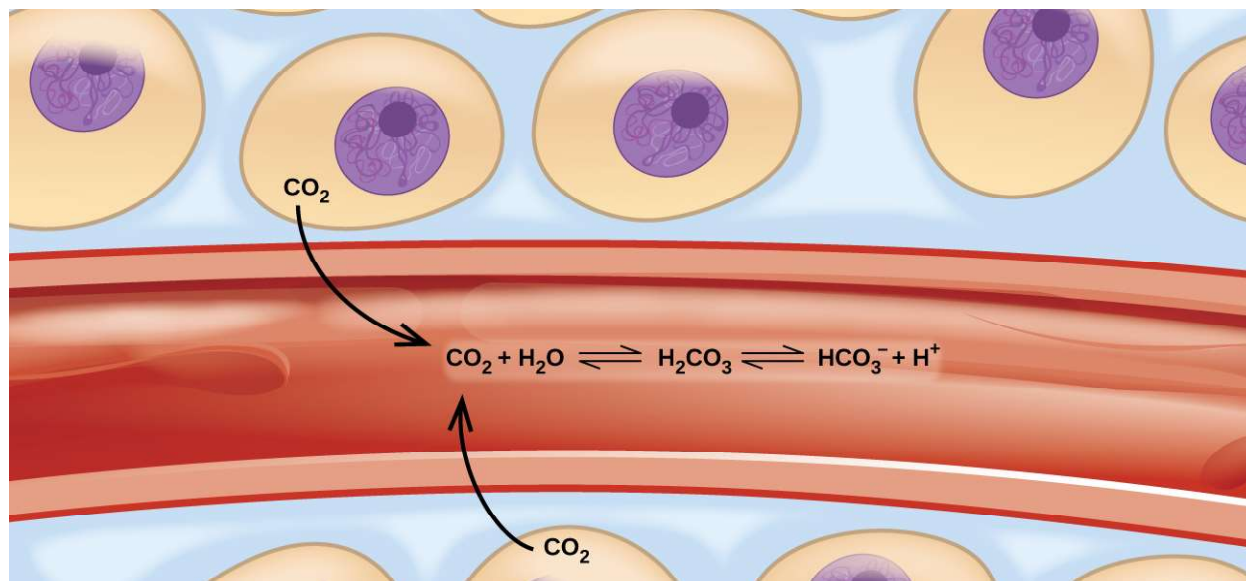# Chapter 13

Fundamental Equilibrium Concepts

Figure 13.1 Transport of carbon dioxide in the body involves several reversible chemical reactions, including hydrolysis and acid ionization (among others).

Chapter Outline

13.1 Chemical Equilibria

13.2 Equilibrium Constants

13.3 Shifting Equilibria: Le Châtelier's Principle

13.4 Equilibrium Calculations

Introduction

Imagine a beach populated with sunbathers and swimmers. As those basking in the sun get too hot, they enter the surf to swim and cool off. As the swimmers tire, they return to the beach to rest. If the rate at which sunbathers enter the surf were to equal the rate at which swimmers return to the sand, then the numbers (though not the identities) of sunbathers and swimmers would remain constant. This scenario illustrates a dynamic phenomenon known as *equilibrium*, in which opposing processes occur at equal rates. Chemical and physical processes are subject to this phenomenon; these processes are at equilibrium when the forward and reverse reaction rates are equal. Equilibrium systems are pervasive in nature; the various reactions involving carbon dioxide dissolved in blood are examples (see **Figure 13.1**). This chapter provides a thorough introduction to the essential aspects of chemical equilibria.

We now have a good understanding of chemical and physical change that allow us to determine, for any given process:

1. Whether the process is endothermic or exothermic

2. Whether the process is accompanied by an increase of decrease in entropy

3. Whether a process will be spontaneous, non-spontaneous, or what we have called an equilibrium process

Recall that when the value ΔG for a reaction is zero, we consider there to be no free energy change—that is, no free energy available to do useful work. Does this mean a reaction where $\Delta G = 0$ comes to a complete halt? No, it does not. Just as a liquid exists in equilibrium with its vapor in a closed container, where the rates of evaporation and condensation are equal, there is a connection to the state of equilibrium for a phase change or a chemical reaction. That is, at equilibrium, the forward and reverse rates of reaction are equal. We will develop that concept and extend it to a relationship between equilibrium and free energy later in this chapter.

In the explanation that follows, we will use the term Q to refer to any reactant or product concentration or pressure. When the concentrations or pressure of reactants and products are at equilibrium, the term K will be used. This will be more clearly explained as we go along in this chapter.

Now we will consider the connection between the free energy change and the equilibrium constant. The fundamental relationship is:

$\Delta G^\circ = -RT \ln K$ —this can be for K_c or K_p (and we will see later, any equilibrium constant we encounter).

We also know that the form of K can be used in non-equilibrium conditions as the reaction quotient, Q. The defining relationship here is

$$\Delta G = \Delta G^\circ + RT \ln Q$$

Without the superscript, the value of ΔG can be calculated for any set of concentrations.

Note that since Q is a mass-action reaction of productions/reactants, as a reaction proceeds from left to right, product concentrations increase as reactant concentrations decrease, until $Q = K$, and at which time ΔG becomes zero: $0 = \Delta G^\circ + RT \ln K$, a relationship that reduces to our defining connection between Q and K.

Thus, we can see clearly that as a reaction moves toward equilibrium, the value of ΔG goes to zero.

Now, think back to the connection between the signs of ΔG° and ΔH°

ΔH°	ΔS°	Result
Negative	Positive	Always spontaneous
Positive	Negative	Never spontaneous
Positive	Positive	Spontaneous at high temperatures
Negative	Negative	Spontaneous at low temperatures

Only in the last two cases is there a point at which the process swings from spontaneous to non-spontaneous (or the reverse); in these cases, the process must pass through equilibrium when the change occurs. The concept of the connection between the free energy change and the equilibrium constant is an important one that we will expand upon in future sections. The fact that the change in free energy for an equilibrium process is zero, and that displacement of a process from that zero point results in a drive to re-establish equilibrium is fundamental to understanding the behavior of chemical reactions and phase changes.

13.1 Chemical Equilibria

By the end of this section, you will be able to:

- Describe the nature of equilibrium systems
- Explain the dynamic nature of a chemical equilibrium

The convention for writing chemical equations involves placing reactant formulas on the left side of a reaction arrow and product formulas on the right side. By this convention, and the definitions of "reactant" and "product," a chemical equation represents the reaction in question as proceeding from left to right. **Reversible reactions**, however, may proceed in both forward (left to right) and reverse (right to left) directions. When the rates of the forward and reverse reactions are equal, the concentrations of the reactant and product species remain constant over time and the system is at **equilibrium**. The relative concentrations of reactants and products in equilibrium systems vary greatly;

some systems contain mostly products at equilibrium, some contain mostly reactants, and some contain appreciable amounts of both.

Figure 13.2 illustrates fundamental equilibrium concepts using the reversible decomposition of colorless dinitrogen tetroxide to yield brown nitrogen dioxide, an elementary reaction described by the equation:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$
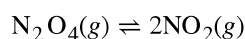
Note that a special double arrow is used to emphasize the reversible nature of the reaction.
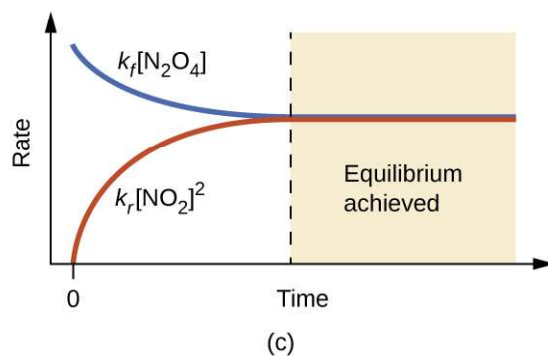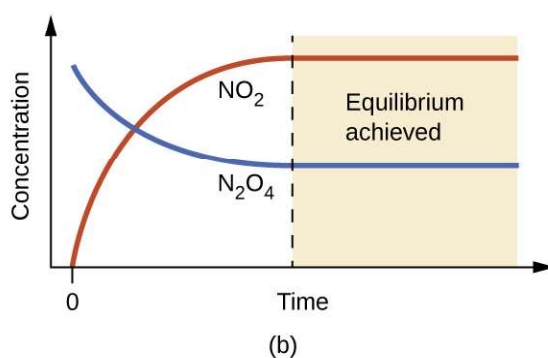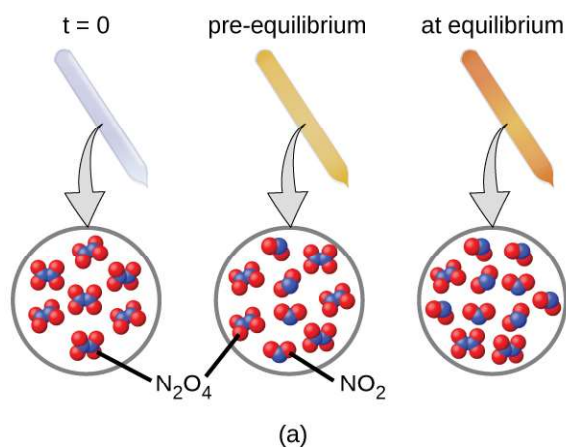

Figure 13.2   (a) A sealed tube containing colorless N_2O_4 darkens as it decomposes to yield brown NO_2. (b) Changes in concentration over time as the decomposition reaction achieves equilibrium. (c) At equilibrium, the forward and reverse reaction rates are equal.

For this elementary process, rate laws for the forward and reverse reactions may be derived directly from the reaction stoichiometry:

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

As the reaction begins ($t = 0$), the concentration of the N_2O_4 reactant is finite and that of the NO_2 product is zero, so the forward reaction proceeds at a finite rate while the reverse reaction rate is zero. As time passes, N_2O_4 is consumed and its concentration falls, while NO_2 is produced and its concentration increases (**Figure 13.2b**). The decreasing concentration of the reactant slows the forward reaction rate, and the increasing product concentration speeds the reverse reaction rate (**Figure 13.2c**). This process continues until *the forward and reverse reaction rates become equal*, at which time the reaction has reached equilibrium, as characterized by constant concentrations of its reactants and products (shaded areas of **Figure 13.2b** and **Figure 13.2c**). It's important to emphasize that chemical equilibria are dynamic; a reaction at equilibrium has not "stopped," but is proceeding in the forward and reverse directions at the same rate. This dynamic nature is essential to understanding equilibrium behavior as discussed in this and subsequent chapters of the text.

Figure 13.3   A two-person juggling act illustrates the dynamic aspect of chemical equilibria. Each person is throwing and catching clubs at the same rate, and each holds a (approximately) constant number of clubs.

Physical changes, such as phase transitions, are also reversible and may establish equilibria. This concept was introduced in another chapter of this text through discussion of the vapor pressure of a condensed phase (liquid or solid). As one example, consider the vaporization of bromine:

$$\text{Br}_2(l) \rightleftharpoons \text{Br}_2(g)$$
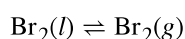
When liquid bromine is added to an otherwise empty container and the container is sealed, the forward process depicted above (vaporization) will commence and continue at a roughly constant rate as long as the exposed surface area of the liquid and its temperature remain constant. As increasing amounts of gaseous bromine are produced, the rate of the reverse process (condensation) will increase until it equals the rate of vaporization and equilibrium is established. A photograph showing this phase transition equilibrium is provided in **Figure 13.4**.

Figure 13.4   A sealed tube containing an equilibrium mixture of liquid and gaseous bromine. (credit: http://images-of-elements.com/bromine.php)

13.2 Equilibrium Constants

The status of a reversible reaction is conveniently assessed by evaluating its **reaction quotient (Q)**. For a reversible reaction described by

$$mA + nB \rightleftharpoons xC + yD,$$
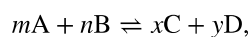
the reaction quotient is derived directly from the stoichiometry of the balanced equation as

$$Q_c = \frac{[C]^x[D]^y}{[A]^m[B]^n},$$

where the subscript c denotes the use of molar concentrations in the expression. If the reactants and products are gaseous, a reaction quotient may be similarly derived using partial pressures:

$$Q_p = \frac{P_{Cx}\, P_{Dy}}{P_{Am}\, P_{Bn}}$$

Note that the reaction quotient equations above are a simplification of more rigorous expressions that use *relative* values for concentrations and pressures rather than *absolute* values. These relative concentration and pressure values are dimensionless (they have no units); consequently, so are the reaction quotients. For purposes of this introductory text, it will suffice to use the simplified equations and to disregard units when computing Q. In most cases, this will introduce only modest errors in calculations involving reaction quotients.

Example 13.1

Writing Reaction Quotient Expressions

Write the concentration-based reaction quotient expression for each of the following reactions:

(a) $3O_2(g) \rightleftharpoons 2O_3(g)$

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

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

Solution

(a) $Q_c = \dfrac{[O_3]^2}{[O_2]^3}$

(b) $Q_c = \dfrac{[NH_3]^2}{[N_2][H_2]^3}$

(c) $Q_c = \dfrac{[NO_2]^4[H_2O]^6}{[NH_3]^4[O_2]^7}$

Check Your Learning

Write the concentration-based reaction quotient expression for each of the following reactions:

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

(b) $C_4H_8(g) \rightleftharpoons 2C_2H_4(g)$

(c) $2C_4H_{10}(g) + 13O_2(g) \rightleftharpoons 8CO_2(g) + 10H_2O(g)$

Answer: (a) $Q_c = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]}$; (b) $Q_c = \dfrac{[C_2H_4]^2}{[C_4H_8]}$; (c) $Q_c = \dfrac{[CO_2]^8[H_2O]^{10}}{[C_4H_{10}]^2[O_2]^{13}}$
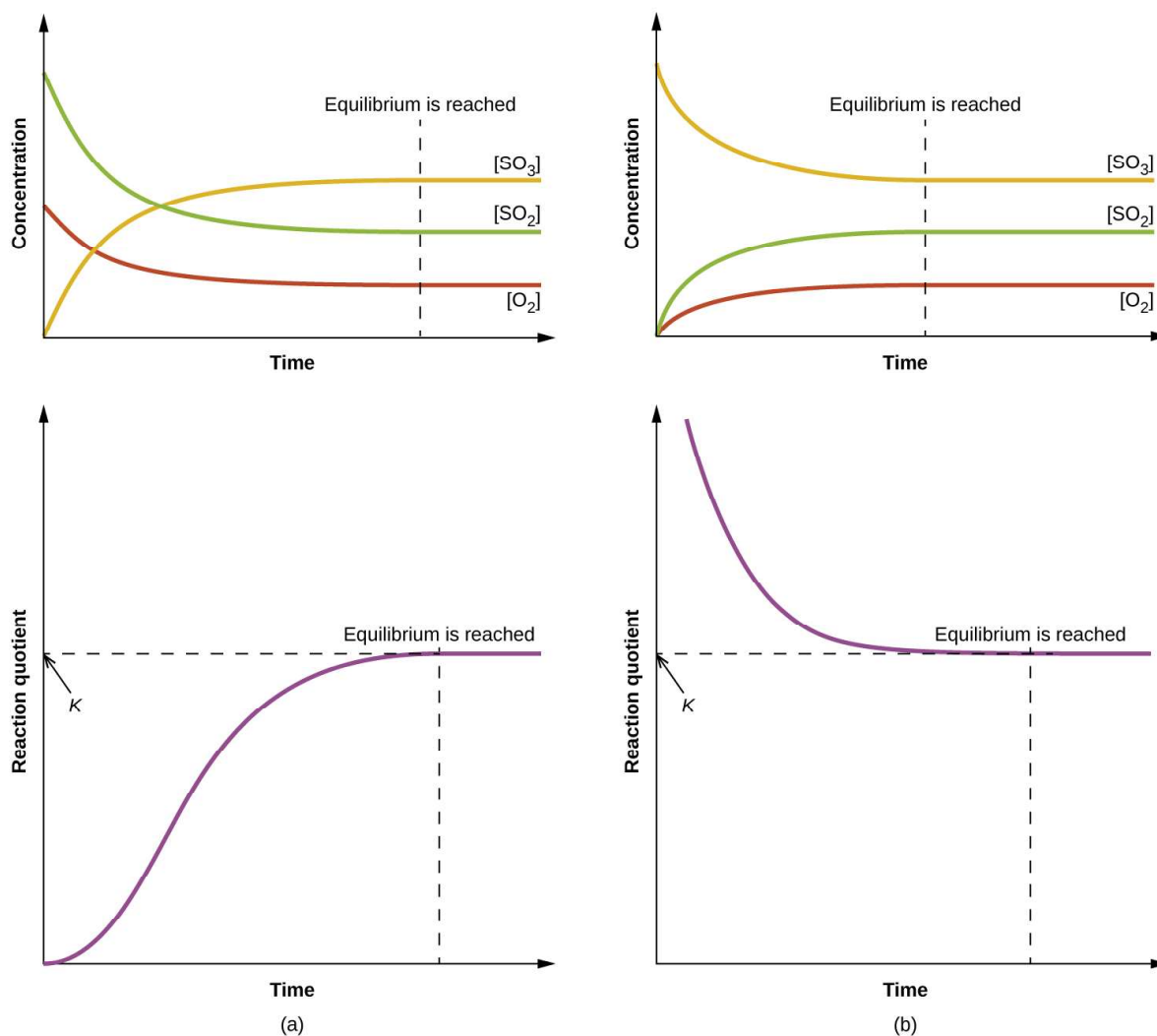
Figure 13.5 Changes in concentrations and Q_c for a chemical equilibrium achieved beginning with (a) a mixture of reactants only and (b) products only.

