UNIT 4

Chemical Systems and Equilibrium

UNIT 4 CONTENTS

UNIT 4 OVERALL EXPECTATIONS

- What are the properties of a system at equilibrium? What factors affect the extent of a chemical reaction?
- How can you measure the position of equilibrium experimentally and predict the concentrations of chemicals in a system at equilibrium?
- How can understanding chemical equilibrium help you explain systems in biology, ecology, and chemical industries?

Unit Issue Prep

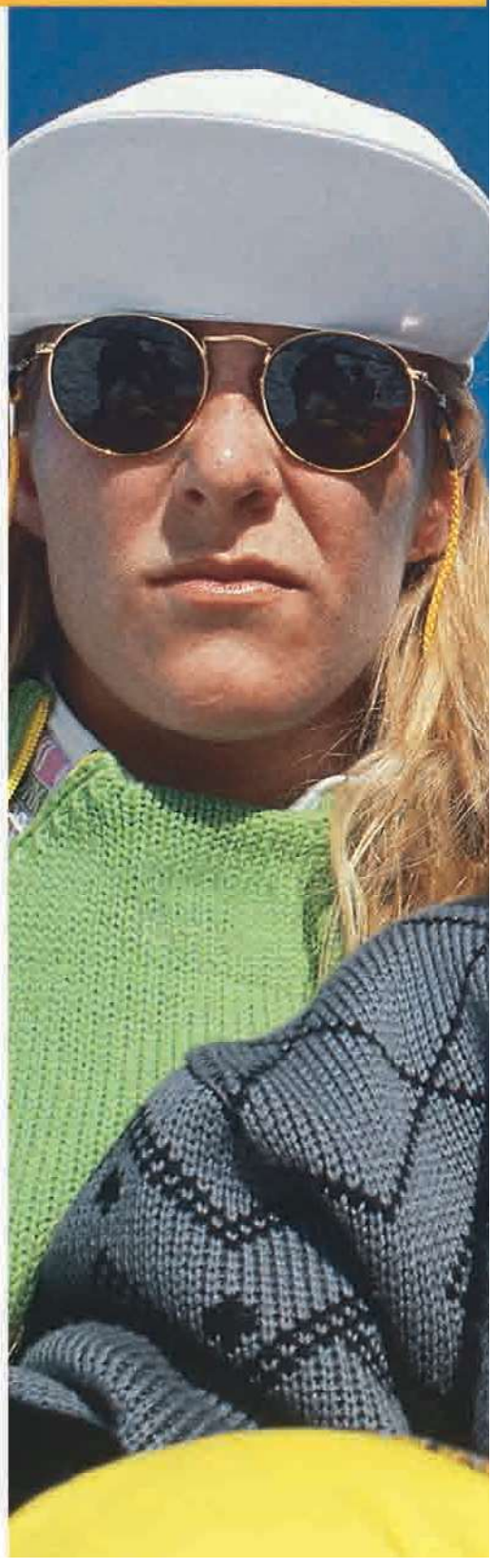
Why is an understanding of Earth's geochemical cycles important? Look at the issue for Unit 4, on page 456. Start preparing now by listing questions that you would like answered. Record additional questions as you progress through this unit.

Photochromic lenses darken in sunlight and then gradually clear in shade and dim light. The change is permanent in constant light conditions, yet reversible if the light intensity changes. How?

The molten glass contains dissolved silver chloride. As the solution cools, silver chloride precipitates, forming tiny silver chloride crystals. Light striking these crystals produces silver and chlorine atoms. The silver atoms tend to clump together to form particles that are big enough to block light and darken the glass.

Adding copper(I) chloride to the molten glass makes the process reversible. When light intensity diminishes, copper ions remove electrons from silver atoms, converting the silver atoms into silver ions. The silver ions then migrate back to the silver chloride crystals. The glass becomes transparent again.

Most of the reactions that you have studied have essentially gone to completion. You can use stoichiometry to calculate the amounts of products formed, assuming that the chemical reaction proceeds only from left to right. In many chemical reactions, however, a mixture of reactants and products form because the reaction can also proceed from right to left. In this unit, you will study the concepts that describe reversible reactions.



CHAPTER 7

Reversible Reactions and Chemical Equilibrium

Chapter Preview

Prerequisite Concepts and Skills

Before you begin this chapter, review the following concepts and skills:

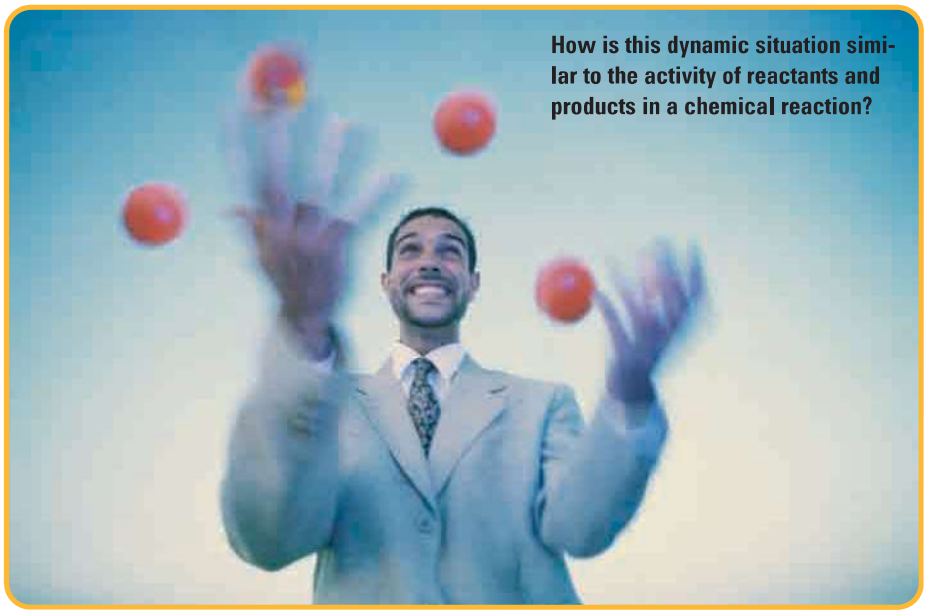
- using the relationship between rate of reaction and concentration (Chapter 6, section 6.2)
- using stoichiometry with chemical equations (previous studies)
- calculating molar concentrations (previous studies)

Your body contains over 1 kg of nitrogen, mainly in the proteins and nucleic acids that make up your cells. Your body, however, cannot absorb nitrogen directly from the atmosphere. You get the nitrogen-containing compounds you need by eating plants and other foods.

Plants cannot absorb nitrogen directly from the atmosphere, either. Their roots absorb nitrogen compounds—mainly nitrates—from the soil. Some of these nitrates result from atmospheric chemical reactions that involve nitrogen and oxygen. First, lightning supplies the energy that is needed to form nitric oxide from nitrogen and oxygen. The resulting nitric oxide combines with oxygen to form nitrogen dioxide, which reacts with rainwater to form nitric acid. Then, in the seas and the soil at Earth's surface, nitric acid ionizes to produce nitrate, NO_3^-. Plants and plant-like organisms can readily absorb nitrate.

Scientists call this chemical "circle of life" the *nitrogen cycle*. There are, as you know, similar, equally important cyclic processes in nature. Each process involves *reversible changes*: changes that may proceed in either direction, from reactants to products or from products to reactants.

In this chapter, you will study factors that affect reversible changes, notably those in chemical reactions. You will learn how to determine the amounts of reactants and products that are present when their proportions no longer change. You will also learn how to make qualitative predictions about the ways that chemists can change these proportions. Finally, you will see how industrial chemists apply their knowledge of reversible changes to increase the yield of chemicals that are important to society.



How is this dynamic situation similar to the activity of reactants and products in a chemical reaction?

Recognizing Equilibrium

7.1

In Unit 3, you learned that the rate of any reaction depends on the concentration of the reacting chemicals. As a reaction proceeds, the concentrations of the "product" chemicals increases, and the reverse reaction may re-form "reactants." Under certain conditions, the rate of the reverse reaction increases as the rate of the forward reaction decreases. Eventually, the rate of the forward reaction equals the rate of the reverse reaction. **Equilibrium** occurs when opposing changes, such as those just described, are occurring simultaneously at the same rate.

How can you recognize equilibrium? In the following paragraphs, you will read about physical changes that may or may not involve a system at equilibrium. As you consider these changes, note which systems are at equilibrium and what changes are taking place. Also note the conditions that would be needed for the changes to occur in the opposite direction at the same rate. The ExpressLab that follows these descriptions will add to your understanding of equilibrium. It will help you recognize systems that are at equilibrium and systems that are not.

- A puddle of water remains after a summer shower. The puddle evaporates because some of the water molecules near the surface have enough kinetic energy to escape from the liquid. At the same time, some water molecules in the air may condense back into the liquid. The chance of this happening is small, however. The puddle soon evaporates completely, as shown in Figure 7.1(A).
- Even if you put a lid on a jar of water, some of the water in the jar evaporates. Careful measurements show that the level of liquid water in the jar initially decreases because more water evaporates than condenses. As the number of water vapour molecules increases, however, some condense back into the liquid. Eventually, the number of evaporating molecules and the number of condensing molecules are equal. The level of water inside the jar remains constant. At this point, shown in Figure 7.1(B), equilibrium has been reached.

