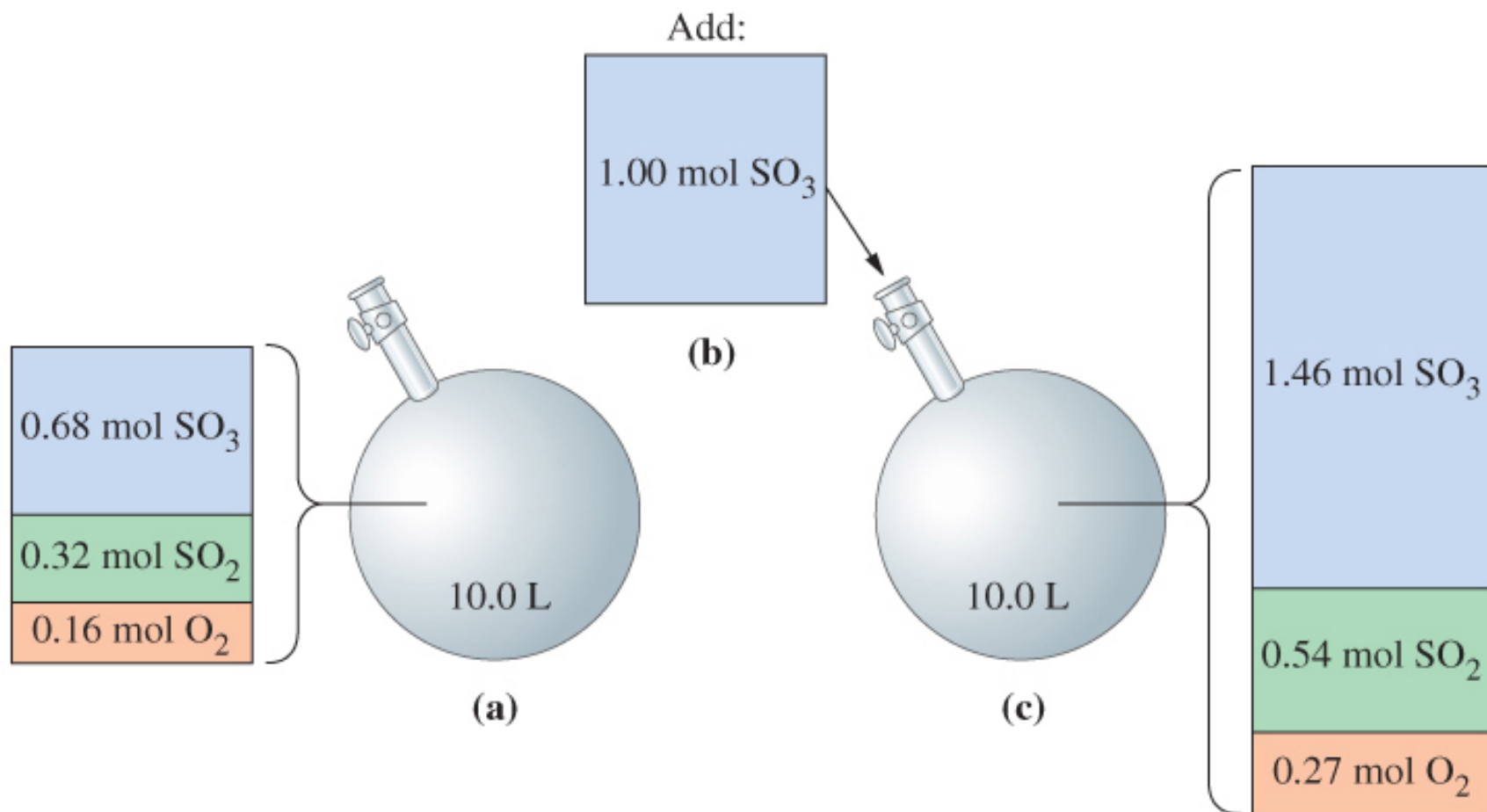
When an equilibrium system is subjected to a change in temperature, pressure, or concentration of a reacting species, the system responds by attaining a new equilibrium that partially offsets the impact of the change.