The numerical value of Q varies as a reaction proceeds towards equilibrium; therefore, it can serve as a useful indicator of the reaction's status. To illustrate this point, consider the oxidation of sulfur dioxide:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$
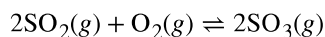
Two different experimental scenarios are depicted in **Figure 13.5**, one in which this reaction is initiated with a mixture of reactants only, SO_2 and O_2, and another that begins with only product, SO_3. For the reaction that begins with a mixture of reactants only, Q is initially equal to zero:

$$Q_c = \frac{[SO_3]^2}{[SO_2]^2 \, [O_2]} = \frac{0^2}{[SO_2]^2 \, [O_2]} = 0$$

As the reaction proceeds toward equilibrium in the forward direction, reactant concentrations decrease (as does the denominator of Q_c), product concentration increases (as does the numerator of Q_c), and the reaction quotient consequently increases. When equilibrium is achieved, the concentrations of reactants and product remain constant, as does the value of Q_c.

If the reaction begins with only product present, the value of Q_c is initially undefined (immeasurably large, or

infinite):

$$Q_c = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]} = \frac{[SO_3]^2}{0} \rightarrow \infty$$

In this case, the reaction proceeds toward equilibrium in the reverse direction. The product concentration and the numerator of Q_c decrease with time, the reactant concentrations and the denominator of Q_c increase, and the reaction quotient consequently decreases until it becomes constant at equilibrium.

The constant value of Q exhibited by a system at equilibrium is called the **equilibrium constant, K**:
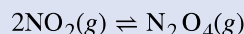
$$K \equiv Q \text{ at equilibrium}$$

Comparison of the data plots in **Figure 13.5** shows that both experimental scenarios resulted in the same value for the equilibrium constant. This is a general observation for all equilibrium systems, known as the **law of mass action**: At a given temperature, the reaction quotient for a system at equilibrium is constant.

Example 13.2

Evaluating a Reaction Quotient

Gaseous nitrogen dioxide forms dinitrogen tetroxide according to this equation:

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

When 0.10 mol NO_2 is added to a 1.0-L flask at 25 °C, the concentration changes so that at equilibrium, $[NO_2] = 0.016\ M$ and $[N_2O_4] = 0.042\ M$.

(a) What is the value of the reaction quotient before any reaction occurs?

(b) What is the value of the equilibrium constant for the reaction?

Solution

As for all equilibrium calculations in this text, use the simplified equations for Q and K and disregard any concentration or pressure units, as noted previously in this section.

(a) Before any product is formed, $[NO_2] = \dfrac{0.10\ \text{mol}}{1.0\ \text{L}} = 0.10\ M$, and $[N_2O_4] = 0\ M$. Thus,

$$Q_c = \frac{[N_2O_4]}{[NO_2]^2} = \frac{0}{0.10^2} = 0$$

(b) At equilibrium, $K_c = Q_c = \dfrac{[N_2O_4]}{[NO_2]^2} = \dfrac{0.042}{0.016^2} = 1.6 \times 10^2$. The equilibrium constant is 1.6×10^2.

Check Your Learning

For the reaction $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$, the concentrations at equilibrium are $[SO_2] = 0.90\ M$, $[O_2] = 0.35\ M$, and $[SO_3] = 1.1\ M$. What is the value of the equilibrium constant, K_c?

Answer: $K_c = 4.3$

By its definition, the magnitude of an equilibrium constant explicitly reflects the composition of a reaction mixture at equilibrium, and it may be interpreted with regard to the extent of the forward reaction. A reaction exhibiting a large K will reach equilibrium when most of the reactant has been converted to product, whereas a small K indicates the reaction achieves equilibrium after very little reactant has been converted. It's important to keep in mind that the magnitude of K does *not* indicate how rapidly or slowly equilibrium will be reached. Some equilibria are established so quickly as to be nearly instantaneous, and others so slowly that no perceptible change is observed over the course of days, years, or longer.

The equilibrium constant for a reaction can be used to predict the behavior of mixtures containing its reactants and/or

products. As demonstrated by the sulfur dioxide oxidation process described above, a chemical reaction will proceed in whatever direction is necessary to achieve equilibrium. Comparing Q to K for an equilibrium system of interest allows prediction of what reaction (forward or reverse), if any, will occur.

To further illustrate this important point, consider the reversible reaction shown below:

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) \qquad K_c = 0.640 \qquad T = 800\,°C$$

The bar charts in **Figure 13.6** represent changes in reactant and product concentrations for three different reaction mixtures. The reaction quotients for mixtures 1 and 3 are initially lesser than the reaction's equilibrium constant, so each of these mixtures will experience a net forward reaction to achieve equilibrium. The reaction quotient for mixture 2 is initially greater than the equilibrium constant, so this mixture will proceed in the reverse direction until equilibrium is established.
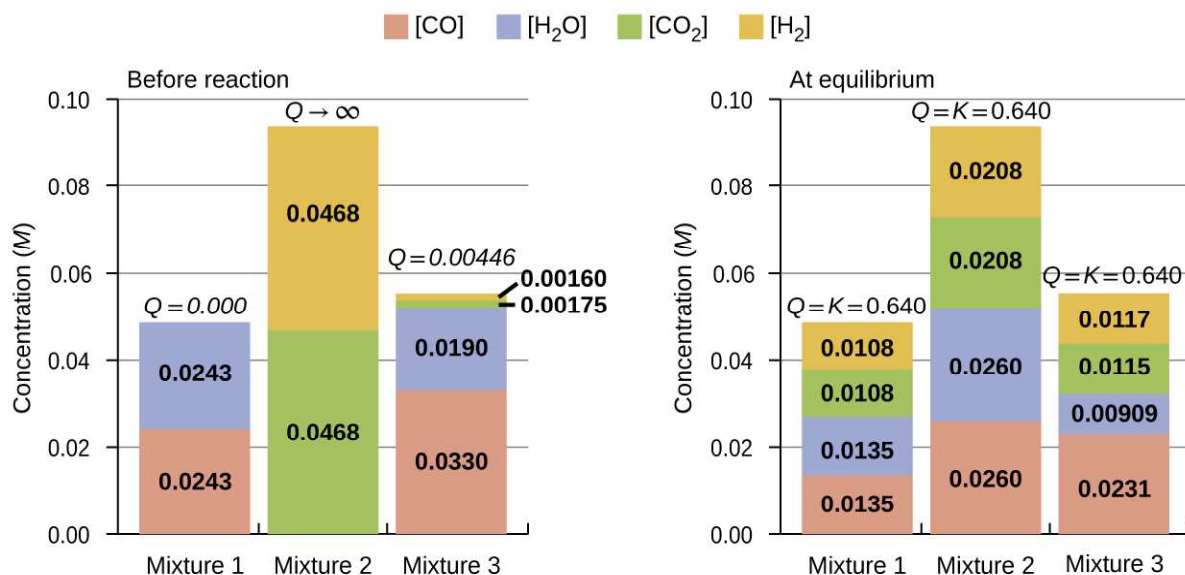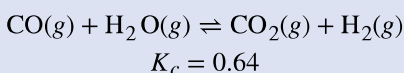
Figure 13.6 Compositions of three mixtures before ($Q_c \neq K_c$) and after ($Q_c = K_c$) equilibrium is established for the reaction $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$.

Example 13.3

Predicting the Direction of Reaction

Given here are the starting concentrations of reactants and products for three experiments involving this reaction:

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$
$$K_c = 0.64$$

Determine in which direction the reaction proceeds as it goes to equilibrium in each of the three experiments shown.

Reactants/Products	Experiment 1	Experiment 2	Experiment 3
$[CO]_i$	0.020 M	0.011 M	0.0094 M
$[H_2O]_i$	0.020 M	0.0011 M	0.0025 M
$[CO_2]_i$	0.0040 M	0.037 M	0.0015 M
$[H_2]_i$	0.0040 M	0.046 M	0.0076 M

Solution

Experiment 1:

$$Q_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(0.0040)(0.0040)}{(0.020)(0.020)} = 0.040.$$

$Q_c < K_c$ (0.040 < 0.64)

The reaction will proceed in the forward direction.

Experiment 2:

$$Q_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(0.037)(0.046)}{(0.011)(0.0011)} = 1.4 \times 10^2$$

$Q_c > K_c$ (140 > 0.64)

The reaction will proceed in the reverse direction.

Experiment 3:

$$Q_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(0.0015)(0.0076)}{(0.0094)(0.0025)} = 0.48$$

$Q_c < K_c$ (0.48 < 0.64)

The reaction will proceed in the forward direction.

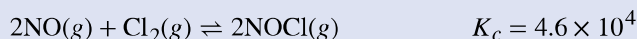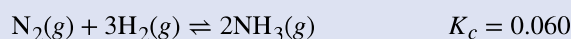### Check Your Learning

Calculate the reaction quotient and determine the direction in which each of the following reactions will proceed to reach equilibrium.
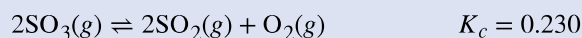
(a) A 1.00-L flask containing 0.0500 mol of NO(g), 0.0155 mol of Cl2(g), and 0.500 mol of NOCl:

$$2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g) \qquad K_c = 4.6 \times 10^4$$

(b) A 5.0-L flask containing 17 g of NH_3, 14 g of N_2, and 12 g of H_2:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad K_c = 0.060$$

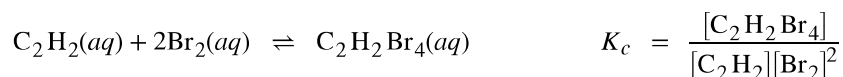(c) A 2.00-L flask containing 230 g of SO_3(g):

$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g) \qquad K_c = 0.230$$

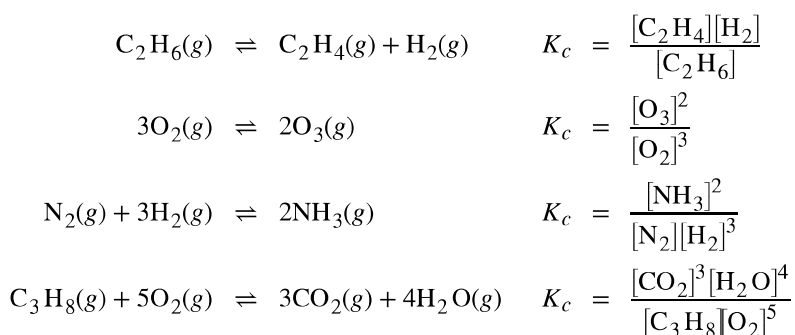**Answer:** (a) $Q_c = 6.45 \times 10^3$, forward. (b) $Q_c = 0.23$, reverse. (c) $Q_c = 0$, forward.

Homogeneous Equilibria

A **homogeneous equilibrium** is one in which all reactants and products (and any catalysts, if applicable) are present in the same phase. By this definition, homogeneous equilibria take place in *solutions*. These solutions are most commonly either liquid or gaseous phases, as shown by the examples below:

$$C_2H_2(aq) + 2Br_2(aq) \rightleftharpoons C_2H_2Br_4(aq) \qquad K_c = \frac{[C_2H_2Br_4]}{[C_2H_2][Br_2]^2}$$

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq) \qquad K_c = \frac{[I_3^-]}{[I_2][I^-]}$$

$$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq) \qquad K_c = \frac{[H_3O^+][F^-]}{[HF]}$$

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad K_c = \frac{[NH_4^+][OH^-]}{[NH_3]}$$
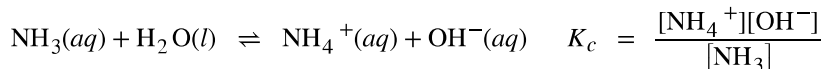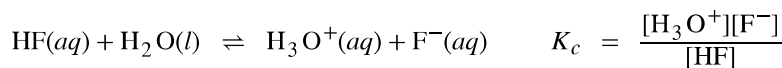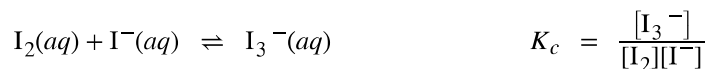
These examples all involve aqueous solutions, those in which water functions as the solvent. In the last two examples, water also functions as a reactant, but its concentration is *not* included in the reaction quotient. The reason for this omission is related to the more rigorous form of the Q (or K) expression mentioned previously in this chapter, in which *relative concentrations for liquids and solids are equal to 1 and needn't be included*. Consequently, reaction quotients include concentration or pressure terms only for gaseous and solute species.

The equilibria below all involve gas-phase solutions:

$$C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g) \qquad K_c = \frac{[C_2H_4][H_2]}{[C_2H_6]}$$

$$3O_2(g) \rightleftharpoons 2O_3(g) \qquad K_c = \frac{[O_3]^2}{[O_2]^3}$$

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$C_3H_8(g) + 5O_2(g) \rightleftharpoons 3CO_2(g) + 4H_2O(g) \qquad K_c = \frac{[CO_2]^3[H_2O]^4}{[C_3H_8][O_2]^5}$$

For gas-phase solutions, the equilibrium constant may be expressed in terms of either the molar concentrations (K_c) or partial pressures (K_p) of the reactants and products. A relation between these two K values may be simply derived from the ideal gas equation and the definition of molarity:

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

where P is partial pressure, V is volume, n is molar amount, R is the gas constant, T is temperature, and M is molar concentration.

For the gas-phase reaction $mA + nB \rightleftharpoons xC + yD$:

$$K_P = \frac{(P_C)^x(P_D)^y}{(P_A)^m(P_B)^n}$$
$$= \frac{([C] \times RT)^x([D] \times RT)^y}{([A] \times RT)^m([B] \times RT)^n}$$
$$= \frac{[C]^x[D]^y}{[A]^m[B]^n} \times \frac{(RT)^{x+y}}{(RT)^{m+n}}$$
$$= K_c(RT)^{(x+y)-(m+n)}$$
$$= K_c(RT)^{\Delta n}$$

And so, the relationship between K_c and K_P is

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

where Δn is the difference in the molar amounts of product and reactant gases, in this case:
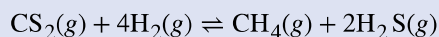
$$\Delta n = (x+y) - (m+n)$$

Example 13.4

Calculation of K_P

Write the equations relating K_c to K_P for each of the following reactions:

(a) $C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g)$

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

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

(d) K_c is equal to 0.28 for the following reaction at 900 °C:

$$CS_2(g) + 4H_2(g) \rightleftharpoons CH_4(g) + 2H_2S(g)$$

What is K_P at this temperature?

Solution

(a) $\Delta n = (2) - (1) = 1$
$K_P = K_c (RT)^{\Delta n} = K_c (RT)^1 = K_c (RT)$

(b) $\Delta n = (2) - (2) = 0$
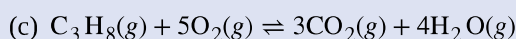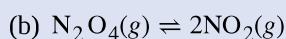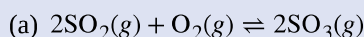$K_P = K_c (RT)^{\Delta n} = K_c (RT)^0 = K_c$

(c) $\Delta n = (2) - (1 + 3) = -2$
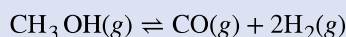$K_P = K_c (RT)^{\Delta n} = K_c (RT)^{-2} = \dfrac{K_c}{(RT)^2}$

(d) $K_P = K_c (RT)^{\Delta n} = (0.28)[(0.0821)(1173)]^{-2} = 3.0 \times 10^{-5}$

Check Your Learning

Write the equations relating K_c to K_P for each of the following reactions:

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

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

(c) $C_3H_8(g) + 5O_2(g) \rightleftharpoons 3CO_2(g) + 4H_2O(g)$

(d) At 227 °C, the following reaction has $K_c = 0.0952$:

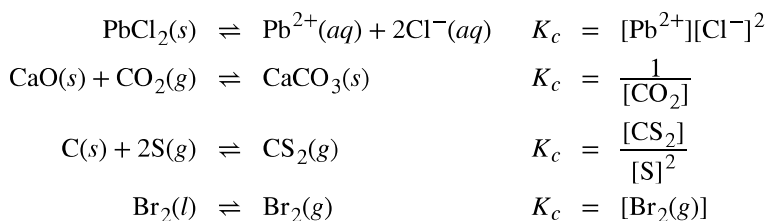$$CH_3OH(g) \rightleftharpoons CO(g) + 2H_2(g)$$

What would be the value of K_P at this temperature?