Section Preview/ Specific Expectations

In this section, you will

- **identify** and **illustrate** equilibrium in various systems and the conditions that lead to equilibrium
- **describe**, in terms of equilibrium, the behaviour of ionic solutes in unsaturated, saturated, and supersaturated solutions
- **communicate** your understanding of the following terms: *equilibrium, homogeneous equilibrium, heterogeneous equilibrium*

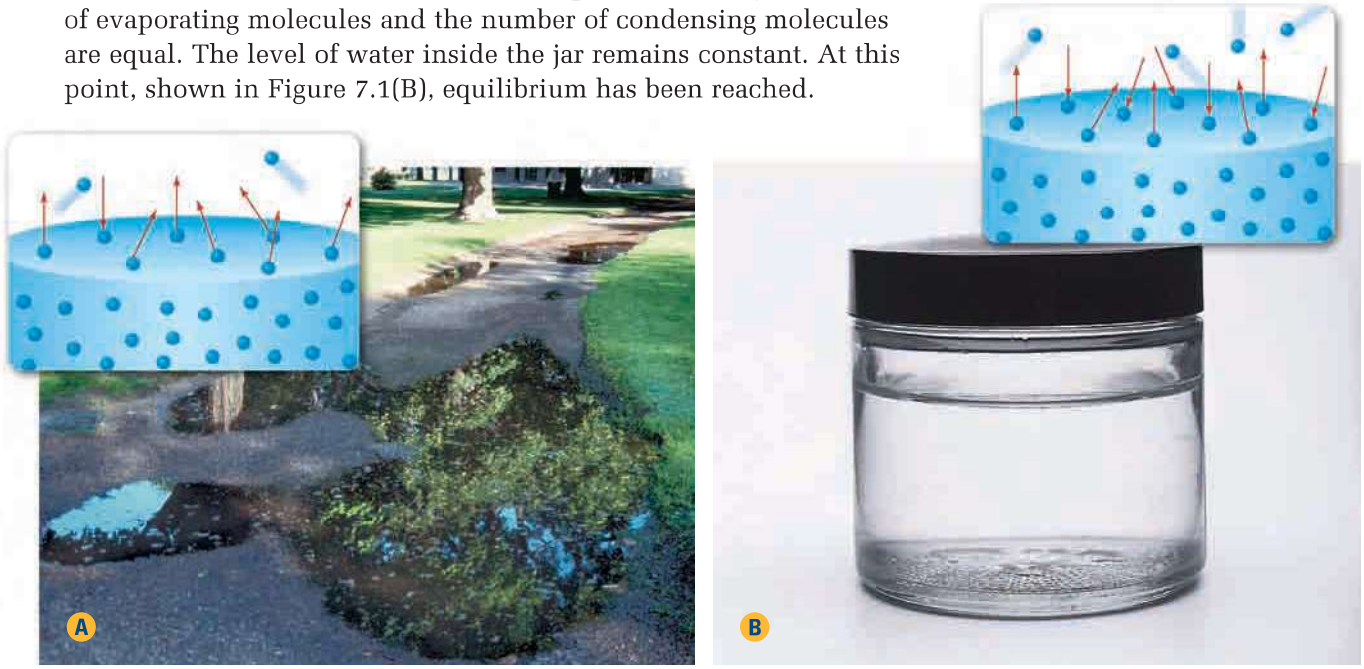


Figure 7.1 Why is (B) an example of equilibrium, while (A) is not?

- Crystals of copper(II) sulfate pentahydrate, $CuSO_4 \cdot 5H_2O$, are blue. If you place a few small crystals in a beaker of water, water molecules break apart the ions and they enter into the solution. A few ions in the solution may re-attach to the crystals. Because more ions enter the solution than re-attach to the crystals, however, all the solid eventually dissolves. If you keep adding crystals of copper(II) sulfate pentahydrate, the solution eventually becomes saturated. Crystals remain at the bottom of the beaker, as shown in Figure 7.2.

Figure 7.2 **Which of these systems, (A) or (B), is at equilibrium? Will changing the temperature affect the concentration of the solution in the equilibrium system?**

- Figure 7.3(A) shows a supersaturated solution of sodium acetate. It was prepared by adding sodium acetate to a saturated aqueous solution. The mixture was heated to dissolve the added crystals. Finally, the solution was left to return slowly to room temperature. In Figure 7.3(B), a single crystal of sodium acetate has been added to the supersaturated solution. As you can see, solute ions rapidly leave the solution, and solid forms.

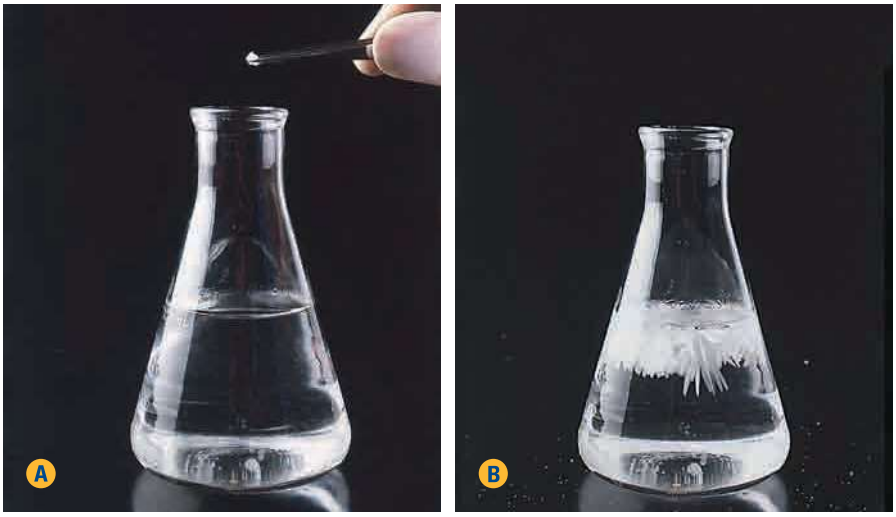


Figure 7.3 **These photographs show a supersaturated solution of sodium acetate and the effect of adding a crystal to it. Is either of these systems at equilibrium?**

ExpressLab Modelling Equilibrium

In this ExpressLab, you will model what happens when forward and reverse reactions occur. You will take measurements to gain quantitative insight into an equilibrium system. Then you will observe the effect of introducing a change to the equilibrium.

Materials

2 graduated cylinders (25 mL)
2 glass tubes with different diameters (for example, 10 mm and 6 mm)
2 labels or a grease pencil
supply of water, coloured with food dye

Procedure

1. Copy the following table into your notebook, to record your observations.

Transfer number	Volume of water in reactant cylinder (mL)	Volume of water in product cylinder (mL)
0	25.0	0.0
1		
2		

2. Label one graduated cylinder "reactant." Label the other "product."
3. Fill the reactant cylinder with coloured water, up to the 25.0 mL mark. Leave the product cylinder empty.
4. With your partner, transfer water simultaneously from one cylinder to the other as follows: Lower the larger-diameter glass tube into the reactant cylinder. Keep the top of the tube open. When the tube touches the bottom of the cylinder, cover the open end with a finger. Then transfer the liquid to the product cylinder. *At the same time* as you are transferring liquid into the product cylinder, your partner must use the smaller-diameter tube to transfer liquid from the product cylinder into the reactant cylinder.
5. Remove the glass tubes. Record the volume of water in each graduated cylinder, to the nearest 0.1 mL.
6. Repeat steps 4 and 5 until there is no further change in the volumes of water in the graduated cylinders.
7. Add approximately 5 mL of water to the reactant cylinder. Record the volume in each cylinder. Then repeat steps 4 and 5 until there is no further change in volume.

Analysis

1. Plot a graph of the data you collected. Put transfer number on the *x*-axis and volume of water on the *y*-axis. Use different symbols or colours to distinguish between the reactant volume and the product volume. Draw the best smooth curve through the data.
2. In this activity, the volume of water is a model for concentration. How can you use your graph to compare the rate of the forward reaction with the rate of the reverse reaction? What happens to these rates as the reaction proceeds?
3. At the point where the two curves cross, is the rate of the forward reaction equal to the rate of the reverse reaction? Explain.
4. How can you recognize when the system is at equilibrium?
5. Were the volumes of water (that is, concentrations of reactants and products) in the two tubes equal at equilibrium? How do you know?
6. In a chemical reaction, what corresponds to the addition of more water to the reactant cylinder? How did the final volume of water in the product cylinder change as a result of adding more water to the reactant cylinder?
7. Determine the ratio $\frac{\text{Volume of product}}{\text{Volume of reactant}}$ at the end of the first equilibrium and at the end of the second equilibrium. Within experimental error, were these two ratios the same or different?
8. In this activity, what do you think determined the relative volumes of water in the graduated cylinders? In a real chemical reaction, what factors might affect the relative concentrations of reactants and products at equilibrium?
9. Explain why the system in this activity is a closed system.

Conditions That Apply to All Equilibrium Systems

The fundamental requirement for equilibrium is that opposing changes must occur at the same rate. There are many processes that reach equilibrium. Three physical processes that reach equilibrium are

- a solid in contact with a solution that contains this solid: for example, sugar crystals in a saturated aqueous sugar solution
- the vapour above a pure liquid: for example, a closed jar that contains liquid water
- the vapour above a pure solid: for example, mothballs in a closed drawer

Two chemical processes that reach equilibrium are

- a reaction with reactants and products in the same phase: for example, a reaction between two gases to produce a gaseous product. In this chapter, you will focus on reactions in which the reactants and products are in the same phase. The equilibrium they reach is called **homogeneous equilibrium**.
- a reaction in which reactants and products are in different phases: for example, an aqueous solution of ions, in which the ions combine to produce a slightly soluble solid that forms a precipitate. In Chapters 8 and 9, you will work extensively with reactions in which the reactants and products are in different phases. The equilibrium they reach is called **heterogeneous equilibrium**.

CONCEPT CHECK

A decomposition reaction is taking place in a closed container, R $\rightarrow$ P. At equilibrium, does the concentration of reactant have to equal the concentration of product? Explain your answer.

What is it that equilibrium systems like these have in common? What conditions are necessary for equilibrium to become established? As outlined in the box below, there are four conditions that apply to all equilibrium systems.