Effect of Changing the Amounts of Reacting Species on Equilibrium



Let's consider the following reaction





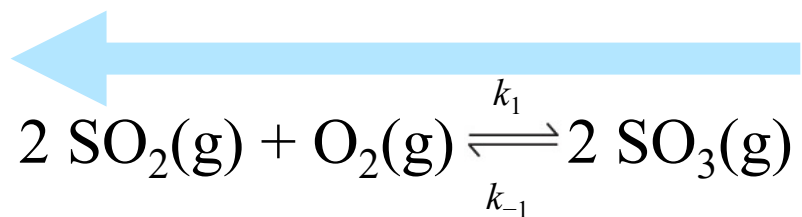
▲ FIGURE 16-5
 Changing equilibrium conditions by changing the amount of a reacting species
 $2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{SO}_3(\text{g}), K_c = 2.8 \times 10^2$ at 1000 K

Original equilibrium

Immediately following disturbance

$$Q = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} = K_c$$

$$Q > K_c$$



Effect of Changes in Pressure or Volume on Equilibrium

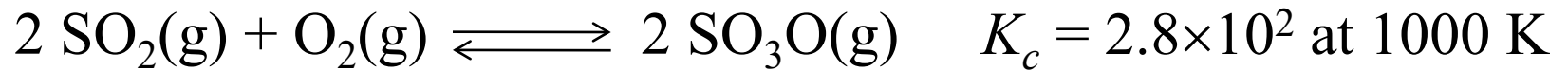
- 1. Add or remove a gaseous reactant or product.**

Changes P_{gas} .

- 2. Adding an inert gas to the constant volume reaction mixture.**

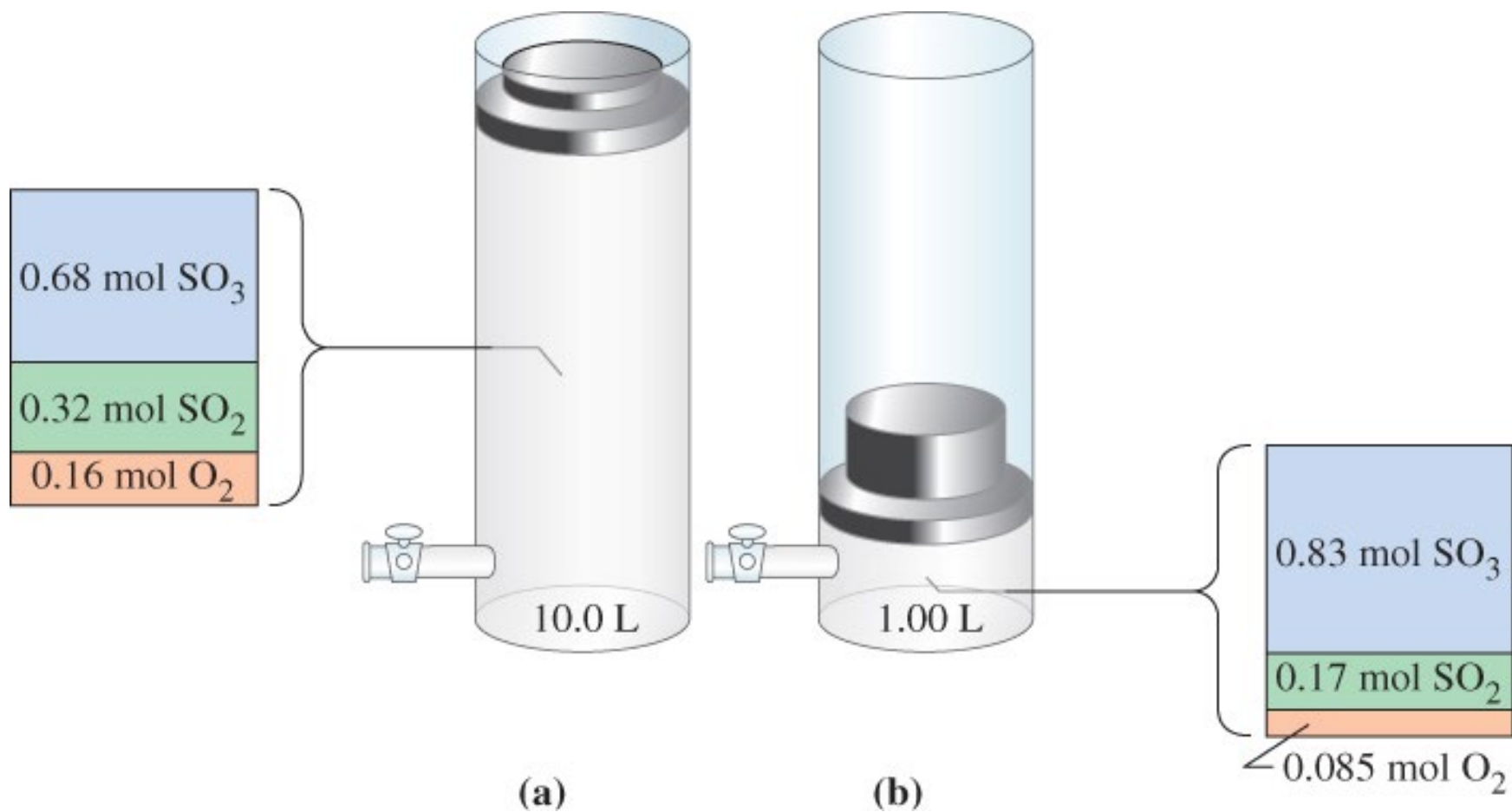
Relative partial pressures are unchanged.