Answer: (a) $K_P = K_c (RT)^{-1}$; (b) $K_P = K_c (RT)$; (c) $K_P = K_c (RT)$; (d) 160 or 1.6×10^2
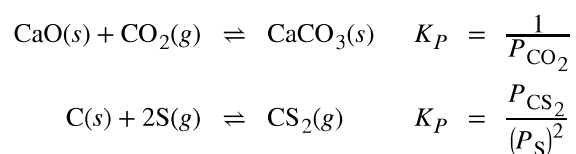
Heterogeneous Equilibria

A **heterogeneous equilibrium** involves reactants and products in two or more different phases, as illustrated by the following examples:

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq) \quad K_c = [Pb^{2+}][Cl^-]^2$$
$$CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s) \quad K_c = \frac{1}{[CO_2]}$$
$$C(s) + 2S(g) \rightleftharpoons CS_2(g) \quad K_c = \frac{[CS_2]}{[S]^2}$$
$$Br_2(l) \rightleftharpoons Br_2(g) \quad K_c = [Br_2(g)]$$

Again, note that concentration terms are only included for gaseous and solute species, as discussed previously.

Two of the above examples include terms for gaseous species only in their equilibrium constants, and so K_P expressions may also be written:

$$CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s) \quad K_P = \frac{1}{P_{CO_2}}$$
$$C(s) + 2S(g) \rightleftharpoons CS_2(g) \quad K_P = \frac{P_{CS_2}}{(P_S)^2}$$

13.3 Shifting Equilibria: Le Châtelier's Principle

By the end of this section, you will be able to:

- Describe the ways in which an equilibrium system can be stressed
- Predict the response of a stressed equilibrium using Le Châtelier's principle

A system at equilibrium is in a state of dynamic balance, with forward and reverse reactions taking place at equal rates. If an equilibrium system is subjected to a change in conditions that affects these reaction rates differently (a *stress*), then the rates are no longer equal and the system is not at equilibrium. The system will subsequently experience a net reaction in the direction of greater rate (a *shift*) that will re-establish the equilibrium. This phenomenon is summarized by **Le Châtelier's principle**: *if an equilibrium system is stressed, the system will experience a shift in response to the stress that re-establishes equilibrium.*
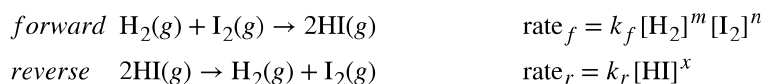
Reaction rates are affected primarily by concentrations, as described by the reaction's rate law, and temperature, as described by the Arrhenius equation. Consequently, changes in concentration and temperature are the two stresses that can shift an equilibrium.

Effect of a Change in Concentration

If an equilibrium system is subjected to a change in the concentration of a reactant or product species, the rate of either the forward or the reverse reaction will change. As an example, consider the equilibrium reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \qquad K_c = 50.0 \text{ at } 400 \text{ °C}$$

The rate laws for the forward and reverse reactions are

$$\textit{forward} \ \ H_2(g) + I_2(g) \rightarrow 2HI(g) \qquad \text{rate}_f = k_f [H_2]^m [I_2]^n$$
$$\textit{reverse} \ \ \ \ 2HI(g) \rightarrow H_2(g) + I_2(g) \qquad \text{rate}_r = k_r [HI]^x$$

When this system is at equilibrium, the forward and reverse reaction rates are equal.

$$\text{rate}_f = \text{rate}_r$$

If the system is stressed by adding reactant, either H_2 or I_2, the resulting increase in concentration causes the rate of the forward reaction to increase, exceeding that of the reverse reaction:

$$\text{rate}_f > \text{rate}_r$$

The system will experience a temporary net reaction in the forward direction to re-establish equilibrium (*the equilibrium will shift right*). This same shift will result if some product HI is removed from the system, which decreases the rate of the reverse reaction, again resulting in the same imbalance in rates.

The same logic can be used to explain the left shift that results from either removing reactant or adding product to an equilibrium system. These stresses both result in an increased rate for the reverse reaction

$$\text{rate}_f < \text{rate}_r$$

and a temporary net reaction in the reverse direction to re-establish equilibrium.

As an alternative to this kinetic interpretation, the effect of changes in concentration on equilibria can be rationalized in terms of reaction quotients. When the system is at equilibrium,

$$Q_c = \frac{[HI]^2}{[H_2][I_2]} = K_c$$

If reactant is added (increasing the denominator of the reaction quotient) or product is removed (decreasing the numerator), then $Q_c < K_c$ and the equilibrium will shift right. Note that the three different ways of inducing this stress result in three different changes in the composition of the equilibrium mixture. If H_2 is added, the right shift will consume I_2 and produce HI as equilibrium is re-established, yielding a mixture with a greater concentrations of H_2

and HI and a lesser concentration of I_2 than was present before. If I_2 is added, the new equilibrium mixture will have greater concentrations of I_2 and HI and a lesser concentration of H_2. Finally, if HI is removed, the new equilibrium mixture will have greater concentrations of H_2 and I_2 and a lesser concentration of HI. Despite these differences in composition, *the value of the equilibrium constant will be the same after the stress as it was before* (per the law of mass action). The same logic may be applied for stresses involving removing reactants or adding product, in which case $Q_c > K_c$ and the equilibrium will shift left.

For gas-phase equilibria such as this one, some additional perspectives on changing the concentrations of reactants and products are worthy of mention. The partial pressure P of an ideal gas is proportional to its molar concentration M,

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

and so changes in the partial pressures of any reactant or product are essentially changes in concentrations and thus yield the same effects on equilibria. Aside from adding or removing reactant or product, the pressures (concentrations) of species in a gas-phase equilibrium can also be changed by *changing the volume occupied by the system*. Since all species of a gas-phase equilibrium occupy the same volume, a given change in volume will cause the same change in concentration for both reactants and products. In order to discern what shift, if any, this type of stress will induce the stoichiometry of the reaction must be considered.

At equilibrium, the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is described by the reaction quotient

$$Q_p = \frac{P_{HI}2}{P_{H}2\,P_{I}2} = K_p$$

If the volume occupied by an equilibrium mixture of these species is decreased by a factor of 3, the partial pressures of all three species will be increased by a factor of 3:

$$Q_p{'} = \frac{(3P_{HI}2)}{3P_{H}2\,3P_{I}2} = \frac{9P_{HI}2}{9P_{H}2\,P_{I}2} = \frac{P_{HI}2}{P_{H}2\,P_{I}2} = Q_p = K_p$$

$$Q_p{'} = Q_p = K_p$$

And so, changing the volume of this gas-phase equilibrium mixture does not result in a shift of the equilibrium.

A similar treatment of a different system, $2NO_2(g) \rightleftharpoons 2\,NO(g) + O_2(g)$, however, yields a different result:

$$Q_p = \frac{P_{NO}2\,P_{O}2}{P_{(NO2)}{}^2} = K_p$$

$$Q_p{'} = \frac{(3P_{NO})^2\,3P_{O}2}{(3P_{NO}2)^2} = \frac{9P_{NO}2\,3P_{O}2}{9P_{(NO2)}{}^2} = \frac{27P_{NO}2\,P_{O}2}{P_{(NO2)}{}^2} = 3Q_p > K_p$$

$$Q_p{'} = 3Q_p > K_p$$

In this case, the change in volume results in a reaction quotient greater than the equilibrium constant, and so the equilibrium will shift left.

These results illustrate the relationship between the stoichiometry of a gas-phase equilibrium and the effect of a volume-induced pressure (concentration) change. If the total molar amounts of reactants and products are equal, as in the first example, a change in volume does not shift the equilibrium. If the molar amounts of reactants and products are different, a change in volume will shift the equilibrium in a direction that better "accommodates" the volume change. In the second example, two moles of reactant (NO_2) yield three moles of product ($2NO + O_2$), and so decreasing the system volume causes the equilibrium to shift left since the reverse reaction produces less gas (2 mol) than the forward reaction (3 mol). Conversely, increasing the volume of this equilibrium system would result in a shift towards products.
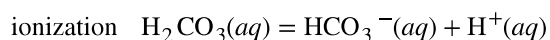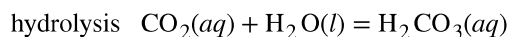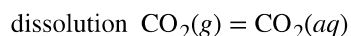
Link to Learning

Check out this **link (http://openstax.org/l/16equichange)** to see a dramatic visual demonstration of how equilibrium changes with pressure changes.

Chemistry in Everyday Life

Equilibrium and Soft Drinks

The connection between chemistry and carbonated soft drinks goes back to 1767, when Joseph Priestley (1733–1804) developed a method of infusing water with carbon dioxide to make carbonated water. Priestly's approach involved production of carbon dioxidey reacting oil of vitriol (sulfuric acid) with chalk (calcium carbonate).

The carbon dioxide was then dissolved in water, reacting to produce hydrogen carbonate, a weak acid that subsequently ionized to yield bicarbonate and hydrogen ions:

$$\text{dissolution} \quad CO_2(g) = CO_2(aq)$$
$$\text{hydrolysis} \quad CO_2(aq) + H_2O(l) = H_2CO_3(aq)$$
$$\text{ionization} \quad H_2CO_3(aq) = HCO_3{}^-(aq) + H^+(aq)$$

These same equilibrium reactions are the basis of today's soft-drink carbonation process. Beverages are exposed to a high pressure of gaseous carbon dioxide during the process to shift the first equilibrium above to the right, resulting in desirably high concentrations of dissolved carbon dioxide and, per similar shifts in the other two equilibria, its hydrolysis and ionization products. A bottle or can is then nearly filled with the carbonated beverage, leaving a relatively small volume of air in the container above the beverage surface (the *headspace*) before it is sealed. The pressure of carbon dioxide in the container headspace is very low immediately after sealing, but it rises as the dissolution equilibrium is re-established by shifting to the left. Since the volume of the beverage is significantly greater than the volume of the headspace, only a relatively small amount of dissolved carbon dioxide is lost to the headspace.

When a carbonated beverage container is opened, a hissing sound is heard as pressurized CO_2 escapes from the headspace. This causes the dissolution equilibrium to shift left, resulting in a decrease in the concentration of dissolved CO_2 and subsequent left-shifts of the hydrolysis and ionization equilibria. Fortunately for the consumer, the dissolution equilibrium is usually re-established slowly, and so the beverage may be enjoyed while its dissolved carbon dioxide concentration remains palatably high. Once the equilibria are re-established, the $CO_2(aq)$ concentration will be significantly lowered, and the beverage acquires a characteristic taste referred to as "flat."
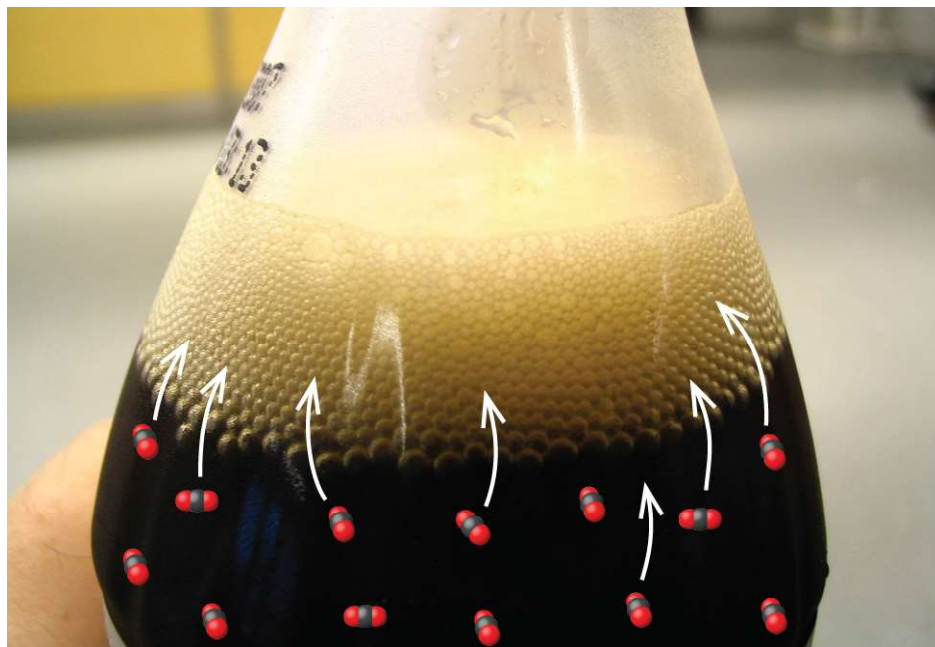
Figure 13.7 Opening a soft-drink bottle lowers the CO_2 pressure above the beverage, shifting the dissolution equilibrium and releasing dissolved CO_2 from the beverage. (credit: modification of work by "D Coetzee"/Flickr)

Effect of a Change in Temperature

Consistent with the law of mass action, an equilibrium stressed by a change in concentration will shift to re-establish equilibrium without any change in the value of the equilibrium constant, K. When an equilibrium shifts in response to a temperature change, however, it is re-established with a different relative composition that exhibits a different value for the equilibrium constant.

To understand this phenomenon, consider the elementary reaction

$$A \rightleftharpoons B$$

Since this is an elementary reaction, the rates laws for the forward and reverse may be derived directly from the balanced equation's stoichiometry:

$$\text{rate}_f = k_f[A]$$
$$\text{rate}_r = k_r[B]$$

When the system is at equilibrium,

$$\text{rate}_r = \text{rate}_f$$

Substituting the rate laws into this equality and rearranging gives

$$k_f[A] \;=\; k_r[B]$$
$$\frac{[B]}{[A]} \;=\; \frac{k_f}{k_r} = K_c$$

The equilibrium constant is seen to be a mathematical function of the rate constants for the forward and reverse reactions. Since the rate constants vary with temperature as described by the Arrhenius equation, is stands to reason that the equilibrium constant will likewise vary with temperature (assuming the rate constants are affected to different

extents by the temperature change). For more complex reactions involving multistep reaction mechanisms, a similar but more complex mathematical relation exists between the equilibrium constant and the rate constants of the steps in the mechanism. Regardless of how complex the reaction may be, the temperature-dependence of its equilibrium constant persists.

Predicting the shift an equilibrium will experience in response to a change in temperature is most conveniently accomplished by considering the enthalpy change of the reaction. For example, the decomposition of dinitrogen tetroxide is an endothermic (heat-consuming) process:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad\qquad \Delta H = 57.20 \text{ kJ}$$

For purposes of applying Le Chatelier's principle, heat (q) may be viewed as a reactant:

$$\text{heat} + N_2O_4(g) \rightleftharpoons 2NO_2(g)$$
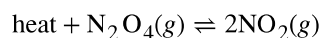
Raising the temperature of the system is akin to increasing the amount of a reactant, and so the equilibrium will shift to the right. Lowering the system temperature will likewise cause the equilibrium to shift left. For exothermic processes, heat is viewed as a product of the reaction and so the opposite temperature dependence is observed.

Link to Learning

This interactive **animation (http://openstax.org/l/16chatelier)** allows you to apply Le Châtelier's principle to predict the effects of changes in concentration, pressure, and temperature on reactant and product concentrations.


13.4 Equilibrium Calculations

By the end of this section, you will be able to:

- Identify the changes in concentration or pressure that occur for chemical species in equilibrium systems
- Calculate equilibrium concentrations or pressures and equilibrium constants, using various algebraic approaches
- Explain how temperature affects the spontaneity of some proceses
- Relate standard free energy changes to equilibrium constants

Having covered the essential concepts of chemical equilibria in the preceding sections of this chapter, this final section will demonstrate the more practical aspect of using these concepts and appropriate mathematical strategies to perform various equilibrium calculations. These types of computations are essential to many areas of science and technology—for example, in the formulation and dosing of pharmaceutical products. After a drug is ingested or injected, it is typically involved in several chemical equilibria that affect its ultimate concentration in the body system of interest. Knowledge of the quantitative aspects of these equilibria is required to compute a dosage amount that will solicit the desired therapeutic effect.