The Four Conditions That Apply to All Equilibrium Systems

1. Equilibrium is achieved in a reversible process when the rates of opposing changes are equal. A double arrow, $\rightleftharpoons$, indicates reversible changes. For example:

$$H_2O_{(\ell)} \rightleftharpoons H_2O_{(g)}$$

$$H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)}$$

2. The observable (macroscopic) properties of a system at equilibrium are constant. At equilibrium, there is no overall change in the properties that depend on the total quantity of matter in the system. Examples of these properties include colour, pressure, concentration, and pH.

You can summarize the first two equilibrium conditions by stating that *equilibrium involves dynamic change at the molecular level but no change at the macroscopic level.*

3. Equilibrium can only be reached in a closed system. A closed system is a system that does not allow the input or escape of any component of the equilibrium system, including energy. For this reason, a system can be at equilibrium only if it is at constant temperature. A common example of a closed system is carbon dioxide gas that is in equilibrium with dissolved carbon dioxide in a soda drink.

The system remains at equilibrium as long as the container is not opened. Note that small changes to the components of a system are sometimes negligible. Thus, equilibrium principles can be applied if a system is not physically closed. For example, consider the equilibrium of a solid in a saturated aqueous solution, such as $CaO_{(s)} + H_2O_{(\ell)} \rightleftharpoons Ca^{2+}{}_{(aq)} + 2OH^-{}_{(aq)}$. You can neglect the small amount of water that vaporizes from the open beaker during an experiment.

4. Equilibrium can be approached from either direction. For example, the proportions of $H_{2(g)}$, $Cl_{2(g)}$, and $HCl_{(g)}$ (in a closed container at constant temperature) are the same at equilibrium, regardless of whether you started with $H_{2(g)}$ and $Cl_{(g)}$ or whether you started with $HCl_{(g)}$.

Section Summary

In this section, you learned how to recognize equilibrium. As well, you learned about the conditions that are needed for equilibrium to be reached. Later in this chapter, you will examine what happens when some equilibrium conditions in a system are changed. You will learn how chemists can control conditions to increase the yield of reactions.

Energy is an important component of most equilibrium systems. The input or output of energy in a system causes the temperature to change. Thus, the requirement that an equilibrium system be closed means that the temperature of the system must remain constant. In the next section, you will examine more closely the effects of thermodynamics on equilibrium systems. In particular, you will examine the factors that affect the amount of reactant and product in a reaction and the factors that determine whether or not a reaction is spontaneous.

Section Review

1. K/U Give two physical and two chemical processes that are examples of reversible changes that are not at equilibrium.

2. K/U Explain, in terms of reaction rates, how the changes that take place in a reversible reaction approach equilibrium.

3. K/U A sealed carbonated-drink bottle contains a liquid drink with a space above it. The space contains carbon dioxide at a pressure of about 405 kPa.
   (a) What changes are taking place at the molecular level?
   (b) Which macroscopic properties are constant?

4. K/U Agree or disagree with the following statement, and give reasons to support your answer: "In a sealed jar of water at equilibrium, the quantity of water molecules in the liquid state equals the quantity of water vapour molecules."

5. I Ice and slush are a feature of Canadian winters. Under what conditions do ice and water form an equilibrium mixture?

Electronic Learning Partner

Observe a molecular view of dynamic equilibrium in your Chemistry 12 Electronic Learning Partner.

7.2 Thermodynamics and Equilibrium

Section Preview/ Specific Expectations

In this section, you will

- **identify** qualitatively entropy changes that are associated with physical and chemical processes
- **describe** how reactions have a tendency to achieve minimum energy and maximum entropy
- **explain** the effect of changes in enthalpy, entropy, and temperature on a chemical reaction
- **communicate** your understanding of the following terms: *favourable change, entropy (S), second law of thermodynamics, free energy*

You can easily predict what will happen in a number of physical and chemical processes. What will happen if you let go of a pencil that you are holding tip-down on a table? What will you observe if you add a few drops of food colouring to some water in a glass? If a piece of paper starts to burn in a plentiful supply of air, what are the products of the reaction? How will an iron nail change if it is left outside? These are all examples of favourable (or *spontaneous*) changes. A **favourable change** is a change that has a natural tendency to happen under certain conditions.

What Conditions Favour a Change?

What conditions determine whether or not a change is favourable? How are different conditions related to equilibrium, where forward and reverse changes occur at the same rate? The answers to these questions are linked to two important concepts in thermodynamics: enthalpy and entropy.

Enthalpy and Favourable Changes

Energy is a key condition in favourable changes. For example, you know that a ball always rolls downhill. Its gravitational potential energy is lower at the bottom of the hill than at the top. For the ball to roll uphill—an unfavourable (or non-spontaneous) change—you have to apply energy to the ball. Chemical reactions are similar. When products have less enthalpy than reactants, the reaction releases energy. Therefore, the reaction is exothermic. Are favourable changes those that are exothermic under certain conditions?

Certainly many favourable physical and chemical changes are exothermic. Some favourable changes, however, involve no release of energy. Others are actually endothermic. For example, a favourable endothermic chemical reaction occurs when barium hydroxide and ammonium thiocyanate are placed in an Erlenmeyer flask, as shown in Figure 7.4.

$$Ba(OH)_2 \cdot 8H_2O_{(s)} + 2NH_4SCN_{(s)} \rightarrow Ba(SCN)_{2(aq)} + 10H_2O_{(\ell)} + 2NH_{3(g)} \qquad \Delta H = +170\ \text{kJ}$$

When the flask is stoppered and the contents are shaken, the solids intermingle. The reaction produces a slush-like mixture. This favourable, but endothermic, reaction absorbs enough energy to freeze a thin layer of water under the flask.

Figure 7.4 **A favourable endothermic reaction occurs when barium hydroxide is mixed with ammonium thiocyanate. If you removed the stopper in photograph (B), you would detect the characteristic odour of ammonia.**

Temperature and Favourable Changes

Another condition that determines whether or not a particular reaction is favoured is temperature. Consider the reversible synthesis reaction between mercury and oxygen, and the decomposition of mercury(II) oxide.

$$Hg_{(\ell)} + \frac{1}{2}O_{2(g)} \rightleftharpoons HgO_{(s)} \quad \Delta H = \pm 90.8 \text{ kJ}$$

From left to right, the reaction is exothermic. Therefore, the enthalpy change, ΔH, is negative. If the enthalpy change was the only condition that determined whether a reaction is favourable, then the synthesis reaction would take place. The synthesis reaction does take place—but only at relatively moderate temperatures. Above 400°C, the reverse reaction is favourable. The decomposition of $HgO_{(s)}$ occurs. Thus, the direction in which this reaction proceeds depends on temperature. This is fundamentally different from the dependence of reaction rate on temperature that you learned about in Unit 3. The reaction between $Hg_{(\ell)}$, $O_{2(g)}$, and $HgO_{(s)}$ does not just change its rate with a change in temperature, it changes its *direction*.

Temperature and Enthalpy Alone Cannot Explain Favourable Reactions

Temperature and enthalpy are not the only conditions that determine whether a change is favourable. Consider the process shown in Figure 7.5. A closed valve links two flasks together. The left flask contains an ideal gas. The right flask is evacuated. When the valve is opened, you expect the gas to diffuse into the evacuated flask until the pressure in both flasks is equal. You do not expect to see the reverse process—with all the gas molecules ending up in one of the flasks—unless work is done on the system.

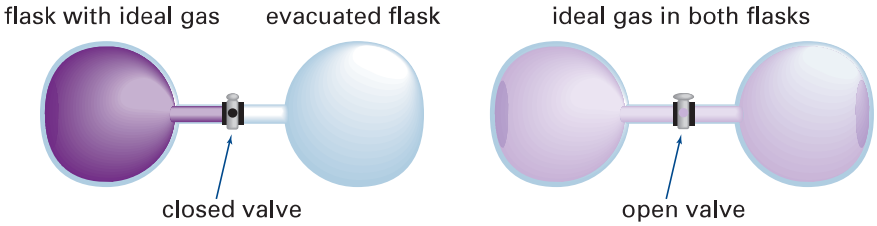


Figure 7.5 **If the gas is ideal, this favourable change involves no change in energy. Why must the gas be ideal?**

The process shown in Figure 7.5 is certainly a favourable change. Yet no exchange of energy is involved. The condition that influences this change is called entropy. It is an important condition in all physical and chemical changes.

Entropy and Favourable Changes

Entropy, ***S***, is the tendency toward randomness or disorder in a system. It is also a thermodynamic property that can be measured. It can be used to describe qualitative changes in energy.

An ordered arrangement of particles (atoms, ions, or molecules) has lower entropy (smaller disorder) than the same number of particles in random arrangements. Thus, the entropy of a pure substance depends on its state. The entropy of a system increases (becomes more disordered) with temperature, because the motion of particles becomes more chaotic at higher temperatures. See Figure 7.6 on the next page.