- 3. Change the pressure by changing the volume of the system.**



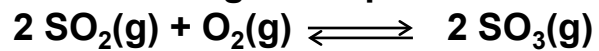
$$K_c = \frac{[\text{SO}_3]}{[\text{SO}_2]^2[\text{O}_2]} = \frac{\left(\frac{n_{\text{SO}_3}}{V}\right)^2}{\left(\frac{n_{\text{SO}_2}}{V}\right)^2 \frac{n_{\text{O}_2}}{V}} = \frac{n_{\text{SO}_3}^2}{n_{\text{SO}_2}^2 n_{\text{O}_2}} V$$

If V is reduced by a factor of 10, then $\frac{n_{\text{SO}_3}^2}{n_{\text{SO}_2}^2 n_{\text{O}_2}}$ must increase by a factor of 10



▲ FIGURE 16-6

Effect of a pressure change on equilibrium in the reaction



When the volume of an equilibrium mixture of gases is reduced, a net change occurs in the direction that produces fewer moles of gas. When the volume is increased, a net change occurs in the direction that produces more moles of gas.

Effect of Temperature on Equilibrium

Raising the temperature of an equilibrium mixture shifts the equilibrium condition in the direction of the *endothermic* reaction. *Lowering the temperature* causes a shift in the direction of the *exothermic* reaction.

For *endothermic* reactions, *K increases* as temperature increases. For *exothermic* reactions, *K decreases* as temperature increases.

Effect of a Catalyst on Equilibrium

A catalyst has no effect on the condition of equilibrium in a reversible reaction.



▲ Sulfuric acid is produced from SO_3
 $\text{SO}_3(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{SO}_4(\text{aq})$

16-7 Equilibrium Calculations: Some Illustrative Examples.

Five numerical examples are given in the text that illustrate ideas that have been presented in this chapter.

Refer to the “comments” which describe the methodology. These will help in subsequent chapters.

Exercise your understanding by working through the examples with a pencil and paper.