Many of the useful equilibrium calculations that will be demonstrated here require terms representing changes in reactant and product concentrations. These terms are derived from the stoichiometry of the reaction, as illustrated by decomposition of ammonia:

$$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$$
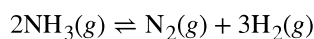
As shown earlier in this chapter, this equilibrium may be established within a sealed container that initially contains either NH_3 only, or a mixture of any two of the three chemical species involved in the equilibrium. Regardless of its initial composition, a reaction mixture will show the same relationships between changes in the concentrations of the

three species involved, as dictated by the reaction stoichiometry (see also the related content on expressing reaction rates in the chapter on kinetics). For example, if the nitrogen concentration increases by an amount x:

$$\Delta[N_2] = + x,$$

the corresponding changes in the other species concentrations are

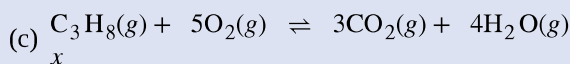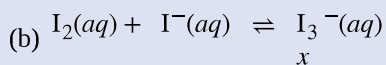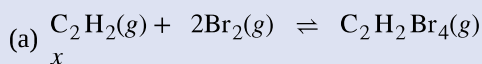$$\Delta[H_2] = \Delta[N_2]\left(\frac{3 \text{ mol } H_2}{1 \text{ mol } N_2}\right) = + 3x$$

$$\Delta[NH_3] = -\Delta[N_2]\left(\frac{2 \text{ mol } NH_3}{1 \text{ mol } N_2}\right) = - 2x,$$

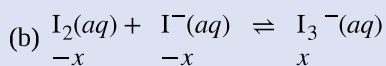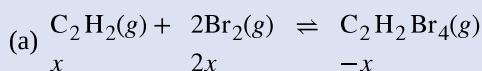where the negative sign indicates a decrease in concentration.

Example 13.5

Determining Relative Changes in Concentration

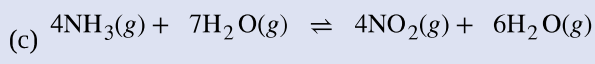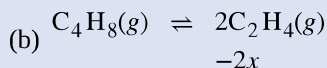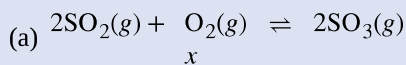Derive the missing terms representing concentration changes for each of the following reactions.

(a)
$$C_2H_2(g) + \ 2Br_2(g) \ \rightleftharpoons \ C_2H_2Br_4(g)$$
$$x \qquad\qquad \underline{\hspace{3em}} \qquad\quad \underline{\hspace{3em}}$$

(b)
$$I_2(aq) + \ I^-(aq) \ \rightleftharpoons \ I_3^-(aq)$$
$$\underline{\hspace{3em}} \quad\ \underline{\hspace{3em}} \qquad x$$

(c)
$$C_3H_8(g) + \ 5O_2(g) \ \rightleftharpoons \ 3CO_2(g) + \ 4H_2O(g)$$
$$x \qquad\qquad \underline{\hspace{3em}} \qquad\quad \underline{\hspace{3em}} \qquad\quad \underline{\hspace{3em}}$$

Solution

(a)
$$C_2H_2(g) + \ 2Br_2(g) \ \rightleftharpoons \ C_2H_2Br_4(g)$$
$$x \qquad\qquad 2x \qquad\qquad -x$$

(b)
$$I_2(aq) + \ I^-(aq) \ \rightleftharpoons \ I_3^-(aq)$$
$$-x \qquad\quad -x \qquad\qquad x$$

(c)
$$C_3H_8(g) + \ 5O_2(g) \ \rightleftharpoons \ 3CO_2(g) + \ 4H_2O(g)$$
$$x \qquad\qquad 5x \qquad\qquad -3x \qquad\qquad -4x$$
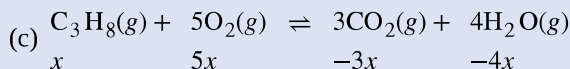
Check Your Learning

Complete the changes in concentrations for each of the following reactions:

(a)
$$2SO_2(g) + \ O_2(g) \ \rightleftharpoons \ 2SO_3(g)$$
$$\underline{\hspace{3em}} \qquad\quad x \qquad\qquad \underline{\hspace{3em}}$$

(b)
$$C_4H_8(g) \ \rightleftharpoons \ 2C_2H_4(g)$$
$$\underline{\hspace{3em}} \qquad\qquad -2x$$

(c)
$$4NH_3(g) + \ 7H_2O(g) \ \rightleftharpoons \ 4NO_2(g) + \ 6H_2O(g)$$
$$\underline{\hspace{3em}} \qquad\quad \underline{\hspace{3em}} \qquad\qquad \underline{\hspace{3em}} \qquad\quad \underline{\hspace{3em}}$$

Answer: (a) $2x$, x, $-2x$; (b) x, $-2x$; (c) $4x$, $7x$, $-4x$, $-6x$ or $-4x$, $-7x$, $4x$, $6x$

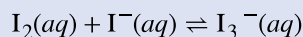## Calculation of an Equilibrium Constant

The equilibrium constant for a reaction is calculated from the equilibrium concentrations (or pressures) of its reactants and products. If these concentrations are known, the calculation simply involves their substitution into the K expression, as was illustrated by **Example 13.2**. A slightly more challenging example is provided next, in which the reaction stoichiometry is used to derive equilibrium concentrations from the information provided. The basic strategy of this computation is helpful for many types of equilibrium computations and relies on the use of terms for the reactant and product concentrations *initially* present, for how they *change* as the reaction proceeds, and for what they

are when the system reaches *equilibrium*. The acronym ICE is commonly used to refer to this mathematical approach, and the concentrations terms are usually gathered in a tabular format called an ICE table.

Example 13.6

Calculation of an Equilibrium Constant

Iodine molecules react reversibly with iodide ions to produce triiodide ions.

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$$

If a solution with the concentrations of I_2 and I^- both equal to 1.000×10^{-3} M before reaction gives an equilibrium concentration of I_2 of 6.61×10^{-4} M, what is the equilibrium constant for the reaction?

Solution

To calculate the equilibrium constants, equilibrium concentrations are needed for all the reactants and products:

$$K_C = \frac{[I_3^-]}{[I_2][I^-]}$$

Provided are the initial concentrations of the reactants and the equilibrium concentration of the product. Use this information to derive terms for the equilibrium concentrations of the reactants, presenting all the information in an ICE table.

	I_2	+	I^-	$\rightleftharpoons$	I_3^-
Initial concentration (M)	1.000×10^{-3}		1.000×10^{-3}		0
Change (M)	$-x$		$-x$		$+x$
Equilibrium concentration (M)	$1.000 \times 10^{-3} - x$		$1.000 \times 10^{-3} - x$		x

At equilibrium the concentration of I_2 is 6.61×10^{-4} M so that

$$1.000 \times 10^{-3} - x = 6.61 \times 10^{-4}$$
$$x = 1.000 \times 10^{-3} - 6.61 \times 10^{-4}$$
$$= 3.39 \times 10^{-4} \ M$$

The ICE table may now be updated with numerical values for all its concentrations:

|	I_2	+	I^-	$\rightleftharpoons$	I_3^-
Initial concentration (M)	1.000×10^{-3}		1.000×10^{-3}		0
Change (M)	-3.39×10^{-4}		-3.39×10^{-4}		$+3.39 \times 10^{-4}$
Equilibrium concentration (M)	6.61×10^{-4}		6.61×10^{-4}		3.39×10^{-4}

Finally, substitute the equilibrium concentrations into the K expression and solve:

$$K_c = \frac{[I_3^-]}{[I_2][I^-]}$$

$$= \frac{3.39 \times 10^{-4} \ M}{(6.61 \times 10^{-4} \ M)(6.61 \times 10^{-4} \ M)} = 776$$

Check Your Learning

Ethanol and acetic acid react and form water and ethyl acetate, the solvent responsible for the odor of some

nail polish removers.

$$C_2H_5OH + CH_3CO_2H \rightleftharpoons CH_3CO_2C_2H_5 + H_2O$$
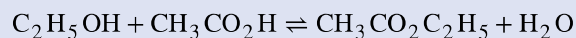
When 1 mol each of C_2H_5OH and CH_3CO_2H are allowed to react in 1 L of the solvent dioxane, equilibrium is established when $\frac{1}{3}$ mol of each of the reactants remains. Calculate the equilibrium constant for the reaction. (Note: Water is a solute in this reaction.)

Answer: $K_c = 4$

Calculation of a Missing Equilibrium Concentration

When the equilibrium constant and all but one equilibrium concentration are provided, the other equilibrium concentration(s) may be calculated. A computation of this sort is illustrated in the next example exercise.

Example 13.7

Calculation of a Missing Equilibrium Concentration

Nitrogen oxides are air pollutants produced by the reaction of nitrogen and oxygen at high temperatures. At 2000 °C, the value of the K_c for the reaction, $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$, is 4.1×10^{-4}. Calculate the equilibrium concentration of $NO(g)$ in air at 1 atm pressure and 2000 °C. The equilibrium concentrations of N_2 and O_2 at this pressure and temperature are 0.036 M and 0.0089 M, respectively.

Solution

Substitute the provided quantities into the equilibrium constant expression and solve for [NO]:

$$K_c = \frac{[NO]^2}{[N_2][O_2]}$$
$$[NO]^2 = K_c[N_2][O_2]$$
$$[NO] = \sqrt{K_c[N_2][O_2]}$$
$$= \sqrt{(4.1 \times 10^{-4})(0.036)(0.0089)}$$
$$= \sqrt{1.31 \times 10^{-7}}$$
$$= 3.6 \times 10^{-4}$$

Thus [NO] is 3.6×10^{-4} mol/L at equilibrium under these conditions.

To confirm this result, it may be used along with the provided equilibrium concentrations to calculate a value for K:

$$K_c = \frac{[NO]^2}{[N_2][O_2]}$$
$$= \frac{(3.6 \times 10^{-4})^2}{(0.036)(0.0089)}$$
$$= 4.0 \times 10^{-4}$$

This result is consistent with the provided value for K within nominal uncertainty, differing by just 1 in the least significant digit's place.

Check Your Learning

The equilibrium constant K_c for the reaction of nitrogen and hydrogen to produce ammonia at a certain temperature is 6.00×10^{-2}. Calculate the equilibrium concentration of ammonia if the equilibrium concentrations of nitrogen and hydrogen are 4.26 M and 2.09 M, respectively.

Answer: 1.53 mol/L

Calculation of Equilibrium Concentrations from Initial Concentrations

Perhaps the most challenging type of equilibrium calculation can be one in which equilibrium concentrations are derived from initial concentrations and an equilibrium constant. For these calculations, a four-step approach is typically useful:

1. Identify the direction in which the reaction will proceed to reach equilibrium.

2. Develop an ICE table.

3. Calculate the concentration changes and, subsequently, the equilibrium concentrations.

4. Confirm the calculated equilibrium concentrations.

The last two example exercises of this chapter demonstrate the application of this strategy.

Example 13.8

Calculation of Equilibrium Concentrations

Under certain conditions, the equilibrium constant K_c for the decomposition of $PCl_5(g)$ into $PCl_3(g)$ and $Cl_2(g)$ is 0.0211. What are the equilibrium concentrations of PCl_5, PCl_3, and Cl_2 in a mixture that initially contained only PCl_5 at a concentration of 1.00 M?

Solution

Use the stepwise process described earlier.

Step 1. *Determine the direction the reaction proceeds.*
The balanced equation for the decomposition of PCl_5 is

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

Because only the reactant is present initially $Q_c = 0$ and the reaction will proceed to the right.

Step 2. *Develop an ICE table.*

	PCl_5 $\rightleftharpoons$	PCl_3 +	Cl_2
Initial concentration (M)	1.00	0	0
Change (M)	$-x$	$+x$	$+x$
Equilibrium concentration (M)	$1.00 - x$	x	x

Step 3. *Solve for the change and the equilibrium concentrations.*
Substituting the equilibrium concentrations into the equilibrium constant equation gives

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = 0.0211$$

$$= \frac{(x)(x)}{(1.00 - x)}$$

$$0.0211 = \frac{(x)(x)}{(1.00 - x)}$$

$$0.0211(1.00 - x) = x^2$$

$$x^2 + 0.0211x - 0.0211 = 0$$

Appendix B shows an equation of the form $ax^2 + bx + c = 0$ can be rearranged to solve for x:

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

In this case, $a = 1$, $b = 0.0211$, and $c = -0.0211$. Substituting the appropriate values for a, b, and c yields:

$$x = \frac{-0.0211 \pm \sqrt{(0.0211)^2 - 4(1)(-0.0211)}}{2(1)}$$

$$= \frac{-0.0211 \pm \sqrt{(4.45 \times 10^{-4}) + (8.44 \times 10^{-2})}}{2}$$

$$= \frac{-0.0211 \pm 0.291}{2}$$

The two roots of the quadratic are, therefore,

$$x = \frac{-0.0211 + 0.291}{2} = 0.135$$

and

$$x = \frac{-0.0211 - 0.291}{2} = -0.156$$

For this scenario, only the positive root is physically meaningful (concentrations are either zero or positive), and so $x = 0.135 \ M$.

The equilibrium concentrations are

$$[PCl_5] = 1.00 - 0.135 = 0.87 \ M$$

$$[PCl_3] = x = 0.135 \ M$$

$$[Cl_2] = x = 0.135 \ M$$

Step 4. *Confirm the calculated equilibrium concentrations.*

Substitution into the expression for K_c (to check the calculation) gives

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{(0.135)(0.135)}{0.87} = 0.021$$

The equilibrium constant calculated from the equilibrium concentrations is equal to the value of K_c given in the problem (when rounded to the proper number of significant figures).

Check Your Learning

Acetic acid, CH_3CO_2H, reacts with ethanol, C_2H_5OH, to form water and ethyl acetate, $CH_3CO_2C_2H_5$.

$$CH_3CO_2H + C_2H_5OH \rightleftharpoons CH_3CO_2C_2H_5 + H_2O$$
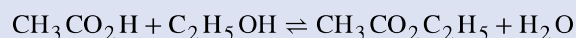
The equilibrium constant for this reaction with dioxane as a solvent is 4.0. What are the equilibrium concentrations for a mixture that is initially 0.15 M in CH_3CO_2H, 0.15 M in C_2H_5OH, 0.40 M in $CH_3CO_2C_2H_5$, and 0.40 M in H_2O?

Answer: $[CH_3CO_2H] = 0.36 \ M$, $[C_2H_5OH] = 0.36 \ M$, $[CH_3CO_2C_2H_5] = 0.17 \ M$, $[H_2O] = 0.17 \ M$

Check Your Learning

A 1.00-L flask is filled with 1.00 moles of H_2 and 2.00 moles of I_2. The value of the equilibrium constant

for the reaction of hydrogen and iodine reacting to form hydrogen iodide is 50.5 under the given conditions. What are the equilibrium concentrations of H_2, I_2, and HI in moles/L?
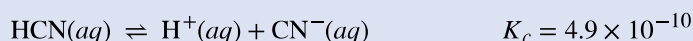
$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$
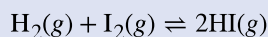
Answer: $[H_2] = 0.06\ M$, $[I_2] = 1.06\ M$, $[HI] = 1.88\ M$

Example 13.9

Calculation of Equilibrium Concentrations Using an Algebra-Simplifying Assumption

What are the concentrations at equilibrium of a 0.15 M solution of HCN?

$$HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq) \qquad\qquad K_c = 4.9 \times 10^{-10}$$

Solution

Using "x" to represent the concentration of each product at equilibrium gives this ICE table.

	$HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq)$		
Initial concentration (*M*)	0.15	0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium concentration (*M*)	$0.15 - x$	x	x

Substitute the equilibrium concentration terms into the K_c expression

$$K_c = \frac{(x)(x)}{0.15 - x}$$

Rearrange to the quadratic form and solve for x

$$x^2 + 4.9 \times 10^{-10} - 7.35 \times 10^{-11} = 0$$
$$x = 8.56 \times 10^{-6}\ M\ (3\ \text{sig. figs.}) = 8.6 \times 10^{-6}\ M\ (2\ \text{sig. figs.})$$

Thus $[H^+] = [CN^-] = x = 8.6 \times 10^{-6}\ M$ and $[HCN] = 0.15 - x = 0.15\ M$.

Note in this case that the change in concentration is significantly less than the initial concentration (a consequence of the small K), and so the initial concentration experiences a negligible change:

$$\text{if } x \ll 0.15\ \text{M},\ \text{then } (0.15 - x) \approx 0.15$$

This approximation allows for a more expedient mathematical approach to the calculation that avoids the need to solve for the roots of a quadratic equation:

$$K_c = \frac{(x)(x)}{0.15 - x} \approx \frac{x^2}{0.15}$$
$$4.9 \times 10^{-10} = \frac{x^2}{0.15}$$
$$x^2 = (0.15)(4.9 \times 10^{-10}) = 7.4 \times 10^{-11}$$
$$x = \sqrt{7.4 \times 10^{-11}} = 8.6 \times 10^{-6}\ M$$

The value of x calculated is, indeed, much less than the initial concentration
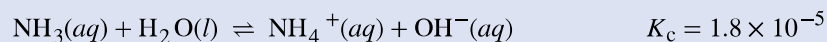
$$8.6 \times 10^{-6} \ll 0.15$$

and so the approximation was justified. If this simplified approach were to yield a value for x that did *not*

justify the approximation, the calculation would need to be repeated without making the approximation.