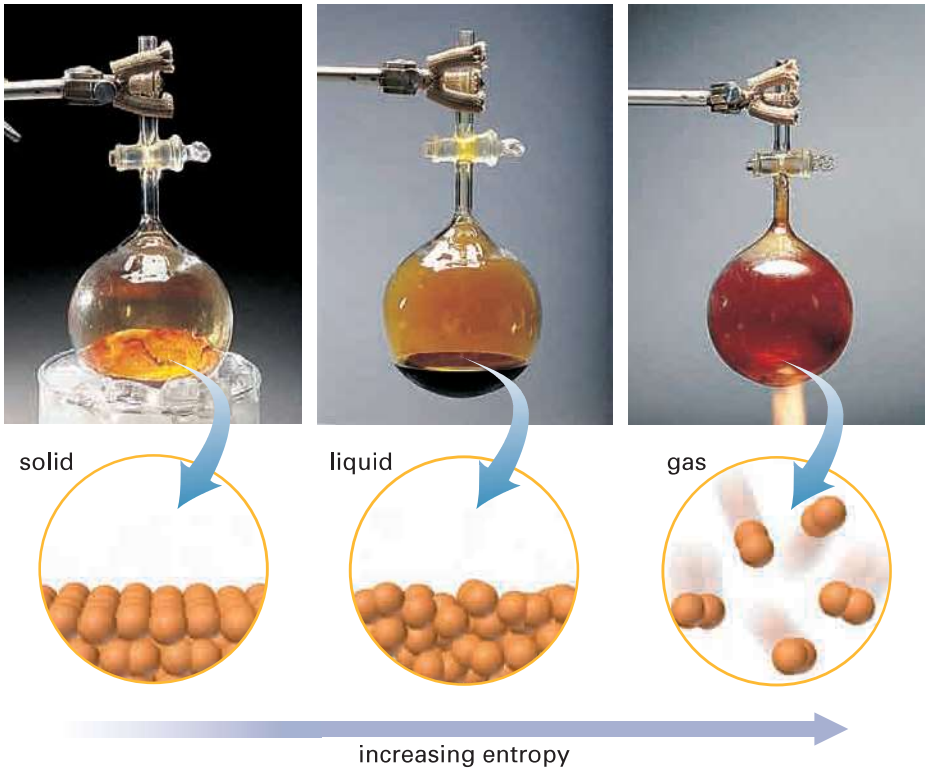


Figure 7.6 **The entropy of the particles in a sample of matter increases as the matter changes state from solid to liquid to gas.**

The mathematical definition of entropy describes the probability of a given arrangement of particles. A system of moving particles with low entropy *probably* has greater order than a similar system with higher entropy. Why say "probably"? Consider gas molecules in a container at room temperature. The gas molecules are moving rapidly, colliding with other molecules and the walls of the container. They have relatively large entropy. What if two different gases occupy the same container? It is possible, in principle, for the gases to separate so they are on opposite sides of the container. Given the huge number of particles, however, the probability of this happening is so close to zero that chemists say it will never happen. Nevertheless, it remains possible. The outcome is not certain.

As you know from Unit 3, chemists often use the terms "system" and "surroundings" to describe a chemical reaction. The system is the reaction itself—the reactants and products. The surroundings are everything else in the universe. According to the first law of thermodynamics (the law of conservation of energy) the algebraic sum of the energy changes in a system and its surroundings is zero. Unlike energy, entropy is not conserved. The total amount of entropy is increasing. This is part of the **second law of thermodynamics**: the total entropy of the universe is constantly increasing. The key word here is "total." If you are studying a system, you must add together changes in the entropy of the system, ΔS_{sys}, and changes in the entropy of the surroundings, ΔS_{surr}.

Consider what happens to you and your classmates (the particles in a "system") on your way to class. Initially, you and your classmates are in different places in the school, walking with different velocities toward the classroom. Going to class represents a relatively large amount of entropy. The final state of the system, when everyone is seated, represents a

smaller amount of entropy. Thus, the entropy of the system decreased. How, then, did the entropy of the universe increase?

The answer to this question involves changes to the surroundings. Each of you, on your way to class, metabolized energy. The movement and heat from your bodies added to the entropy of the air particles around you. In fact, the increase in the entropy of the surroundings was greater than the decrease in the entropy of the system. Therefore, the total entropy of the universe increased.

What does entropy have to do with favourable chemical changes and equilibrium systems? *All favourable changes involve an increase in the total amount of entropy.* Recall the endothermic reaction in Figure 7.4.

$$Ba(OH)_2 \cdot 8H_2O_{(s)} + 2NH_4SCN_{(s)} \rightarrow Ba(SCN)_{2(aq)} + 10H_2O_{(\ell)} + 2NH_{3(g)} \qquad \Delta H = +170\ \text{kJ}$$

The reaction is favourable, partly because the reactants are two solids and the products are a solution, water, and a gas. The products have a much larger entropy than the reactants. This helps to make the reaction favourable.

Now recall the reaction between mercury and oxygen. It favours the formation of HgO below about 400°C, but the decomposition of HgO above 400°C. This reaction highlights the importance of temperature to favourable change. Enthalpy, entropy, and temperature are linked in a concept called free energy.

Free Energy and Equilibrium

Imagine a perfect engine—an engine without any friction between its moving parts. This engine would still be unable to convert all the energy in a fuel into useful work. The reason is that some energy, such as the energy of the hot exhaust, is used to increase the entropy of the surroundings. The term **free energy** means available energy. In a chemical change, free energy is a measure of the useful work that can be obtained from a reaction. Free energy is often called *Gibbs free energy*, and given the symbol G, in honour of Josiah Willard Gibbs (1839–1903). Gibbs, a professor of chemistry at Harvard University, developed the concept of free energy and the equations that describe it.

The change in the free energy of a system, ΔG, at constant temperature is given by the equation $\Delta G = \Delta H - T\Delta S$. In this equation, as in most chemistry equations, the temperature, T, must be in Kelvin degrees. The symbol ΔH represents the change in enthalpy. The symbol ΔS represents the change in entropy.

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

change in free energy

change in enthalpy

change in entropy

Kelvin temperature

The value of ΔG for a chemical reaction tells us whether the reaction is a source of useful energy. Such energy can be converted into another form, such as mechanical energy to drive machinery or electrical energy in a battery. The rest of the energy from the reaction enters the environment as heat. It increases the entropy of the surroundings.

Biology LINK

The concept of free energy appears in other areas of science, notably biology. Find out the meanings of the terms "exergonic" and "endergonic." How are these terms related to free energy?

The equation $\Delta G = \Delta H - T\Delta S$, and the sign of ΔG, can help to explain why some chemical reactions are favourable at room temperature, why others are not, and how temperature affects the direction of a reaction. The change in the free energy of a chemical reaction is related to the direction of the reaction and to equilibrium as follows:

- When ΔG is negative, the forward reaction is favourable.
- When ΔG is zero, the reaction is at equilibrium.
- When ΔG is positive, the reaction is favourable in the reverse direction but not in the forward direction.

Exothermic reactions are often favourable because the sign of ΔH is negative. The equation shows that exothermic reactions are unfavourable only when ΔS is negative and the value of $-T\Delta S$ is large enough to make ΔG positive. This is what happens in the reaction between mercury and oxygen.

$$Hg_{(\ell)} + \frac{1}{2}O_{2(g)} \rightarrow HgO_{(s)} \quad \Delta H = -90.8 \text{ kJ}$$

From left to right, the reaction is exothermic. There is a decrease in entropy because gas molecules react to form a solid. At temperatures greater than about 400°C (673 K), the value of $-T\Delta S$ is positive and greater than 90.8 kJ. Thus, ΔG becomes positive. The forward reaction is no longer favourable, as experiments confirm.

In most reactions, the entropy of the system increases (S is positive), so the value of $-T\Delta S$ is negative. Therefore, most reactions tend to be more favourable at higher temperatures. At low temperatures, reactions are likely to be favourable only if they are highly exothermic.

Section Summary

Table 7.1 shows how you can use the signs of ΔH and ΔS to determine whether a chemical reaction is favourable. It also shows how ΔH and ΔS may vary with temperature. Keep in mind that a favourable reaction may be fast or slow. Thermodynamics makes no prediction about the rate of a reaction, only whether or not it can take place. Also, before any reaction begins, the activation energy must be supplied.

Table 7.1 How the Signs of ΔH and ΔS Affect the Favourability of a Reaction

ΔH	ΔS	$-T\Delta S$	Comments and examples
−	+	−	Both ΔH and ΔS favour the reaction. The reaction is favourable at all temperatures. Example: $2O_{3(g)} \rightarrow 3O_{2(g)}$
+	−	+	Neither ΔH nor ΔS favours the reaction. The reaction is unfavourable at all temperatures. Example: $3O_{2(g)} \rightarrow 2O_{3(g)}$
−	−	+	ΔH is favourable, but ΔS is not. The reaction is likely to be favourable at relatively low temperatures. Example: $Hg_{(\ell)} + \frac{1}{2}O_{2(g)} \rightarrow HgO_{(s)}$
+	+	−	ΔS is favourable, but ΔH is not. The reaction is likely to be favourable at higher temperatures. Example: $HgO_{(s)} \rightarrow Hg_{(\ell)} + \frac{1}{2}O_{2(g)}$

Note that the entropy of a system cannot increase forever. Eventually, a maximum state of disorder is reached. When this happens, the system appears to have constant properties, even though changes are still taking place at the molecular level. We say that a chemical system is at equilibrium when it has constant observable properties. Therefore, equilibrium occurs when a system has reached its maximum entropy. In the next section, you will look more closely at the reactants and products of chemical systems and learn how equilibrium is measured.

Section Review

1. K/U Explain the difference between a favourable chemical change and an unfavourable chemical change. Give two examples of each type of change.

2. C Write a short paragraph, or use a graphic organizer, to show the relationship among the following concepts: favourable chemical change, temperature, enthalpy, entropy, free energy.

3. K/U In each process, how does the entropy of the system change?
   - **(a)** ice melting
   - **(b)** water vapour condensing
   - **(c)** sugar dissolving in water
   - **(d)** $HCl_{(g)} + NH_{3(g)} \rightarrow NH_4Cl_{(s)}$
   - **(e)** $CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$

4. K/U What is the sign of the entropy change in each chemical reaction?
   - **(a)** $N_2O_{4(g)} \rightarrow 2NO_{2(g)}$
   - **(b)** $PCl_{3(g)} + Cl_{2(g)} \rightarrow PCl_{5(g)}$
   - **(c)** $2Al_{(s)} + \frac{3}{2}O_{2(g)} \rightarrow Al_2O_{3(s)}$
   - **(d)** $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$
   - **(e)** $S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)}$

5. I When water freezes, the phase change that occurs is exothermic.

   $H_2O_{(\ell)} \rightarrow H_2O_{(s)} \quad \Delta H = -6.02\ \text{kJ}$

   Based on the change in enthalpy, you would expect that water would always freeze. Use the concepts of entropy and free energy to explain why this phase change is favourable only below 0°C.

7.3 The Equilibrium Constant

Section Preview/ Specific Expectations

In this section, you will

- **express** your understanding of the law of chemical equilibrium as it applies to concentrations of reactants and products at equilibrium
- **collect** experimental data to determine an equilibrium constant for concentration
- **solve** equilibrium problems involving concentrations of reactants and products
- **communicate** your understanding of the following terms: *law of chemical equilibrium, equilibrium constant (K_c), ICE table*

Chemists use both thermodynamics and rate to study chemical reactions. Thermodynamics determines *whether* a reaction will occur at a certain temperature and *when* equilibrium will be reached. The rate of a reaction determines the *time it takes* for a certain concentration of product to form. In this section, you will learn about the *extent* of a reaction: the relative concentrations of products to reactants at equilibrium.

Opposing Rates and the Law of Chemical Equilibrium

In 1864, two Norwegian chemists, Cato Guldberg and Peter Waage, summarized their experiments on chemical equilibrium in the **law of chemical equilibrium**: *At equilibrium, there is a constant ratio between the concentrations of the products and reactants in any change.* Figure 7.7 shows how the law of chemical equilibrium applies to one chemical system. Chemists have studied this system extensively. It involves the reversible reaction between two gases: dinitrogen tetroxide, which is colourless, and nitrogen dioxide, which is dark brown.

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

colourless **brown**

By observing the intensity of the brown colour in the mixture, chemists can determine the concentration of nitrogen dioxide.

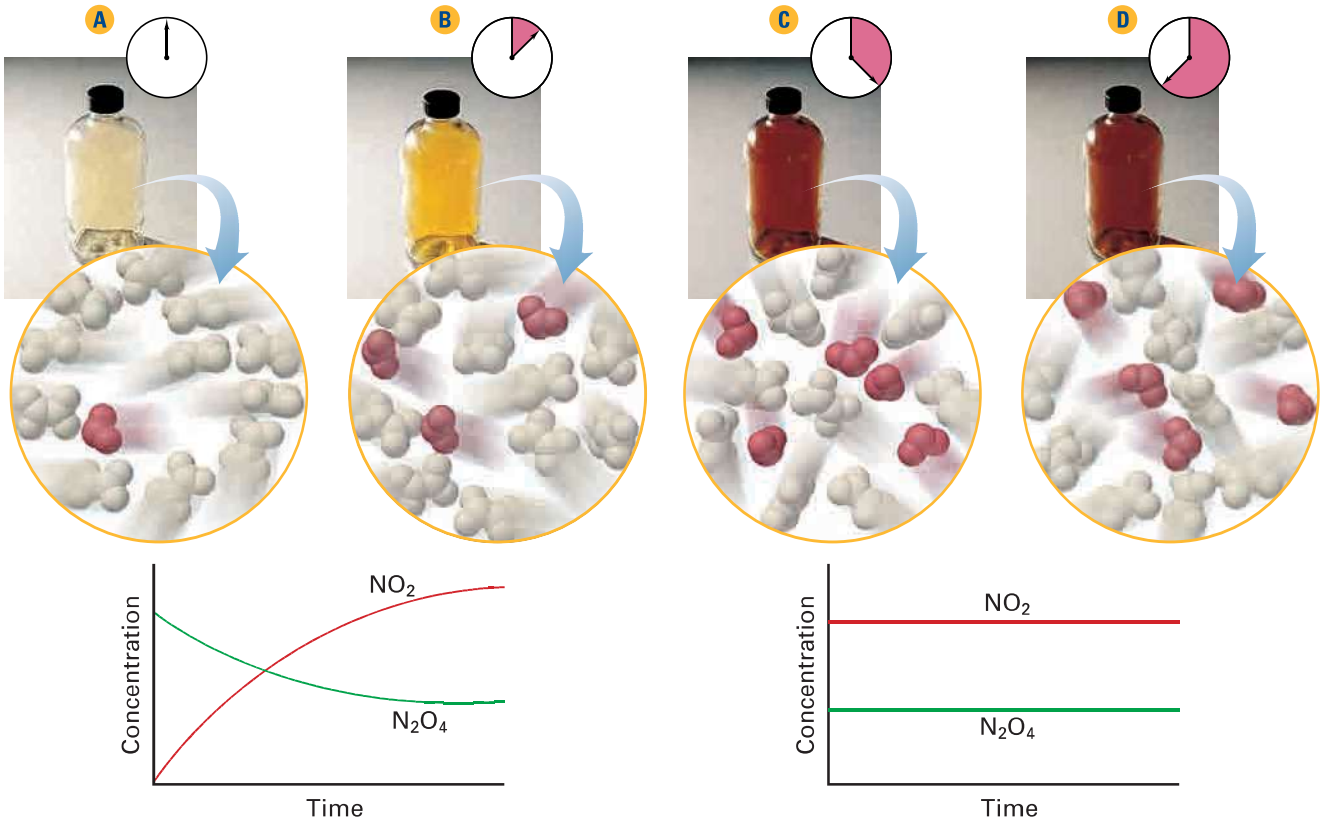


Figure 7.7 **As this system nears equilibrium, the rate of the forward reaction decreases and the rate of the reverse reaction increases. At equilibrium, the macroscopic properties of this system are constant. Changes at the molecular level take place at equal rates.**

Dinitrogen tetroxide gas is produced by vaporizing dinitrogen tetroxide liquid. Dinitrogen tetroxide liquid boils at 21°C. If a small quantity is placed in a sealed flask at 100°C, it vaporizes, filling the flask with dinitrogen tetroxide gas.

Suppose that the initial concentration of $N_2O_{4(g)}$ is 0.0200 mol/L. The initial concentration of $NO_{2(g)}$ is zero. The initial rate of the forward reaction, k_f, is relatively large, while the initial rate of the reverse reaction, k_r, is zero. The initial conditions correspond to the first exchange in the ExpressLab on page 325, where the reactant cylinder was full and the product cylinder was empty. As the reaction proceeds, the rate of the forward reaction decreases because the concentration of $N_2O_{4(g)}$ decreases. At the same time, the rate of the reverse reaction increases because the concentration of $NO_{2(g)}$ increases. At equilibrium, $k_f = k_r$. There are no further changes in the relative amounts of N_2O_4 and NO_2.

CONCEPT CHECK

How did the ExpressLab on page 325 model a reaction approaching equilibrium? How did it model the situation when equilibrium was reached?

The Equilibrium Constant

From other experiments involving the reaction between nitrogen tetroxide and nitrogen dioxide, chemists know that both the forward and reverse reactions involve elementary steps. Thus, you can write rate equations for the reactions.

Forward reaction: $N_2O_{4(g)} \rightarrow 2NO_{2(g)}$ Reverse reaction: $2NO_{2(g)} \rightarrow N_2O_{4(g)}$

Forward rate: $k_f[N_2O_4]$ Reverse rate: $k_f[NO_2]^2$

At equilibrium,

$$\text{Foward rate} = \text{Reverse rate}$$

$$k_f[N_2O_4] = k_r[NO_2]^2$$

The ratio of rate constants is another constant. The forward rate constant, k_f, divided by the reverse rate constant, k_r, is called the **equilibrium constant**, K_{eq}.

$$\frac{k_f}{k_r} = K_{eq} = \frac{[NO_2]^2}{[N_2O_4]}$$

You can write rate equations for these reactions because they are elementary mechanisms. Guldberg and Waage, however, showed that similar results are found for any reaction, regardless of the mechanism. For any general equilibrium equation, let P, Q, R, and S represent chemical formulas and a, b, c, and d represent their respective coefficients in the chemical equation.

$$aP + bQ \rightleftharpoons cR + dS$$

Recall that molar concentrations are indicated by square brackets. The equilibrium expression is usually expressed in terms of molar concentrations. Thus, the subscript "c" is usually used instead of "eq" in the equilibrium constant.

$$K_c = \frac{[R]^c[S]^d}{[P]^a[Q]^b}$$

This equilibrium expression depends only on the stoichiometry of the reaction. By convention, chemists always write the concentrations of the products in the numerator and the concentrations of the reactants in the denominator. Each concentration term is raised to the power of the coefficient in the chemical equation. The terms are multiplied, never added.

The following Sample Problem shows how to find the equilibrium expression for a reaction. In this chapter, you will use equilibrium expressions for homogeneous reactions (mostly reactions between gases). In Chapters 8 and 9, you will learn how to use equilibrium expressions for heterogeneous systems.

CHEM FACT

The law of chemical equilibrium is sometimes known as the law of mass action. Before the term "concentration" was used, the concept of amount per unit volume was called "active mass."

Sample Problem

Writing Equilibrium Expressions

Problem

One of the steps in the production of sulfuric acid involves the catalytic oxidation of sulfur dioxide.

$$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$$

Write the equilibrium expression.

What Is Required?

You need to find an expression for K_c.

What Is Given?

You know the balanced chemical equation.

Plan Your Strategy

The expression for K_c is a fraction. The concentration of the product is in the numerator, and the concentrations of the reactants are in the denominator. Each concentration term must be raised to the power of the coefficient in the balanced equation.

Act on Your Strategy

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

Check Your Solution

The square brackets indicate concentrations. The product is in the numerator, and each term is raised to the power of the coefficient in the chemical equation. The coefficient or power of 1 is not written, thus following chemistry conventions.

Practice Problems

Write the equilibrium expression for each homogeneous reaction.