Check Your Learning

What are the equilibrium concentrations in a 0.25 M NH$_3$ solution?

$$\text{NH}_3(aq) + \text{H}_2\text{O}(l) \;\rightleftharpoons\; \text{NH}_4{}^+(aq) + \text{OH}^-(aq) \qquad K_c = 1.8 \times 10^{-5}$$

Answer: $[\text{OH}^-] = [\text{NH}_4{}^+] = 0.0021\ M;\ [\text{NH}_3] = 0.25\ M$

Temperature Dependence of Spontaneity

As was previously demonstrated in the section on entropy in an earlier chapter, the spontaneity of a process may depend upon the temperature of the system. Phase transitions, for example, will proceed spontaneously in one direction or the other depending upon the temperature of the substance in question. Likewise, some chemical reactions can also exhibit temperature dependent spontaneities. To illustrate this concept, the equation relating free energy change to the enthalpy and entropy changes for the process is considered:

$$\Delta G = \Delta H - T\Delta S$$

The spontaneity of a process, as reflected in the arithmetic sign of its free energy change, is then determined by the signs of the enthalpy and entropy changes and, in some cases, the absolute temperature. Since T is the absolute (kelvin) temperature, it can only have positive values. Four possibilities therefore exist with regard to the signs of the enthalpy and entropy changes:

1. **Both ΔH and ΔS are positive.** This condition describes an endothermic process that involves an increase in system entropy. In this case, ΔG will be negative if the magnitude of the $T\Delta S$ term is greater than ΔH. If the $T\Delta S$ term is less than ΔH, the free energy change will be positive. Such a process is *spontaneous at high temperatures and nonspontaneous at low temperatures.*

2. **Both ΔH and ΔS are negative.** This condition describes an exothermic process that involves a decrease in system entropy. In this case, ΔG will be negative if the magnitude of the $T\Delta S$ term is less than ΔH. If the $T\Delta S$ term's magnitude is greater than ΔH, the free energy change will be positive. Such a process is *spontaneous at low temperatures and nonspontaneous at high temperatures.*

3. **ΔH is positive and ΔS is negative.** This condition describes an endothermic process that involves a decrease in system entropy. In this case, ΔG will be positive regardless of the temperature. Such a process is *nonspontaneous at all temperatures.*

4. **ΔH is negative and ΔS is positive.** This condition describes an exothermic process that involves an increase in system entropy. In this case, ΔG will be negative regardless of the temperature. Such a process is *spontaneous at all temperatures.*

These four scenarios are summarized in **Figure 13.8**.

Summary of the Four Scenarios for Enthalpy and Entropy Changes

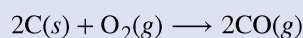|	$\Delta H > 0$ (endothermic)	$\Delta H < 0$ (exothermic)
$\Delta S > 0$ (increase in entropy)	$\Delta G < 0$ at high temperature $\Delta G > 0$ at low temperature Process is spontaneous at high temperature	$\Delta G < 0$ at any temperature Process is spontaneous at any temperature
$\Delta S < 0$ (decrease in entropy)	$\Delta G > 0$ at any temperature Process is nonspontaneous at any temperature	$\Delta G < 0$ at low temperature $\Delta G > 0$ at high temperature Process is spontaneous at low temperature

Figure 13.8   There are four possibilities regarding the signs of enthalpy and entropy changes.

Example 13.10

Predicting the Temperature Dependence of Spontaneity

The incomplete combustion of carbon is described by the following equation:

$$2C(s) + O_2(g) \longrightarrow 2CO(g)$$

How does the spontaneity of this process depend upon temperature?

Solution

Combustion processes are exothermic ($\Delta H < 0$). This particular reaction involves an increase in entropy due to the accompanying increase in the amount of gaseous species (net gain of one mole of gas, $\Delta S > 0$). The reaction is therefore spontaneous ($\Delta G < 0$) at all temperatures.

Check Your Learning

Popular chemical hand warmers generate heat by the air-oxidation of iron:

$$4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s)$$
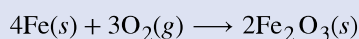
How does the spontaneity of this process depend upon temperature?

Answer: ΔH and ΔS are negative; the reaction is spontaneous at low temperatures.

When considering the conclusions drawn regarding the temperature dependence of spontaneity, it is important to keep in mind what the terms "high" and "low" mean. Since these terms are adjectives, the temperatures in question are deemed high or low relative to some reference temperature. A process that is nonspontaneous at one temperature but spontaneous at another will necessarily undergo a change in "spontaneity" (as reflected by its ΔG) as temperature varies. This is clearly illustrated by a graphical presentation of the free energy change equation, in which ΔG is plotted on the y axis versus T on the x axis:

$$\Delta G = \Delta H - T\Delta S$$
$$y = b + mx$$

Such a plot is shown in **Figure 13.9**. A process whose enthalpy and entropy changes are of the same arithmetic sign will exhibit a temperature-dependent spontaneity as depicted by the two yellow lines in the plot. Each line crosses from one spontaneity domain (positive or negative ΔG) to the other at a temperature that is characteristic of the process in question. This temperature is represented by the x-intercept of the line, that is, the value of T for which ΔG is zero:

$$\Delta G = 0 = \Delta H - T\Delta S$$
$$T = \frac{\Delta H}{\Delta S}$$

So, saying a process is spontaneous at "high" or "low" temperatures means the temperature is above or below, respectively, that temperature at which ΔG for the process is zero. As noted earlier, the condition of $\Delta G = 0$ describes a system at equilibrium.
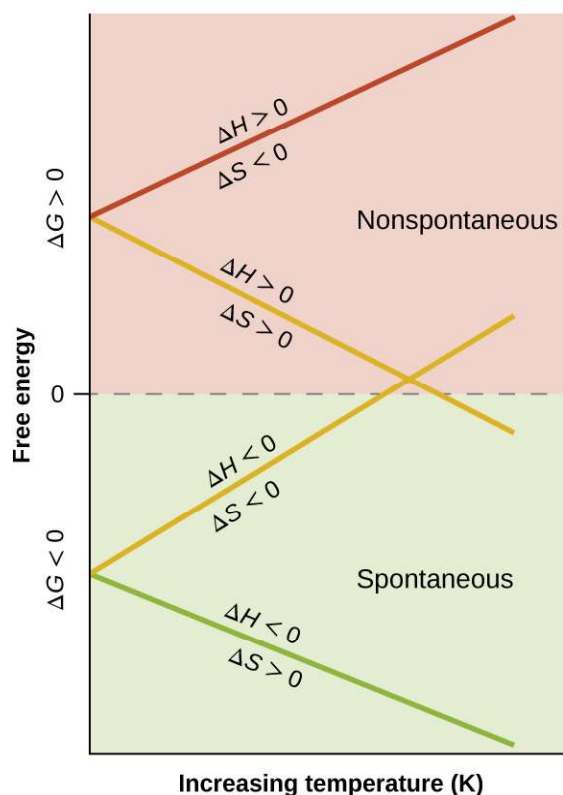

**Figure 13.9** These plots show the variation in ΔG with temperature for the four possible combinations of arithmetic sign for ΔH and ΔS.

Example 13.11

Equilibrium Temperature for a Phase Transition

As defined in the chapter on liquids and solids, the boiling point of a liquid is the temperature at which its liquid and gaseous phases are in equilibrium (that is, when vaporization and condensation occur at equal rates). Use the information in **Appendix G** to estimate the boiling point of water.

Solution

The process of interest is the following phase change:

$$H_2O(l) \longrightarrow H_2O(g)$$
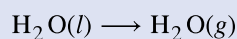
When this process is at equilibrium, $\Delta G = 0$, so the following is true:

$$0 = \Delta H° - T\Delta S° \qquad \text{or} \qquad T = \frac{\Delta H°}{\Delta S°}$$

Using the standard thermodynamic data from **Appendix G**,

$$\Delta H° = 1 \text{ mol} \times \Delta H_f° \ (H_2O(g)) - 1 \text{ mol} \times \Delta H_f° \ (H_2O(l))$$
$$= (1 \text{ mol}) - 241.82 \text{ kJ/mol} - (1 \text{ mol})(-241.82 \text{ kJ/mol}) = 44.01 \text{ kJ}$$
$$\Delta S° = 1 \text{ mol} \times \Delta S° \ (H_2O(g)) - 1 \text{ mol} \times \Delta S° \ (H_2O(l))$$
$$= (1 \text{ mol})188.8 \text{ J/K·mol} - (1 \text{ mol})70.0 \text{ J/K·mol} = 118.8 \text{ J/K}$$
$$T = \frac{\Delta H°}{\Delta S°} = \frac{44.01 \times 10^3 \text{ J}}{118.8 \text{ J/K}} = 370.5 \text{ K} = 97.3 \text{ °C}$$

The accepted value for water's normal boiling point is 373.2 K (100.0 °C), and so this calculation is in reasonable agreement. Note that the values for enthalpy and entropy changes data used were derived from standard data at 298 K (**Appendix G**). If desired, you could obtain more accurate results by using enthalpy and entropy changes determined at (or at least closer to) the actual boiling point.

Check Your Learning

Use the information in **Appendix G** to estimate the boiling point of CS_2.

Answer: 313 K (accepted value 319 K)

Free Energy and Equilibrium

The free energy change for a process may be viewed as a measure of its driving force. A negative value for ΔG represents a driving force for the process in the forward direction, while a positive value represents a driving force for the process in the reverse direction. When ΔG is zero, the forward and reverse driving forces are equal, and the process occurs in both directions at the same rate (the system is at equilibrium).

In the section on equilibrium, the *reaction quotient, Q,* was introduced as a convenient measure of the status of an equilibrium system. Recall that Q is the numerical value of the mass action expression for the system, and that you may use its value to identify the direction in which a reaction will proceed in order to achieve equilibrium. When Q is lesser than the equilibrium constant, K, the reaction will proceed in the forward direction until equilibrium is reached and $Q = K$. Conversely, if $Q > K$, the process will proceed in the reverse direction until equilibrium is achieved.

The free energy change for a process taking place with reactants and products present under *nonstandard conditions* (pressures other than 1 bar; concentrations other than 1 M) is related to the standard free energy change, according to this equation:

$$\Delta G = \Delta G° + RT \ln Q$$

R is the gas constant (8.314 J/K mol), T is the kelvin or absolute temperature, and Q is the reaction quotient. This equation may be used to predict the spontaneity for a process under any given set of conditions as illustrated in **Example 13.12**.

Example 13.12

Calculating Δ*G* under Nonstandard Conditions

What is the free energy change for the process shown here under the specified conditions?

$T = 25 °C$, $P_{N_2} = 0.870$ atm, $P_{H_2} = 0.250$ atm,   and $P_{NH_3} = 12.9$ atm

$$2NH_3(g) \longrightarrow 3H_2(g) + N_2(g) \qquad \Delta G° = 33.0 \text{ kJ/mol}$$
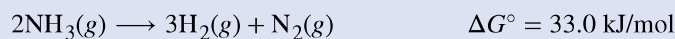
Solution

The equation relating free energy change to standard free energy change and reaction quotient may be used directly:

$$\Delta G = \Delta G° + RT \ln Q = 33.0 \frac{\text{kJ}}{\text{mol}} + \left(8.314 \frac{\text{J}}{\text{mol K}} \times 298 \text{ K} \times \ln \frac{(0.250^3) \times 0.870}{12.9^2}\right) = 9680 \frac{\text{J}}{\text{mol}} \text{ or } 9.68 \text{ kJ/mol}$$

Since the computed value for ΔG is positive, the reaction is nonspontaneous under these conditions.

Check Your Learning

Calculate the free energy change for this same reaction at 875 °C in a 5.00 L mixture containing 0.100 mol of each gas. Is the reaction spontaneous under these conditions?

Answer: $\Delta G = -47$ kJ/mol; yes

For a system at equilibrium, $Q = K$ and $\Delta G = 0$, and the previous equation may be written as

$$0 = \Delta G° + RT \ln K \qquad \text{(at equilibrium)}$$

$$\Delta G° = -RT \ln K \qquad \text{or} \qquad K = e^{-\frac{\Delta G°}{RT}}$$

This form of the equation provides a useful link between these two essential thermodynamic properties, and it can be used to derive equilibrium constants from standard free energy changes and vice versa. The relations between standard free energy changes and equilibrium constants are summarized in **Table 13.1**.

Relations between Standard Free Energy Changes and Equilibrium Constants

K	$\Delta G°$	Composition of an Equilibrium Mixture
> 1	< 0	Products are more abundant
< 1	> 0	Reactants are more abundant
= 1	= 0	Reactants and products are comparably abundant

Table 13.1

Example 13.13

Calculating an Equilibrium Constant using Standard Free Energy Change

Given that the standard free energies of formation of $Ag^+(aq)$, $Cl^-(aq)$, and $AgCl(s)$ are 77.1 kJ/mol, −131.2 kJ/mol, and −109.8 kJ/mol, respectively, calculate the solubility product, K_{sp}, for AgCl.

Solution

The reaction of interest is the following:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \qquad K_{sp} = [Ag^+][Cl^-]$$
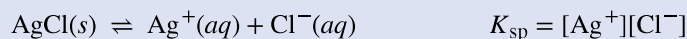
The standard free energy change for this reaction is first computed using standard free energies of formation for its reactants and products:

$$\Delta G° = \left[\Delta G_f° \left(Ag^+(aq)\right) + \Delta G_f° \left(Cl^-(aq)\right)\right] - \left[\Delta G_f° \left(AgCl(s)\right)\right]$$
$$= [77.1 \text{ kJ/mol} - 131.2 \text{ kJ/mol}] - [-109.8 \text{ kJ/mol}] = 55.7 \text{ kJ/mol}$$

The equilibrium constant for the reaction may then be derived from its standard free energy change:

$$K_{sp} = e^{-\frac{\Delta G°}{RT}} = \exp\left(-\frac{\Delta G°}{RT}\right) = \exp\left(-\frac{55.7 \times 10^3 \text{ J/mol}}{8.314 \text{ J/mol·K} \times 298.15 \text{ K}}\right) = \exp(-22.470) = e^{-22.470} = 1.74 \times 10^{-10}$$

This result is in reasonable agreement with the value provided in **Appendix J**.

Check Your Learning

Use the thermodynamic data provided in **Appendix G** to calculate the equilibrium constant for the dissociation of dinitrogen tetroxide at 25 °C.

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$
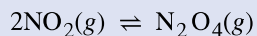
Answer: $K = 6.9$

To further illustrate the relation between these two essential thermodynamic concepts, consider the observation that reactions spontaneously proceed in a direction that ultimately establishes equilibrium. As may be shown by plotting the free energy change versus the extent of the reaction (for example, as reflected in the value of Q), equilibrium is established when the system's free energy is minimized (**Figure 13.10**). If a system consists of reactants and products in nonequilibrium amounts ($Q \neq K$), the reaction will proceed spontaneously in the direction necessary to establish equilibrium.
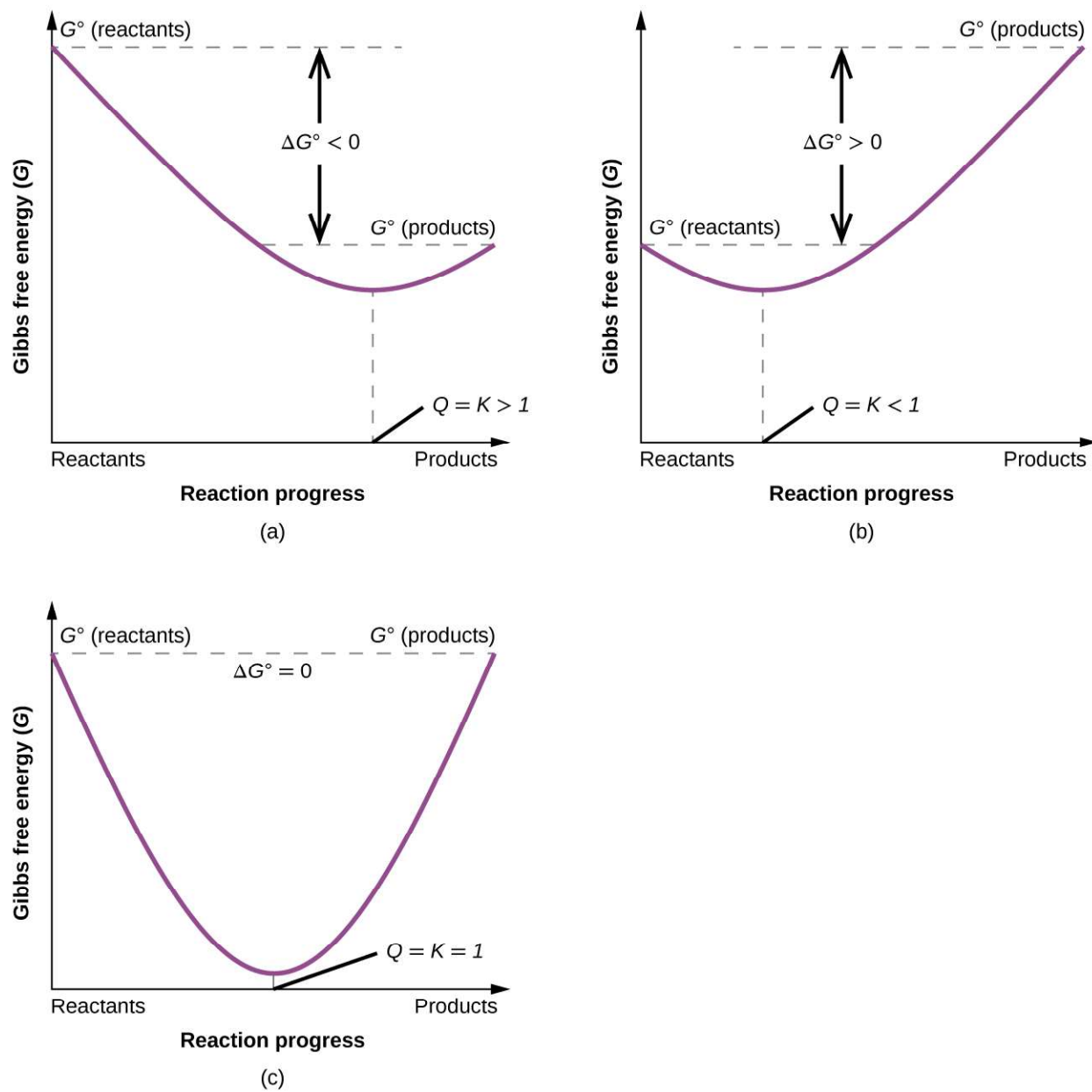
Figure 13.10 These plots show the free energy versus reaction progress for systems whose standard free changes are (a) negative, (b) positive, and (c) zero. Nonequilibrium systems will proceed spontaneously in whatever direction is necessary to minimize free energy and establish equilibrium.