1. The reaction between ethanol and ethanoic acid to form ethyl ethanoate and water:
   $CH_3CH_2OH_{(\ell)} + CH_3COOH_{(\ell)} \rightleftharpoons CH_3CHOOCH_2CH_{3(\ell)} + H_2O_{(\ell)}$
2. The reaction between nitrogen gas and oxygen gas at high temperatures:
   $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$
3. The reaction between hydrogen gas and oxygen gas to form water vapour:
   $2H_{2(g)} + O_{2(g)} \rightleftharpoons 2H_2O_{(g)}$
4. The reduction-oxidation equilibrium of iron and iodine ions in aqueous solution:
   $2Fe^{3+}_{(aq)} + 2I^-_{(aq)} \rightleftharpoons 2Fe^{2+}_{(aq)} + I_{2(aq)}$
   Note: You will learn about reduction-oxidation reactions in the next unit.
5. The oxidation of ammonia (one of the reactions in the production of nitric acid):
   $4NH_{3(g)} + 5O_{2(g)} \rightleftharpoons 4NO_{(g)} + 6H_2O_{(g)}$

The Equilibrium Constant and Temperature

Adding a chemical that is involved in a reaction at equilibrium increases the rate at which this chemical reacts. The rate, however, decreases as the concentration of the added chemical decreases. Eventually, equilibrium is re-established with the same equilibrium constant. For a given system at equilibrium, the value of the equilibrium constant depends only on temperature. Changing the temperature of a reacting mixture changes the rate of the forward and reverse reactions by different amounts, because the forward and reverse reactions have different activation energies. A reacting mixture at one temperature has an equilibrium constant whose value changes if the mixture is allowed to reach equilibrium at a different temperature.

The numerical value of the equilibrium constant does not depend on whether the starting point involves reactants or products. These are just labels that chemists use to identify particular chemicals in the reaction mixture. Also, at a given temperature, the value of K_c does not depend on the starting concentrations. The reaction gives the same ratio of products and reactants according to the equilibrium law. Remember, however, that K_c is calculated using *concentration* values when the system is at *equilibrium*.

Sample Problem

Calculating an Equilibrium Constant

Problem

A mixture of nitrogen and chlorine gases was kept at a certain temperature in a 5.0 L reaction flask.

$$N_{2(g)} + 3Cl_{2(g)} \rightleftharpoons 2NCl_{3(g)}$$

When the equilibrium mixture was analyzed, it was found to contain 0.0070 mol of $N_{2(g)}$, 0.0022 mol of $Cl_{2(g)}$, and 0.95 mol of $NCl_{3(g)}$. Calculate the equilibrium constant for this reaction.

What Is Required?

You need to calculate the value of K_c.

What Is Given?

You have the balanced chemical equation and the amount of each substance at equilibrium.

Plan Your Strategy

Step 1 Calculate the molar concentration of each compound at equilibrium.

Step 2 Write the equilibrium expression. Then substitute the equilibrium molar concentrations into the expression.

Act on Your Strategy

Step 1 The reaction takes place in a 5.0 L flask. Calculate the molar concentrations at equilibrium.

$$[N_2] = \frac{0.0070 \text{ mol}}{5.0 \text{ L}} = 1.4 \times 10^{-3} \text{ mol/L}$$

Continued ...

Continued ...

$$[Cl_2] = \frac{0.0022 \text{ mol}}{5.0 \text{ L}} = 1.9 \times 10^{-1} \text{ mol/L}$$

$$[NCl_3] = \frac{0.95 \text{ mol}}{5.0 \text{ L}} = 1.9 \times 10^{-1} \text{ mol/L}$$

Step 2 Write the equilibrium expression. Substitute the equilibrium molar concentrations into the expression.

$$K_c = \frac{[NCl_3]^2}{[N_2][Cl_2]^3}$$

$$= \frac{(1.9 \times 10^{-1})^2}{(1.4 \times 10^{-3}) \times (4.4 \times 10^{-4})^3}$$

$$= 3.0 \times 10^{11}$$

PROBLEM TIP

Notice that units are not included when using or calculating the value of K_c. This is the usual practice. The units do not help you check your solution.

Check Your Solution

The equilibrium expression has the product terms in the numerator and the reactant terms in the denominator. The exponents in the equilibrium expression match the corresponding coefficients in the chemical equation. The molar concentrations at equilibrium were substituted into the expression.

Practice Problems

6. The following reaction took place in a sealed flask at 250°C.

   $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

   At equilibrium, the gases in the flask had the following concentrations: $[PCl_5] = 1.2 \times 10^{-2}$ mol/L, $[PCl_3] = 1.5 \times 10^{-2}$ mol/L, and $[Cl_2] = 1.5 \times 10^{-2}$ mol/L. Calculate the value of K_c at 250°C.

7. Iodine and bromine react to form iodine monobromide, IBr.

   $I_{2(g)} + Br_{2(g)} \rightleftharpoons 2IBr_{(g)}$

   At 250°C, an equilibrium mixture in a 2.0 L flask contained 0.024 mol of $I_{2(g)}$, 0.050 mol of $Br_{2(g)}$, and 0.38 mol of $IBr_{(g)}$. What is the value of K_c for the reaction at 250°C?

8. At high temperatures, carbon dioxide gas decomposes into carbon monoxide and oxygen gas. At equilibrium, the gases have the following concentrations: $[CO_{2(g)}] = 1.2$ mol/L, $[CO_{(g)}] = 0.35$ mol/L, and $[O_{2(g)}] = 0.15$ mol/L. Determine K_c at the temperature of the reaction.

9. Hydrogen sulfide is a pungent, poisonous gas. At 1400 K, an equilibrium mixture was found to contain 0.013 mol/L hydrogen, 0.046 mol/L sulfur in the form of $S_{2(g)}$, and 0.18 mol/L hydrogen sulfide. Calculate the equilibrium constant, at 1400 K, for the following reaction.

   $2H_2S_{(g)} \rightleftharpoons 2H_{2(g)} + S_{2(g)}$

10. Methane, ethyne, and hydrogen form the following equilibrium mixture.

    $2CH_{4(g)} \rightleftharpoons C_2H_{2(g)} + 3H_{2(g)}$

    While studying this reaction mixture, a chemist analyzed a 4.0 L sealed flask at 1700°C. The chemist found 0.46 mol of $CH_{4(g)}$, 0.64 mol of $C_2H_{2(g)}$, and 0.92 mol of $H_{2(g)}$. What is the value of K_c for the reaction at 1700°C?

Measuring Equilibrium Concentrations

The equilibrium constant, K_c, is calculated by substituting equilibrium concentrations into the equilibrium expression. Experimentally, this means that a reaction mixture must come to equilibrium. Then one or more properties are measured. The properties that are measured depend on the reaction. Common examples for gaseous reactions include colour, pH, and pressure. From these measurements, the concentrations of the reacting substances can be determined. Thus, you do not need to measure all the concentrations in the mixture at equilibrium. You can determine some equilibrium concentrations if you know the initial concentrations of the reactants and the concentration of one product at equilibrium.

For example, a mixture of iron(III) nitrate and potassium thiocyanate, in aqueous solution, react to form the iron(III) thiocyanate ion, $Fe(SCN)^{2+}_{(aq)}$. The reactant solutions are nearly colourless. The product solution ranges in colour from orange to blood-red, depending on its concentration. The nitrate and potassium ions are spectators. Therefore, the net ionic equation is

$$Fe^{3+}_{(aq)} + SCN^{-}_{(aq)} \rightleftharpoons Fe(SCN)^{2+}_{(aq)}$$

colourless **red**

Because the reaction involves a colour change, you can determine the concentration of $Fe(SCN)^{2+}_{(aq)}$ by measuring the intensity of the colour. You will find out how to do this in Investigation 7-A. For now, assume that it can be done. From the measurements of colour intensity, you can calculate the equilibrium concentration of $Fe(SCN)^{2+}_{(aq)}$. Then, knowing the initial concentration of each solution, you can calculate the equilibrium concentration of each ion using the chemical equation.

Suppose, for instance, that the initial concentration of $Fe^{3+}_{(aq)}$ is 0.0064 mol/L and the initial concentration of $SCN^{-}_{(aq)}$ is 0.0010 mol/L. When the solutions are mixed, the red complex ion forms. By measuring the intensity of its colour, you can determine that the concentration of $Fe(SCN)^{2+}_{(aq)}$ is 4.5×10^{-4} mol/L. From the stoichiometry of the equation, each mole of $Fe(SCN)^{2+}_{(aq)}$ forms when equal amounts of $Fe^{3+}_{(aq)}$ and $SCN^{-}_{(aq)}$ react. So, if there is 4.5×10^{-4} mol/L of $Fe(SCN)^{2+}_{(aq)}$ at equilibrium, then the same amounts of both $Fe^{3+}_{(aq)}$ and $SCN^{-}_{(aq)}$ must have reacted. This represents the change in their concentrations. The equilibrium concentration of a reacting species is the sum of its initial concentration and the change that results from the reaction. Therefore, the concentration of $Fe^{3+}_{(aq)}$ at equilibrium is (0.0064 – 0.000 45) mol/L = 0.005 95 mol/L, or 0.0060 mol/L. You can calculate the equilibrium concentration of $SCN^{-}_{(aq)}$ the same way, and complete the table below.

Concentration (mol/L)	$Fe^{3+}_{(aq)}$	+	$SCN^{-}_{(aq)}$	$\rightleftharpoons$	$Fe(SCN)^{2+}_{(aq)}$
Initial	0.0064		0.0010		0
Change	-4.5×10^{-4}		-4.5×10^{-4}		4.5×10^{-4}
Equilibrium	0.0060		5.5×10^{-4}		4.5×10^{-4}

Finally, you can calculate K_c by substituting the equilibrium concentrations into the equilibrium expression.

In the following investigation, you will collect experimental data to determine an equilibrium constant.

CONCEPT CHECK

Think about a chemical system at equilibrium. Are the concentrations of the reactants and products in the same ratio as the coefficients in the chemical equation? Explain your answer.