Key Terms

equilibrium state of a reversible reaction in which the forward and reverse processes occur at equal rates

equilibrium constant (K) value of the reaction quotient for a system at equilibrium; may be expressed using concentrations (K_c) or partial pressures (K_p)

heterogeneous equilibria equilibria in which reactants and products occupy two or more different phases

homogeneous equilibria equilibria in which all reactants and products occupy the same phase

law of mass action when a reversible reaction has attained equilibrium at a given temperature, the reaction quotient remains constant

Le Châtelier's principle an equilibrium subjected to stress will shift in a way to counter the stress and re-establish equilibrium

reaction quotient (Q) mathematical function describing the relative amounts of reactants and products in a reaction mixture; may be expressed in terms of concentrations (Q_c) or pressures (Q_p)

reversible reaction chemical reaction that can proceed in both the forward and reverse directions under given conditions

Key Equations

- $Q_c = \dfrac{[C]^x[D]^y}{[A]^m[B]^n}$ for the reaction $m\text{A} + n\text{B} \rightleftharpoons x\text{C} + y\text{D}$

- $Q_P = \dfrac{(P_C)^x(P_D)^y}{(P_A)^m(P_B)^n}$ for the reaction $m\text{A} + n\text{B} \rightleftharpoons x\text{C} + y\text{D}$

- $P = MRT$

- $K_c = Q_c$ at equilibrium

- $K_p = Q_p$ at equilibrium

- $K_P = K_c\,(RT)^{\Delta n}$

Summary

13.1 Chemical Equilibria

A reversible reaction is at equilibrium when the forward and reverse processes occur at equal rates. Chemical equilibria are dynamic processes characterized by constant amounts of reactant and product species.

13.2 Equilibrium Constants

The composition of a reaction mixture may be represented by a mathematical function known as the reaction quotient, Q. For a reaction at equilibrium, the composition is constant, and Q is called the equilibrium constant, K.

A homogeneous equilibrium is an equilibrium in which all components are in the same phase. A heterogeneous equilibrium is an equilibrium in which components are in two or more phases.

13.3 Shifting Equilibria: Le Châtelier's Principle

Systems at equilibrium can be disturbed by changes to temperature, concentration, and, in some cases, volume and pressure. The system's response to these disturbances is described by Le Châtelier's principle: An equilibrium system subjected to a disturbance will shift in a way that counters the disturbance and re-establishes equilibrium. A catalyst will increase the rate of both the forward and reverse reactions of a reversible process, increasing the rate at which

equilibrium is reached but not altering the equilibrium mixture's composition (K does not change).

13.4 Equilibrium Calculations

Calculating values for equilibrium constants and/or equilibrium concentrations is of practical benefit to many applications. A mathematical strategy that uses initial concentrations, changes in concentrations, and equilibrium concentrations (and goes by the acronym ICE) is useful for several types of equilibrium calculations. We also learned that a negative value for ΔG indicates a spontaneous process; a positive ΔG indicates a nonspontaneous process; and a ΔG of zero indicates that the system is at equilibrium. We also saw how free energy, spontaneity, and equilibrium relate.

Exercises

13.1 Chemical Equilibria

1. What does it mean to describe a reaction as "reversible"?

2. When writing an equation, how is a reversible reaction distinguished from a nonreversible reaction?

3. If a reaction is reversible, when can it be said to have reached equilibrium?

4. Is a system at equilibrium if the rate constants of the forward and reverse reactions are equal?

5. If the concentrations of products and reactants are equal, is the system at equilibrium?

13.2 Equilibrium Constants

6. Explain why there may be an infinite number of values for the reaction quotient of a reaction at a given temperature but there can be only one value for the equilibrium constant at that temperature.

7. Explain why an equilibrium between $Br_2(l)$ and $Br_2(g)$ would not be established if the container were not a closed vessel shown in **Figure 13.4**.

8. If you observe the following reaction at equilibrium, is it possible to tell whether the reaction started with pure NO_2 or with pure N_2O_4?
$2NO_2(g) \rightleftharpoons N_2O_4(g)$

9. Among the solubility rules previously discussed is the statement: All chlorides are soluble except Hg_2Cl_2, $AgCl$, $PbCl_2$, and $CuCl$.

(a) Write the expression for the equilibrium constant for the reaction represented by the equation
$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$. Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.

(b) Write the expression for the equilibrium constant for the reaction represented by the equation
$Pb^{2+}(aq) + 2Cl^-(aq) \rightleftharpoons PbCl_2(s)$. Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.

10. Among the solubility rules previously discussed is the statement: Carbonates, phosphates, borates, and arsenates—except those of the ammonium ion and the alkali metals—are insoluble.

(a) Write the expression for the equilibrium constant for the reaction represented by the equation
$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3{}^{2-}(aq)$. Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.

(b) Write the expression for the equilibrium constant for the reaction represented by the equation
$3Ba^{2+}(aq) + 2PO_4{}^{3-}(aq) \rightleftharpoons Ba_3(PO_4)_2(s)$. Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.

11. Benzene is one of the compounds used as octane enhancers in unleaded gasoline. It is manufactured by the catalytic conversion of acetylene to benzene: $3C_2H_2(g) \rightleftharpoons C_6H_6(g)$. Which value of K_c would make this reaction most useful commercially? $K_c \approx 0.01$, $K_c \approx 1$, or $K_c \approx 10$. Explain your answer.

12. Show that the complete chemical equation, the total ionic equation, and the net ionic equation for the reaction represented by the equation $KI(aq) + I_2(aq) \rightleftharpoons KI_3(aq)$ give the same expression for the reaction quotient. KI_3 is composed of the ions K^+ and $I_3{}^-$.
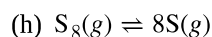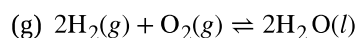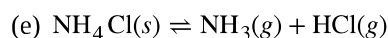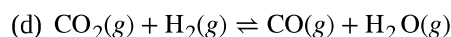
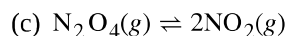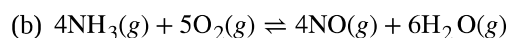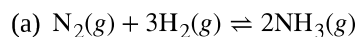**13.** For a titration to be effective, the reaction must be rapid and the yield of the reaction must essentially be 100%. Is $K_c > 1$, < 1, or ≈ 1 for a titration reaction?

14. For a precipitation reaction to be useful in a gravimetric analysis, the product of the reaction must be insoluble. Is $K_c > 1$, < 1, or ≈ 1 for a useful precipitation reaction?
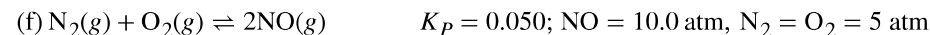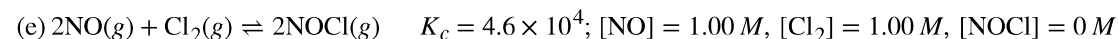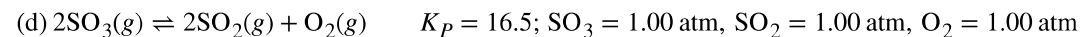
15. Write the mathematical expression for the reaction quotient, Q_c, for each of the following reactions:

(a) $CH_4(g) + Cl_2(g) \rightleftharpoons CH_3Cl(g) + HCl(g)$
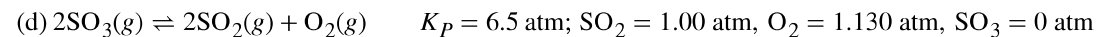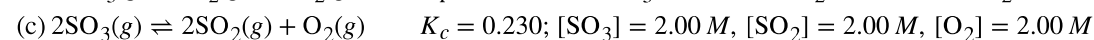
(b) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

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

(d) $BaSO_3(s) \rightleftharpoons BaO(s) + SO_2(g)$

(e) $P_4(g) + 5O_2(g) \rightleftharpoons P_4O_{10}(s)$

(f) $Br_2(g) \rightleftharpoons 2Br(g)$

(g) $CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(l)$

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

16. Write the mathematical expression for the reaction quotient, Q_c, for each of the following reactions:

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

(b) $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$

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

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

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

(f) $2Pb(NO_3)_2(s) \rightleftharpoons 2PbO(s) + 4NO_2(g) + O_2(g)$

(g) $2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(l)$
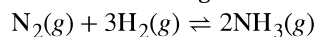
(h) $S_8(g) \rightleftharpoons 8S(g)$

17. The initial concentrations or pressures of reactants and products are given for each of the following systems. Calculate the reaction quotient and determine the direction in which each system will proceed to reach equilibrium.

(a) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ $K_c = 17$; $[NH_3] = 0.20\,M$, $[N_2] = 1.00\,M$, $[H_2] = 1.00\,M$

(b) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ $K_P = 6.8 \times 10^4$; $NH_3 = 3.0$ atm, $N_2 = 2.0$ atm, $H_2 = 1.0$ atm

(c) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ $K_c = 0.230$; $[SO_3] = 0.00\,M$, $[SO_2] = 1.00\,M$, $[O_2] = 1.00\,M$

(d) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ $K_P = 16.5$; $SO_3 = 1.00$ atm, $SO_2 = 1.00$ atm, $O_2 = 1.00$ atm

(e) $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$ $K_c = 4.6 \times 10^4$; $[NO] = 1.00\,M$, $[Cl_2] = 1.00\,M$, $[NOCl] = 0\,M$

(f) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $K_P = 0.050$; $NO = 10.0$ atm, $N_2 = O_2 = 5$ atm

18. The initial concentrations or pressures of reactants and products are given for each of the following systems. Calculate the reaction quotient and determine the direction in which each system will proceed to reach equilibrium.

(a) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ $K_c = 17$; $[NH_3] = 0.50\,M$, $[N_2] = 0.15\,M$, $[H_2] = 0.12\,M$

(b) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ $K_P = 6.8 \times 10^4$; $NH_3 = 2.00$ atm, $N_2 = 10.00$ atm, $H_2 = 10.00$ atm

(c) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ $K_c = 0.230$; $[SO_3] = 2.00\,M$, $[SO_2] = 2.00\,M$, $[O_2] = 2.00\,M$

(d) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ $K_P = 6.5$ atm; $SO_2 = 1.00$ atm, $O_2 = 1.130$ atm, $SO_3 = 0$ atm

(e) $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$ $K_P = 2.5 \times 10^3$; $NO = 1.00$ atm, $Cl_2 = 1.00$ atm, $NOCl = 0$ atm

(f) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $K_c = 0.050$; $[N_2] = 0.100\,M$, $[O_2] = 0.200\,M$, $[NO] = 1.00\,M$

19. The following reaction has $K_P = 4.50 \times 10^{-5}$ at 720 K.

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

If a reaction vessel is filled with each gas to the partial pressures listed, in which direction will it shift to reach equilibrium? $P(NH_3) = 93$ atm, $P(N_2) = 48$ atm, and $P(H_2) = 52$ atm

20. Determine if the following system is at equilibrium. If not, in which direction will the system need to shift to reach equilibrium?

$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$
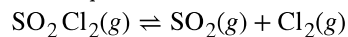
$[SO_2Cl_2] = 0.12$ M, $[Cl_2] = 0.16$ M and $[SO_2] = 0.050$ M. K_c for the reaction is 0.078.

21. Which of the systems described in **Exercise 13.15** are homogeneous equilibria? Which are heterogeneous equilibria?

22. Which of the systems described in **Exercise 13.16** are homogeneous equilibria? Which are heterogeneous equilibria?

23. For which of the reactions in **Exercise 13.15** does K_c (calculated using concentrations) equal K_P (calculated using pressures)?

24. For which of the reactions in **Exercise 13.16** does K_c (calculated using concentrations) equal K_P (calculated using pressures)?

25. Convert the values of K_c to values of K_P or the values of K_P to values of K_c.

(a) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $K_c = 0.50$ at 400 °C

(b) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ $K_c = 50.2$ at 448 °C

(c) $Na_2SO_4 \cdot 10H_2O(s) \rightleftharpoons Na_2SO_4(s) + 10H_2O(g)$ $K_P = 4.08 \times 10^{-25}$ at 25 °C
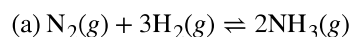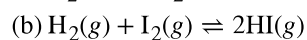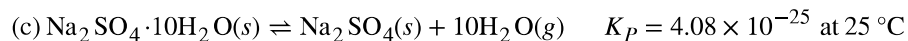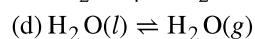
(d) $H_2O(l) \rightleftharpoons H_2O(g)$ $K_P = 0.122$ at 50 °C

26. Convert the values of K_c to values of K_P or the values of K_P to values of K_c.

(a) $Cl_2(g) + Br_2(g) \rightleftharpoons 2BrCl(g)$ $K_c = 4.7 \times 10^{-2}$ at 25 °C

(b) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $K_P = 48.2$ at 500 °C

(c) $CaCl_2 \cdot 6H_2O(s) \rightleftharpoons CaCl_2(s) + 6H_2O(g)$ $K_P = 5.09 \times 10^{-44}$ at 25 °C
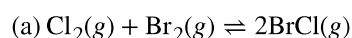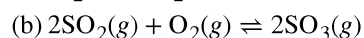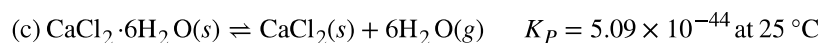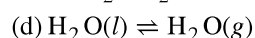
(d) $H_2O(l) \rightleftharpoons H_2O(g)$ $K_P = 0.196$ at 60 °C

27. What is the value of the equilibrium constant expression for the change $H_2O(l) \rightleftharpoons H_2O(g)$ at 30 °C? (See **Appendix E**.)

28. Write the expression of the reaction quotient for the ionization of HOCN in water.

29. Write the reaction quotient expression for the ionization of NH_3 in water.

30. What is the approximate value of the equilibrium constant K_P for the change $C_2H_5OC_2H_5(l) \rightleftharpoons C_2H_5OC_2H_5(g)$ at 25 °C. (The equilibrium vapor pressure for this substance is 570 torr at 25 °C.)

13.3 Shifting Equilibria: Le Châtelier's Principle

31. The following equation represents a reversible decomposition:

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

Under what conditions will decomposition in a closed container proceed to completion so that no $CaCO_3$ remains?

32. Explain how to recognize the conditions under which changes in volume will affect gas-phase systems at equilibrium.

33. What property of a reaction can we use to predict the effect of a change in temperature on the value of an equilibrium constant?

34. The following reaction occurs when a burner on a gas stove is lit:

$$CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(g)$$
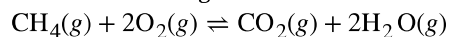
Is an equilibrium among CH_4, O_2, CO_2, and H_2O established under these conditions? Explain your answer.

35. A necessary step in the manufacture of sulfuric acid is the formation of sulfur trioxide, SO_3, from sulfur dioxide, SO_2, and oxygen, O_2, shown here. At high temperatures, the rate of formation of SO_3 is higher, but the equilibrium amount (concentration or partial pressure) of SO_3 is lower than it would be at lower temperatures.

$$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$$
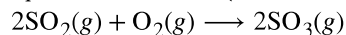
(a) Does the equilibrium constant for the reaction increase, decrease, or remain about the same as the temperature increases?
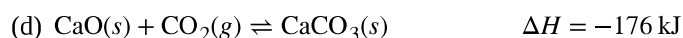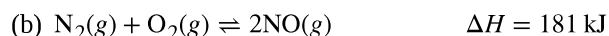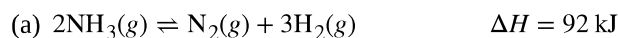
(b) Is the reaction endothermic or exothermic?

36. Suggest four ways in which the concentration of hydrazine, N_2H_4, could be increased in an equilibrium described by the following equation:
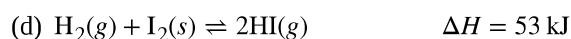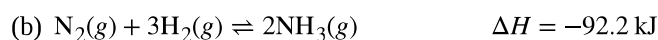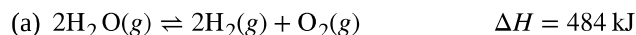
$$N_2(g) + 2H_2(g) \rightleftharpoons N_2H_4(g) \qquad \Delta H = 95 \text{ kJ}$$
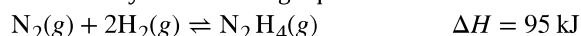
37. Suggest four ways in which the concentration of PH_3 could be increased in an equilibrium described by the following equation:
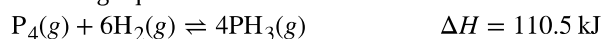
$$P_4(g) + 6H_2(g) \rightleftharpoons 4PH_3(g) \qquad \Delta H = 110.5 \text{ kJ}$$

38. How will an increase in temperature affect each of the following equilibria? How will a decrease in the volume of the reaction vessel affect each?

(a) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g) \qquad \Delta H = 92 \text{ kJ}$

(b) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \qquad \Delta H = 181 \text{ kJ}$

(c) $2O_3(g) \rightleftharpoons 3O_2(g) \qquad \Delta H = -285 \text{ kJ}$

(d) $CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s) \qquad \Delta H = -176 \text{ kJ}$

39. How will an increase in temperature affect each of the following equilibria? How will a decrease in the volume of the reaction vessel affect each?

(a) $2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g) \qquad \Delta H = 484 \text{ kJ}$

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

(c) $2Br(g) \rightleftharpoons Br_2(g) \qquad \Delta H = -224 \text{ kJ}$

(d) $H_2(g) + I_2(s) \rightleftharpoons 2HI(g) \qquad \Delta H = 53 \text{ kJ}$

40. Methanol can be prepared from carbon monoxide and hydrogen at high temperature and pressure in the presence of a suitable catalyst.

(a) Write the expression for the equilibrium constant (K_c) for the reversible reaction

$$2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g) \qquad \Delta H = -90.2 \text{ kJ}$$
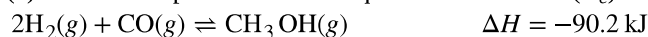
(b) What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if more H_2 is added?
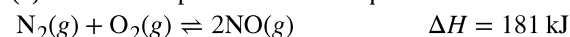
(c) What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if CO is removed?

(d) What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if CH_3OH is added?

(e) What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if the temperature of the system is increased?

41. Nitrogen and oxygen react at high temperatures.

(a) Write the expression for the equilibrium constant (K_c) for the reversible reaction

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \qquad\qquad \Delta H = 181 \text{ kJ}$$

(b) What will happen to the concentrations of N_2, O_2, and NO at equilibrium if more O_2 is added?

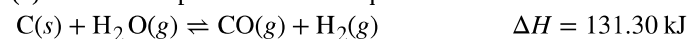(c) What will happen to the concentrations of N_2, O_2, and NO at equilibrium if N_2 is removed?

(d) What will happen to the concentrations of N_2, O_2, and NO at equilibrium if NO is added?

(e) What will happen to the concentrations of N_2, O_2, and NO at equilibrium if the volume of the reaction vessel is decreased?

(f) What will happen to the concentrations of N_2, O_2, and NO at equilibrium if the temperature of the system is increased?

42. Water gas, a mixture of H_2 and CO, is an important industrial fuel produced by the reaction of steam with red hot coke, essentially pure carbon.

(a) Write the expression for the equilibrium constant for the reversible reaction

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g) \qquad\qquad \Delta H = 131.30 \text{ kJ}$$

(b) What will happen to the concentration of each reactant and product at equilibrium if more C is added?
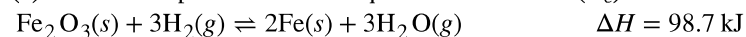
(c) What will happen to the concentration of each reactant and product at equilibrium if H_2O is removed?

(d) What will happen to the concentration of each reactant and product at equilibrium if CO is added?

(e) What will happen to the concentration of each reactant and product at equilibrium if the temperature of the system is increased?

43. Pure iron metal can be produced by the reduction of iron(III) oxide with hydrogen gas.

(a) Write the expression for the equilibrium constant (K_c) for the reversible reaction

$$Fe_2O_3(s) + 3H_2(g) \rightleftharpoons 2Fe(s) + 3H_2O(g) \qquad\qquad \Delta H = 98.7 \text{ kJ}$$

(b) What will happen to the concentration of each reactant and product at equilibrium if more Fe is added?

(c) What will happen to the concentration of each reactant and product at equilibrium if H_2O is removed?

(d) What will happen to the concentration of each reactant and product at equilibrium if H_2 is added?

(e) What will happen to the concentration of each reactant and product at equilibrium if the volume of the reaction vessel is decreased?

(f) What will happen to the concentration of each reactant and product at equilibrium if the temperature of the system is increased?

44. Ammonia is a weak base that reacts with water according to this equation:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^{+}(aq) + OH^{-}(aq)$$
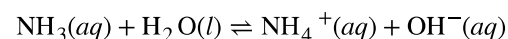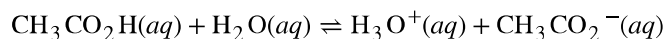
Will any of the following increase the percent of ammonia that is converted to the ammonium ion in water?

(a) Addition of NaOH

(b) Addition of HCl

(c) Addition of NH_4Cl

45. Acetic acid is a weak acid that reacts with water according to this equation:

$$CH_3CO_2H(aq) + H_2O(aq) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$$

Will any of the following increase the percent of acetic acid that reacts and produces $CH_3CO_2^-$ ion?

(a) Addition of HCl

(b) Addition of NaOH

(c) Addition of $NaCH_3CO_2$

46. Suggest two ways in which the equilibrium concentration of Ag^+ can be reduced in a solution of Na^+, Cl^-, Ag^+, and NO_3^-, in contact with solid AgCl.

$$Na^+(aq) + Cl^-(aq) + Ag^+(aq) + NO_3^-(aq) \rightleftharpoons AgCl(s) + Na^+(aq) + NO_3^-(aq)$$
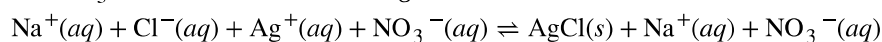
$$\Delta H = -65.9 \text{ kJ}$$

47. How can the pressure of water vapor be increased in the following equilibrium?

$$H_2O(l) \rightleftharpoons H_2O(g) \qquad \Delta H = 41 \text{ kJ}$$

48. A solution is saturated with silver sulfate and contains excess solid silver sulfate:

$$Ag_2SO_4(s) \rightleftharpoons 2Ag^+(aq) + SO_4^{2-}(aq)$$
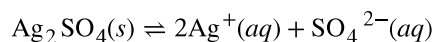
A small amount of solid silver sulfate containing a radioactive isotope of silver is added to this solution. Within a few minutes, a portion of the solution phase is sampled and tests positive for radioactive Ag^+ ions. Explain this observation.

49. The amino acid alanine has two isomers, α-alanine and β-alanine. When equal masses of these two compounds are dissolved in equal amounts of a solvent, the solution of α-alanine freezes at the lowest temperature. Which form, α-alanine or β-alanine, has the larger equilibrium constant for ionization $(HX \rightleftharpoons H^+ + X^-)$?

13.4 Equilibrium Calculations

**50.** A reaction is represented by this equation: $A(aq) + 2B(aq) \rightleftharpoons 2C(aq) \qquad K_c = 1 \times 10^3$

(a) Write the mathematical expression for the equilibrium constant.

(b) Using concentrations ≤1 M, identify two sets of concentrations that describe a mixture of A, B, and C at equilibrium.

51. A reaction is represented by this equation: $2W(aq) \rightleftharpoons X(aq) + 2Y(aq) \qquad K_c = 5 \times 10^{-4}$

(a) Write the mathematical expression for the equilibrium constant.

(b) Using concentrations of ≤1 M, identify two sets of concentrations that describe a mixture of W, X, and Y at equilibrium.

52. What is the value of the equilibrium constant at 500 °C for the formation of NH_3 according to the following equation?

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
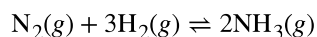
An equilibrium mixture of $NH_3(g)$, $H_2(g)$, and $N_2(g)$ at 500 °C was found to contain 1.35 M H_2, 1.15 M N_2, and 4.12 $\times$ 10^{-1} M NH_3.

53. Hydrogen is prepared commercially by the reaction of methane and water vapor at elevated temperatures.

$$CH_4(g) + H_2O(g) \rightleftharpoons 3H_2(g) + CO(g)$$
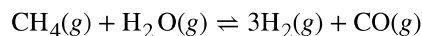
What is the equilibrium constant for the reaction if a mixture at equilibrium contains gases with the following concentrations: CH_4, 0.126 M; H_2O, 0.242 M; CO, 0.126 M; H_2 1.15 M, at a temperature of 760 °C?

54. A 0.72-mol sample of PCl_5 is put into a 1.00-L vessel and heated. At equilibrium, the vessel contains 0.40 mol of $PCl_3(g)$ and 0.40 mol of $Cl_2(g)$. Calculate the value of the equilibrium constant for the decomposition of PCl_5 to PCl_3 and Cl_2 at this temperature.

55. At 1 atm and 25 °C, NO_2 with an initial concentration of 1.00 M is 0.0033% decomposed into NO and O_2. Calculate the value of the equilibrium constant for the reaction.

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

56. Calculate the value of the equilibrium constant K_P for the reaction $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$ from these equilibrium pressures: NO, 0.050 atm; Cl_2, 0.30 atm; NOCl, 1.2 atm.

57. When heated, iodine vapor dissociates according to this equation:

$$I_2(g) \rightleftharpoons 2I(g)$$
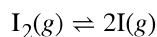
At 1274 K, a sample exhibits a partial pressure of I_2 of 0.1122 atm and a partial pressure due to I atoms of 0.1378 atm. Determine the value of the equilibrium constant, K_P, for the decomposition at 1274 K.

58. A sample of ammonium chloride was heated in a closed container.

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$$
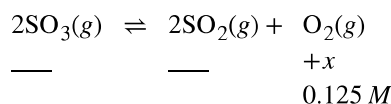
At equilibrium, the pressure of $NH_3(g)$ was found to be 1.75 atm. What is the value of the equilibrium constant K_P for the decomposition at this temperature?

59. At a temperature of 60 °C, the vapor pressure of water is 0.196 atm. What is the value of the equilibrium constant K_P for the vaporization equilibrium at 60 °C?
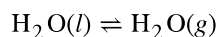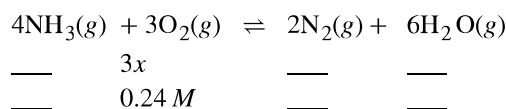
$$H_2O(l) \rightleftharpoons H_2O(g)$$

60. Complete the changes in concentrations (or pressure, if requested) for each of the following reactions.

(a)

$$2SO_3(g) \quad \rightleftharpoons \quad 2SO_2(g) + \quad O_2(g)$$
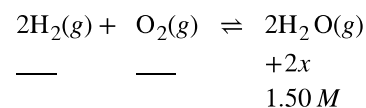
		$+x$
___	___	0.125 M

(b)

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

	$3x$		
___	0.24 M	___	___

(c) Change in pressure:

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

	x	
___	25 torr	___

(d) Change in pressure:

$$CH_4(g) + \quad H_2O(g) \quad \rightleftharpoons \quad CO(g) + \quad 3H_2(g)$$

	x		
___	5 atm	___	___

(e)

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

	x	
	1.03×10^{-4} M	___

(f) change in pressure:

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

	$4x$	
	0.40 atm	___

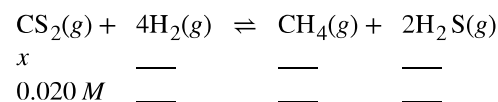**61.** Complete the changes in concentrations (or pressure, if requested) for each of the following reactions.

(a)

$$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$$
$$\underline{\quad} \quad \underline{\quad} \qquad +2x$$
$$\underline{\quad} \quad \underline{\quad} \qquad 1.50\,M$$

(b)

$$CS_2(g) + 4H_2(g) \rightleftharpoons CH_4(g) + 2H_2S(g)$$
$$x \qquad \underline{\quad} \qquad \underline{\quad} \qquad \underline{\quad}$$
$$0.020\,M \quad \underline{\quad} \qquad \underline{\quad} \qquad \underline{\quad}$$

(c) Change in pressure:

$$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$$
$$x \qquad \underline{\quad} \qquad \underline{\quad}$$
$$1.50\,\text{atm} \quad \underline{\quad} \qquad \underline{\quad}$$

(d) Change in pressure:

$$2NH_3(g) + 2O_2(g) \rightleftharpoons N_2O(g) + 3H_2O(g)$$
$$\underline{\quad} \qquad \underline{\quad} \qquad \underline{\quad} \qquad x$$
$$\underline{\quad} \qquad \underline{\quad} \qquad \underline{\quad} \qquad 60.6\,\text{torr}$$

(e)

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$$
$$\qquad\qquad x \qquad \underline{\quad}$$
$$\qquad\qquad 9.8 \times 10^{-6}\,M \quad \underline{\quad}$$

(f) Change in pressure:

$$Fe(s) + 5CO(g) \rightleftharpoons Fe(CO)_5(g)$$
$$\qquad \underline{\quad} \qquad x$$
$$\qquad \underline{\quad} \qquad 0.012\,\text{atm}$$
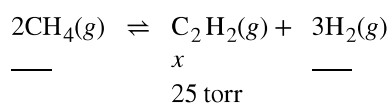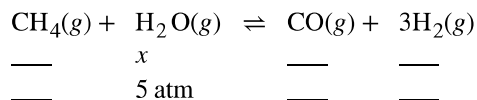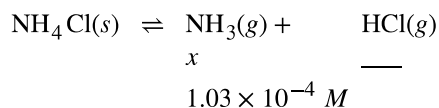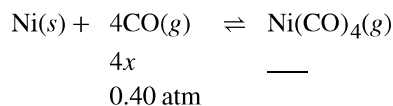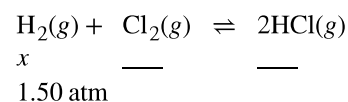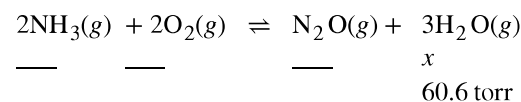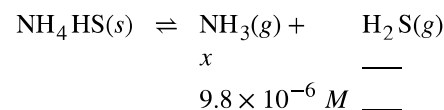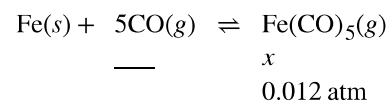
62. Why are there no changes specified for Ni in **Exercise 13.60**, part (f)? What property of Ni does change?

63. Why are there no changes specified for NH_4HS in **Exercise 13.61**, part (e)? What property of NH_4HS does change?

64. Analysis of the gases in a sealed reaction vessel containing NH_3, N_2, and H_2 at equilibrium at 400 °C established the concentration of N_2 to be 1.2 M and the concentration of H_2 to be 0.24 M.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad\qquad K_c = 0.50 \text{ at } 400\,°C$$

Calculate the equilibrium molar concentration of NH_3.

65. Calculate the number of moles of HI that are at equilibrium with 1.25 mol of H_2 and 1.25 mol of I_2 in a 5.00−L flask at 448 °C.

$$H_2 + I_2 \rightleftharpoons 2HI \qquad\qquad K_c = 50.2 \text{ at } 448\,°C$$

66. What is the pressure of BrCl in an equilibrium mixture of Cl_2, Br_2, and BrCl if the pressure of Cl_2 in the mixture is 0.115 atm and the pressure of Br_2 in the mixture is 0.450 atm?

$$Cl_2(g) + Br_2(g) \rightleftharpoons 2BrCl(g) \qquad\qquad K_P = 4.7 \times 10^{-2}$$
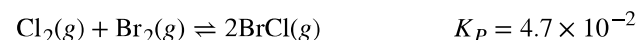
67. What is the pressure of CO_2 in a mixture at equilibrium that contains 0.50 atm H_2, 2.0 atm of H_2O, and 1.0 atm of CO at 990 °C?