Investigation 7-A

SKILL FOCUS

- Predicting
- Performing and recording
- Analyzing and interpreting
- Communicating results

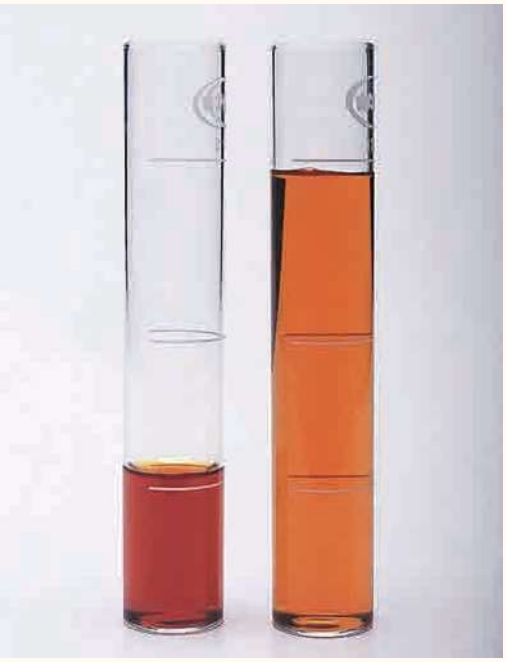
Measuring an Equilibrium Constant

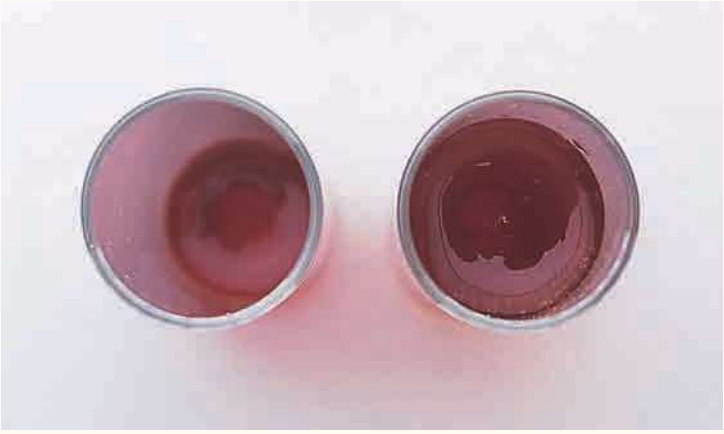
The colour intensity of a solution is related to the concentration of the ions and the depth of the solution. By adjusting the depth of a solution with unknown concentration until it has the same intensity as a solution with known concentration, you can determine the concentration of the unknown solution. For example, if the concentration of a solution is lower than the standard, the depth of the solution has to be greater in order to have the same colour intensity. Thus, the ratio of the concentrations of two solutions with the same colour intensity is inversely proportional to the ratio of their depths.

In this investigation, you will examine the homogeneous equilibrium between iron(III) (ferric) ions, thiocyanate ions, and ferrithiocyanate ions, $Fe(SCN)^{2+}$.

$$Fe^{3+}_{(aq)} + SCN^{-}_{(aq)} \rightleftharpoons Fe(SCN)^{2+}_{(aq)}$$

You will prepare four equilibrium mixtures with different initial concentrations of $Fe^{3+}_{(aq)}$ ions and $SCN^{-}_{(aq)}$ ions. You will calculate the initial concentrations of these reacting ions from the volumes and concentrations of the stock solutions used, and the *total* volumes of the equilibrium mixtures. Then you will determine the concentration of $Fe(SCN)^{2+}$ ions in each mixture by comparing the colour intensity of the mixture with the colour intensity of a solution that has known concentration. After you find the concentration of $Fe(SCN)^{2+}$ ions, you will use it to calculate the concentrations of the other two ions at equilibrium. You will substitute the three concentrations for each mixture into the equilibrium expression to determine the equilibrium constant.





Which solution is the least concentrated? Why is the colour intensity the same when you look vertically through the solutions?

Question

What is the value of the equilibrium constant at room temperature for the following reaction?

$$Fe^{3+}_{(aq)} + SCN^{-}_{(aq)} \rightleftharpoons Fe(SCN)^{2+}_{(aq)}$$

Prediction

Write the equilibrium expression for this reaction.

Safety Precautions

- The $Fe(NO_3)_3$ solution is acidified with nitric acid. It should be handled with care. Wash any spills on your skin or clothing with plenty of water, and inform your teacher.
- All glassware must be clean and dry before using it.

Materials

3 beakers (100 mL)
5 test tubes (18 mm × 150 mm)
5 flat-bottom vials
test tube rack
labels or grease pencil
thermometer
stirring rod
strip of paper
diffuse light source, such as a light box
medicine dropper
3 Mohr pipettes (5.0 mL)
20.0 mL Mohr pipette
pipette bulb
30 mL 0.0020 mol/L $KSCN_{(aq)}$
30 mL 0.0020 mol/L $Fe(NO_3)_{3(aq)}$ (acidified)
25 mL 0.200 mol/L $Fe(NO_3)_{3(aq)}$ (acidified)
distilled water

Procedure

1. Copy the following tables into your notebook, and give them titles. You will use the tables to record your measurements and calculations.
2. Label five test tubes and five vials with the numbers 1 through 5. Label three beakers with the names and concentrations of the stock solutions: 2.00×10^{-3} mol/L KSCN, 2.00×10^{-3} mol/L $Fe(NO_3)_3$, and 0.200 mol/L $Fe(NO_3)_3$. Pour about 30 mL of each stock solution into its labelled beaker. Be sure to distinguish between the different concentrations of the iron(III) nitrate solutions. Make sure that you choose the correct solution when needed in the investigation. Measure the volume of each solution as carefully as possible to ensure the accuracy of your results.

Test tube	$Fe(NO_3)_3$ (mL)	H_2O (mL)	KSCN (mL)	Initial $[SCN^-]$ (mol/L)
2	5.0	3.0	2.0	
3	5.0	2.0	3.0	
4	5.0	1.0	4.0	
5	5.0	0	5.0	

Vial	Depth of solution in vial (mm)	Depth of standard solution (mm)	$\frac{\text{Depth of standard solution}}{\text{Depth of solution in vial}}$
2			
3			
4			
5			

3. Prepare the standard solution of $FeSCN^{2+}$ in test tube 1. Use the 20 mL Mohr pipette to transfer 18.0 mL of 0.200 mol/L $Fe(NO_3)_{3(aq)}$ into the test tube. Then use a 5 mL pipette to add 2.0 mL of 2.00×10^{-3} mol/L KSCN. The large excess of $Fe^{3+}_{(aq)}$ is to ensure that all the $SCN^-_{(aq)}$ will react to form $Fe(SCN)^{2+}_{(aq)}$.

4. Pipette 5.0 mL of 2.0×10^{-3} mol/L $Fe(NO_3)_{3(aq)}$ into each of the other four test tubes (labelled 2 to 5).

5. Pipette 3.0 mL, 2.0 mL, 1.0 mL, and 0 mL of distilled water into test tubes 2 to 5.

6. Pipette 2.0 mL, 3.0 mL, 4.0 mL, and 5.0 mL of 2.0×10^{-3} mol/L $KSCN_{(aq)}$ into test tubes 2 to 5. Each of these test tubes should now contain 10.0 mL of solution. Notice that the first table you prepared (in step 1) shows the volumes of the liquids you added to the test tubes. Use a stirring rod to mix each solution. (Remember to rinse the stirring rod with water and then dry it with a paper towel before you stir each solution. Measure and record the temperature of one of the solutions. Assume that all the solutions are at the same temperature.

7. Pour about 5 mL of the standard solution from test tube 1 into vial 1.

8. Pour some of the solution from test tube 2 into vial 2. Look down through vials 1 and 2. Add enough solution to vial 2 to make its colour intensity about the same as the colour intensity of the solution in vial 1. Use a sheet of white paper as background to make your rough colour intensity comparison.

9. Wrap a sheet of paper around vials 1 and 2 to prevent light from entering the sides of the solutions. Looking down through the vials over a diffuse light source, adjust the volume of the standard solution in vial 1 until the colour intensity in the vials is the same. Use a medicine dropper to remove or add standard solution. Be careful not to add standard solution to vial 2.

10. When the colour intensity is the same in both vials, measure and record the depth of solution in each vial as carefully as possible.

11. Repeat steps 9 and 10 using vials 3 to 5.

12. Discard the solutions into the container supplied by your teacher. Rinse the test tubes and vials with distilled water. Then return all the equipment. Wash your hands.

13. Copy the following table into your notebook, to summarize the results of your calculations.

    (a) Calculate the equilibrium concentration of $Fe(SCN)^{2+}$ in the standard solution you prepared in test tube 1. The $[Fe(SCN)^{2+}]_{standard}$ is essentially the same as the starting concentration of $SCN^-_{(aq)}$ in test tube 1. The large excess of $Fe^{3+}_{(aq)}$ ensured that the reaction of SCN^- was almost complete. Remember, however, to include the volume of $Fe(NO_3)_{3(aq)}$ in the total volume of the solution for your calculation.

Test tube	Initial concentrations		Equilibrium concentrations			Equilibrium constant, K_c
	$[Fe^{3+}]_i$	$[SCN^-]_i$	$[Fe^{3+}]_{eq}$	$[SCN^-]_{eq}$	$[Fe(SCN)^{2+}]_{eq}$	
2						
3						
4						
5						

(b) Calculate the initial concentration of $Fe^{3+}_{(aq)}$ in test tubes 2 to 5. $[Fe^{3+}]_i$ is the same in these four test tubes. They all contained the same volume of $Fe(NO_3)_{3(aq)}$, and the total final volume was the same. Remember to use the total volume of the solution in your calculation.

(c) Calculate the initial concentration of $SCN^-_{(aq)}$ in test tubes 2 to 5. $[SCN^-]_i$ is different in each test tube.

(d) Calculate the equilibrium concentration of $Fe(SCN)^{2+}$ in test tubes 2 to 5. Use the following equation:

$$[FeSCN^{2+}]_{eq} = \frac{\text{Depth of standard solution}}{\text{Depth of solution in vial}} \times [FeSCN^{2+}]_{standard}$$

(e) Based on the stoichiometry of the reaction, each mole of $Fe(SCN)^{2+}$ is formed by the reaction of one mole of Fe^{3+} with one mole of SCN^-. Thus, you can find the equilibrium concentrations of these ions by using the equations below:

$$[Fe^{3+}]_{eq} = [Fe^{3+}]_i - [Fe(SCN)^{2+}]_{eq}$$

$$[SCN^-]_{eq} = [SCN^-]_i - [Fe(SCN)^{2+}]_{eq}$$

(f) Calculate four values for the equilibrium constant, K_c, by substituting the equilibrium concentrations into the equilibrium expression. Find the average of your four values for K_c.