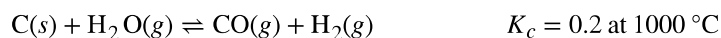$$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g) \qquad\qquad K_P = 1.6 \text{ at } 990\,°C$$
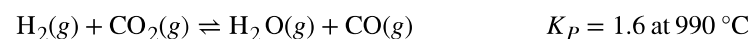
68. Cobalt metal can be prepared by reducing cobalt(II) oxide with carbon monoxide.

$$CoO(s) + CO(g) \rightleftharpoons Co(s) + CO_2(g) \qquad K_c = 4.90 \times 10^2 \text{ at } 550\ ^\circ C$$
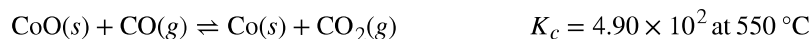
What concentration of CO remains in an equilibrium mixture with $[CO_2] = 0.100\ M$?

**69.** Carbon reacts with water vapor at elevated temperatures.

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g) \qquad K_c = 0.2 \text{ at } 1000\ ^\circ C$$

Assuming a reaction mixture initially contains only reactants, what is the concentration of CO in an equilibrium mixture with $[H_2O] = 0.500\ M$ at 1000 °C?

70. Sodium sulfate 10−hydrate, $Na_2SO_4 \cdot 10H_2O$, dehydrates according to the equation

$$Na_2SO_4 \cdot 10H_2O(s) \rightleftharpoons Na_2SO_4(s) + 10H_2O(g) \qquad K_P = 4.08 \times 10^{-25} \text{ at } 25\ ^\circ C$$
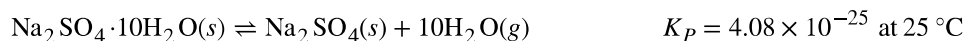
What is the pressure of water vapor at equilibrium with a mixture of $Na_2SO_4 \cdot 10H_2O$ and $NaSO_4$?

71. Calcium chloride 6−hydrate, $CaCl_2 \cdot 6H_2O$, dehydrates according to the equation

$$CaCl_2 \cdot 6H_2O(s) \rightleftharpoons CaCl_2(s) + 6H_2O(g) \qquad K_P = 5.09 \times 10^{-44} \text{ at } 25\ ^\circ C$$
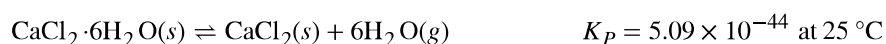
What is the pressure of water vapor at equilibrium with a mixture of $CaCl_2 \cdot 6H_2O$ and $CaCl_2$ at 25 °C?

72. A student solved the following problem and found the equilibrium concentrations to be $[SO_2] = 0.590\ M$, $[O_2] = 0.0450\ M$, and $[SO_3] = 0.260\ M$. How could this student check the work without reworking the problem? The problem was: For the following reaction at 600 °C:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad K_c = 4.32$$
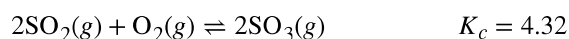
What are the equilibrium concentrations of all species in a mixture that was prepared with $[SO_3] = 0.500\ M$, $[SO_2] = 0\ M$, and $[O_2] = 0.350\ M$?

73. A student solved the following problem and found $[N_2O_4] = 0.16\ M$ at equilibrium. How could this student recognize that the answer was wrong without reworking the problem? The problem was: What is the equilibrium concentration of N_2O_4 in a mixture formed from a sample of NO_2 with a concentration of 0.10 M?

$$2NO_2(g) \rightleftharpoons N_2O_4(g) \qquad K_c = 160$$
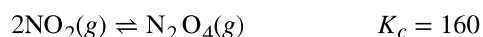
74. Assume that the change in concentration of N_2O_4 is small enough to be neglected in the following problem.

(a) Calculate the equilibrium concentration of both species in 1.00 L of a solution prepared from 0.129 mol of N_2O_4 with chloroform as the solvent.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad K_c = 1.07 \times 10^{-5} \text{ in chloroform}$$
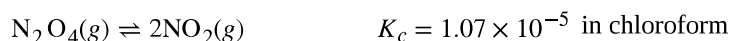
(b) Confirm that the change is small enough to be neglected.

75. Assume that the change in concentration of $COCl_2$ is small enough to be neglected in the following problem.
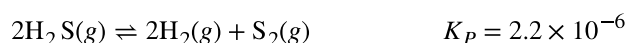
(a) Calculate the equilibrium concentration of all species in an equilibrium mixture that results from the decomposition of $COCl_2$ with an initial concentration of 0.3166 M.

$$COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g) \qquad K_c = 2.2 \times 10^{-10}$$
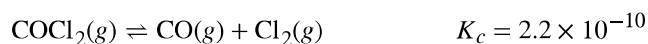
(b) Confirm that the change is small enough to be neglected.

76. Assume that the change in pressure of H_2S is small enough to be neglected in the following problem.

(a) Calculate the equilibrium pressures of all species in an equilibrium mixture that results from the decomposition of H_2S with an initial pressure of 0.824 atm.

$$2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g) \qquad K_P = 2.2 \times 10^{-6}$$

(b) Confirm that the change is small enough to be neglected.

77. What are all concentrations after a mixture that contains $[H_2O] = 1.00\ M$ and $[Cl_2O] = 1.00\ M$ comes to equilibrium at 25 °C?

$$H_2O(g) + Cl_2O(g) \rightleftharpoons 2HOCl(g) \qquad\qquad K_c = 0.0900$$

78. Calculate the number of grams of HI that are at equilibrium with 1.25 mol of H_2 and 63.5 g of iodine at 448 °C.

$$H_2 + I_2 \rightleftharpoons 2HI \qquad\qquad K_c = 50.2 \text{ at } 448\ °C$$

79. Butane exists as two isomers, *n*−butane and isobutane.
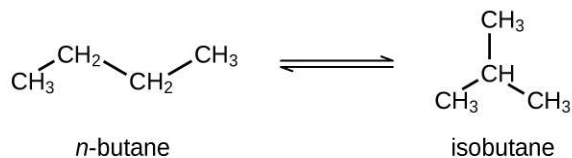
n-butane   isobutane

$K_P = 2.5$ at 25 °C

What is the pressure of isobutane in a container of the two isomers at equilibrium with a total pressure of 1.22 atm?

80. What is the minimum mass of $CaCO_3$ required to establish equilibrium at a certain temperature in a 6.50-L container if the equilibrium constant (K_c) is 0.50 for the decomposition reaction of $CaCO_3$ at that temperature?

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

81. The equilibrium constant (K_c) for this reaction is 1.60 at 990 °C:

$$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$$
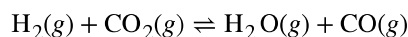
Calculate the number of moles of each component in the final equilibrium mixture obtained from adding 1.00 mol of H_2, 2.00 mol of CO_2, 0.750 mol of H_2O, and 1.00 mol of CO to a 5.00-L container at 990 °C.

82. In a 3.0-L vessel, the following equilibrium partial pressures are measured: N_2, 190 torr; H_2, 317 torr; NH_3, 1.00×10^3 torr.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
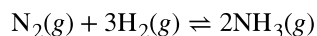
(a) How will the partial pressures of H_2, N_2, and NH_3 change if H_2 is removed from the system? Will they increase, decrease, or remain the same?

(b) Hydrogen is removed from the vessel until the partial pressure of nitrogen, at equilibrium, is 250 torr. Calculate the partial pressures of the other substances under the new conditions.

83. The equilibrium constant (K_c) for this reaction is 5.0 at a given temperature.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$
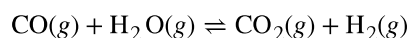
(a) On analysis, an equilibrium mixture of the substances present at the given temperature was found to contain 0.20 mol of CO, 0.30 mol of water vapor, and 0.90 mol of H_2 in a liter. How many moles of CO_2 were there in the equilibrium mixture?

(b) Maintaining the same temperature, additional H_2 was added to the system, and some water vapor was removed by drying. A new equilibrium mixture was thereby established containing 0.40 mol of CO, 0.30 mol of water vapor, and 1.2 mol of H_2 in a liter. How many moles of CO_2 were in the new equilibrium mixture? Compare this with the quantity in part (a), and discuss whether the second value is reasonable. Explain how it is possible for the water vapor concentration to be the same in the two equilibrium solutions even though some vapor was removed before the second equilibrium was established.

84. Antimony pentachloride decomposes according to this equation:

$$SbCl_5(g) \rightleftharpoons SbCl_3(g) + Cl_2(g)$$

An equilibrium mixture in a 5.00-L flask at 448 °C contains 3.85 g of $SbCl_5$, 9.14 g of $SbCl_3$, and 2.84 g of Cl_2. How many grams of each will be found if the mixture is transferred into a 2.00-L flask at the same temperature?

85. Consider the equilibrium

$$4NO_2(g) + 6H_2O(g) \rightleftharpoons 4NH_3(g) + 7O_2(g)$$
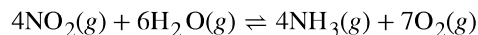
(a) What is the expression for the equilibrium constant (K_c) of the reaction?

(b) How must the concentration of NH_3 change to reach equilibrium if the reaction quotient is less than the equilibrium constant?

(c) If the reaction were at equilibrium, how would an increase in the volume of the reaction vessel affect the pressure of NO_2?

(d) If the change in the pressure of NO_2 is 28 torr as a mixture of the four gases reaches equilibrium, how much will the pressure of O_2 change?

86. The binding of oxygen by hemoglobin (Hb), giving oxyhemoglobin (HbO_2), is partially regulated by the concentration of H_3O^+ and dissolved CO_2 in the blood. Although the equilibrium is complicated, it can be summarized as

$$HbO_2(aq) + H_3O^+(aq) + CO_2(g) \rightleftharpoons CO_2-Hb-H^+ + O_2(g) + H_2O(l)$$
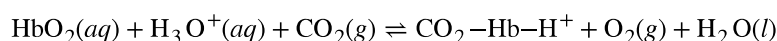
(a) Write the equilibrium constant expression for this reaction.

(b) Explain why the production of lactic acid and CO_2 in a muscle during exertion stimulates release of O_2 from the oxyhemoglobin in the blood passing through the muscle.

87. Liquid N_2O_3 is dark blue at low temperatures, but the color fades and becomes greenish at higher temperatures as the compound decomposes to NO and NO_2. At 25 °C, a value of $K_P = 1.91$ has been established for this decomposition. If 0.236 moles of N_2O_3 are placed in a 1.52-L vessel at 25 °C, calculate the equilibrium partial pressures of $N_2O_3(g)$, $NO_2(g)$, and $NO(g)$.

88. A 1.00-L vessel at 400 °C contains the following equilibrium concentrations: N_2, 1.00 *M*; H_2, 0.50 *M*; and NH_3, 0.25 *M*. How many moles of hydrogen must be removed from the vessel to increase the concentration of nitrogen to 1.1 *M*? The equilibrium reaction is
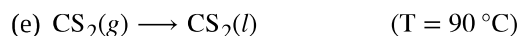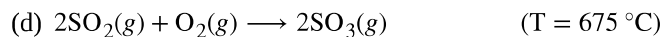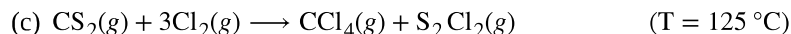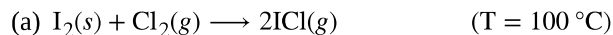
$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
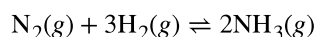
89. Calculate the equilibrium constant at 25 °C for each of the following reactions from the value of $\Delta G°$ given.

(a) $I_2(s) + Cl_2(g) \longrightarrow 2ICl(g)$ $\Delta G° = -10.88$ kJ

(b) $H_2(g) + I_2(s) \longrightarrow 2HI(g)$ $\Delta G° = 3.4$ kJ

(c) $CS_2(g) + 3Cl_2(g) \longrightarrow CCl_4(g) + S_2Cl_2(g)$ $\Delta G° = -39$ kJ

(d) $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$ $\Delta G° = -141.82$ kJ
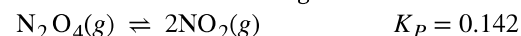
(e) $CS_2(g) \longrightarrow CS_2(l)$ $\Delta G° = -1.88$ kJ

90. Calculate the equilibrium constant at the temperature given.

(a) $O_2(g) + 2F_2(g) \longrightarrow 2F_2O(g)$ (T = 100 °C)

(b) $I_2(s) + Br_2(l) \longrightarrow 2IBr(g)$ (T = 0.0 °C)

(c) $2LiOH(s) + CO_2(g) \longrightarrow Li_2CO_3(s) + H_2O(g)$ (T = 575 °C)

(d) $N_2O_3(g) \longrightarrow NO(g) + NO_2(g)$ (T = -10.0 °C)

(e) $SnCl_4(l) \longrightarrow SnCl_4(g)$ (T = 200 °C)

91. Calculate the equilibrium constant at the temperature given.

(a) $I_2(s) + Cl_2(g) \longrightarrow 2ICl(g)$ (T = 100 °C)

(b) $H_2(g) + I_2(s) \longrightarrow 2HI(g)$ (T = 0.0 °C)

(c) $CS_2(g) + 3Cl_2(g) \longrightarrow CCl_4(g) + S_2Cl_2(g)$ (T = 125 °C)

(d) $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$ (T = 675 °C)

(e) $CS_2(g) \longrightarrow CS_2(l)$ (T = 90 °C)

92. Consider the following reaction at 298 K:
$N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $K_P = 0.142$

What is the standard free energy change at this temperature? Describe what happens to the initial system, where the reactants and products are in standard states, as it approaches equilibrium.

93. Determine the normal boiling point (in kelvin) of dichloroethane, CH_2Cl_2. Find the actual boiling point using the Internet or some other source, and calculate the percent error in the temperature. Explain the differences, if any, between the two values.

94. Under what conditions is $N_2O_3(g) \longrightarrow NO(g) + NO_2(g)$ spontaneous?

95. At room temperature, the equilibrium constant (K_w) for the self-ionization of water is 1.00×10^{-14}. Using this information, calculate the standard free energy change for the aqueous reaction of hydrogen ion with hydroxide ion to produce water. (Hint: The reaction is the reverse of the self-ionization reaction.)

96. Hydrogen sulfide is a pollutant found in natural gas. Following its removal, it is converted to sulfur by the reaction $2H_2S(g) + SO_2(g) \rightleftharpoons \frac{3}{8}S_8(s, \text{ rhombic}) + 2H_2O(l)$. What is the equilibrium constant for this reaction? Is the reaction endothermic or exothermic?

97. Consider the decomposition of $CaCO_3(s)$ into $CaO(s)$ and $CO_2(g)$. What is the equilibrium partial pressure of CO_2 at room temperature?

98. In the laboratory, hydrogen chloride ($HCl(g)$) and ammonia ($NH_3(g)$) often escape from bottles of their solutions and react to form the ammonium chloride ($NH_4Cl(s)$), the white glaze often seen on glassware. Assuming that the number of moles of each gas that escapes into the room is the same, what is the maximum partial pressure of HCl and NH_3 in the laboratory at room temperature? (Hint: The partial pressures will be equal and are at their maximum value when at equilibrium.)

99. Benzene can be prepared from acetylene. $3C_2H_2(g) \rightleftharpoons C_6H_6(g)$. Determine the equilibrium constant at 25 °C and at 850 °C. Is the reaction spontaneous at either of these temperatures? Why is all acetylene not found as benzene?

100. Carbon dioxide decomposes into CO and O_2 at elevated temperatures. What is the equilibrium partial pressure of oxygen in a sample at 1000 °C for which the initial pressure of CO_2 was 1.15 atm?

101. Carbon tetrachloride, an important industrial solvent, is prepared by the chlorination of methane at 850 K.
$CH_4(g) + 4Cl_2(g) \longrightarrow CCl_4(g) + 4HCl(g)$

What is the equilibrium constant for the reaction at 850 K? Would the reaction vessel need to be heated or cooled to keep the temperature of the reaction constant?

102. Acetic acid, CH_3CO_2H, can form a dimer, $(CH_3CO_2H)_2$, in the gas phase.
$2CH_3CO_2H(g) \longrightarrow (CH_3CO_2H)_2(g)$
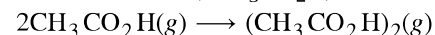
The dimer is held together by two hydrogen bonds with a total strength of 66.5 kJ per mole of dimer.
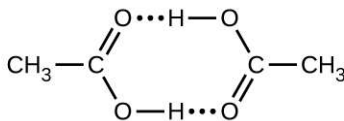
At 25 °C, the equilibrium constant for the dimerization is 1.3×10^3 (pressure in atm). What is $\Delta S°$ for the reaction?