Analysis

1. How did the colour intensity of the solutions in test tubes 2 to 5 vary at equilibrium? Explain your observation.

2. How consistent are the four values you calculated for K_c? Suggest reasons that could account for any differences.

3. Use your four sets of data to evaluate the following expressions:

   $[Fe(SCN)^{2+}][Fe^{3+}][SCN^-]$

   $$\frac{[Fe^{3+}] + [SCN^-]}{[Fe(SCN)^{2+}]}$$

   Do these expressions give a value that is more constant than your equilibrium constant? Make up another expression, and evaluate it using your four sets of data. How constant is its value?

4. Suppose that the following reaction was the equilibrium reaction.

   $Fe^{3+}_{(aq)} + 2SCN^-_{(aq)} \rightleftharpoons Fe(SCN)_2{}^+_{(aq)}$

   (a) Would the equilibrium concentration of the product be different from the concentration of the product in the actual reaction? Explain.

   (b) Would the value of K_c be different from the value you calculated earlier? Explain.

Conclusion

5. Write a short conclusion, summarizing your results for this investigation.

Equilibrium Calculations

The Sample Problems that follow all involve homogeneous equilibrium systems. Each problem illustrates a particular type of system and includes brief tips. Each problem also includes a table like the one on page 339 to organize the data. Because this table is used to record the **i**nitial, **c**hange, and **e**quilibrium values of the reacting species, it is often called an **ICE table**. In Chapters 8 and 9, you will use ICE tables again to help you solve problems that involve heterogeneous equilibrium systems.

Sample Problem

Finding Equilibrium Amounts From Initial Amounts and K_c

Problem

The following reaction increases the proportion of hydrogen gas for use as a fuel.

$$CO_{(g)} + H_2O_{(g)} \rightleftharpoons H_{2(g)} + CO_{2(g)}$$

This reaction has been studied at different temperatures to find the optimum conditions. At 700 K, the equilibrium constant is 8.3. Suppose that you start with 1.0 mol of $CO_{(g)}$ and 1.0 mol of $H_2O_{(g)}$ in a 5.0 L container. What amount of each substance will be present in the container when the gases are at equilibrium, at 700 K?

What Is Required?

You need to find the amount (in moles) of $CO_{(g)}$, $H_2O_{(g)}$, $H_{2(g)}$, and $CO_{2(g)}$ at equilibrium.

What Is Given?

You have the balanced chemical equation. You know the initial amount of each gas, the volume of the container, and the equilibrium constant.

Plan Your Strategy

Step 1 Calculate the initial concentrations.

Step 2 Set up an ICE table. Record the initial concentrations you calculated in step 1 in your ICE table. Let the change in molar concentrations of the reactants be x. Use the stoichiometry of the chemical equation to write and record expressions for the equilibrium concentrations.

Step 3 Write the equilibrium expression. Substitute the expressions for the equilibrium concentrations into the equilibrium expression. Solve the equilibrium expression for x.

Step 4 Calculate the equilibrium concentration of each gas. Then use the volume of the container to find the amount of each gas.

Act on Your Strategy

Step 1 The initial amount of CO is equal to the initial amount of H_2O.

$$\therefore [CO] = [H_2O] = \frac{1.0 \text{ mol}}{5.0 \text{ L}} = 0.20 \text{ mol/L}$$

PROBLEM TIP

Generally, it is best to let x represent the substance with the smallest coefficient in the chemical equation. This helps to avoid fractional values of x in the equilibrium expression. Fractional values make solving the expression more difficult.

Step 2 Set up an ICE table.

Concentration (mol/L)	$CO_{(g)}$	+	$H_2O_{(g)}$	$\rightleftharpoons$	$H_{2(g)}$	+	$CO_{2(g)}$
Initial	0.20		0.20		0		0
Change	$-x$		$-x$		$+x$		$+x$
Equilibrium	$0.20 - x$		$0.20 - x$		$0 + x$		$0 + x$

Step 3

$$K_c = \frac{[H_2][CO_2]}{[CO][H_2O]}$$

$$0.83 = \frac{(x)(x)}{(0.20 - x)(0.20 - x)} = \frac{(x)^2}{(0.20 - x)^2}$$

$$\pm 0.911 = \frac{(x)}{(0.20 - x)}$$

Solving for both values,
$x = 0.148$ and $x = 0.306$

Step 4 The value $x = 0.306$ is physically impossible because it would result in a negative concentration of both CO and H_2O at equilibrium.

$\therefore [H_2] = [CO_2] = 0.15$ mol/L

$[CO] = [H_2O] = 0.20 - 0.15 = 0.05$ mol/L

To find the amount of each gas, multiply the concentration of each gas by the volume of the container (5.0 L).

Amount of $H_{2(g)} = CO_{2(g)} = 0.75$ mol

Amount of $CO_{(g)} = H_2O_{(g)} = 0.25$ mol

Check Your Solution

The equilibrium expression has product terms in the numerator and reactant terms in the denominator. The amounts of chemicals at equilibrium are given in moles. Check K_c.

$$K_c = \frac{(0.75)^2}{(0.25)^2} = 9.0$$

This is close to the given value, $K_c = 8.3$. The difference is due to mathematical rounding.

PROBLEM TIP

In this problem, the right-hand side of the equilibrium expression is a perfect square. Noticing perfect squares, then taking the square root of both sides, makes solving the equation easier. It avoids solving a quadratic equation.

Many problems do not involve perfect squares. You may need to use a quadratic equation to solve the equilibrium expression.

Sample Problem

Solving an Equilibrium Expression Using a Quadratic Equation

Problem

The following reaction has an equilibrium constant of 25.0 at 1100 K.

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

2.00 mol of $H_{2(g)}$ and 3.00 mol of $I_{2(g)}$ are placed in a 1.00 L reaction vessel at 1100 K. What is the equilibrium concentration of each gas?

Continued ...

Continued ...

What Is Required?

You need to find $[H_2]$, $[I_2]$, and $[HI]$.

What Is Given?

You have the balanced chemical equation. You know the equilibrium constant for the reaction, $K_c = 25$. You also know the concentrations of the reactants and product: $[H_2]_i = 2.00$ mol/L, $[I_2]_i = 3.00$ mol/L, and $[HI]_i = 0$.

Plan Your Strategy

Step 1 Set up an ICE table. Let the change in molar concentrations of the reactants be x. Use the stoichiometry of the chemical equation to write expressions for the equilibrium concentrations. Record these expressions in your ICE table.

Step 2 Write the equilibrium expression. Substitute the expressions for the equilibrium concentrations into the equilibrium expression. Rearrange the equilibrium expression into the form of a quadratic equation. Solve the quadratic equation for x.

Step 3 Substitute x into the equilibrium line of the ICE table to find the equilibrium concentrations.

Act on Your Strategy

Step 1 Set up an ICE table.

Concentration (mol/L)	$H_{2(g)}$	+	$I_{2(g)}$	$\rightleftharpoons$	$2HI_{(g)}$
Initial	2.00		3.00		0
Change	$-x$		$-x$		$+2x$
Equilibrium	$2.00 - x$		$3.00 - x$		$+2x$

Step 2 Write and solve the equilibrium expression.

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

$$25.0 = \frac{(2x)^2}{(2.00 - x)(3.00 - x)}$$

This equation does not involve a perfect square. It must be re-arranged into a quadratic equation.

$$0.840x^2 - 5.00x + 6.00 = 0$$

Recall that a quadratic equation of the form $ax^2 + bx + c = 0$ has the following solution:

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

$$\therefore x = \frac{-(-5.00) \pm \sqrt{25.0 - 20.16}}{1.68}$$

$$= \frac{5.00 \pm 2.2}{1.68}$$

$x = 4.3$ and $x = 1.7$

PROBLEM TIP

In the equilibrium expression, the numerator is $[HI]^2$. The concentration is $2x$, so the substitution is $(2x)^2 = 4x^2$. A common mistake is to write $2x^2$. You can avoid this mistake by using brackets.

Step 3 The value $x = 4.3$ is not physically possible. It would result in negative concentrations of H_2 and I_2 at equilibrium. The concentration of each substance at equilibrium is found by substituting $x = 1.7$ into the last line of the ICE table.

Concentration (mol/L)	$H_{2(g)}$	+	$I_{2(g)}$	$\rightleftharpoons$	$2HI_{(g)}$
Equilibrium	2.00 − 1.7		3.00 − 1.7		3.4

Applying the rule for subtraction involving measured values,
$[H_2] = 0.3$ mol/L

$[I_2] = 1.3$ mol/L

$[HI] = 3.4$ mol/L

Check Your Solution

The coefficients in the chemical equation match the exponents in the equilibrium expression. To check your concentrations, substitute them back into the equilibrium expression.

$$K_c = \frac{3.4^2}{0.3 \times 1.3} = 30$$

Solving the quadratic equation gives a value of x, correct to one decimal place. As a result, $[H_2]$ can have only one significant figure. The calculated value of K_c is equal to the given value, within the error introduced by rounding.

Practice Problems

11. At 25°C, the value of K_c for the following reaction is 82.

$I_{2(g)} + Cl_{2(g)} \rightleftharpoons 2ICl_{(g)}$

0.83 mol of $I_{2(g)}$ and 0.83 mol of $Cl_{2(g)}$ are placed in a 10 L container at 25°C. What are the concentrations of the three gases at equilibrium?

12. At a certain temperature, $K_c = 4.0$ for the following reaction.

$2HF_{(g)} \rightleftharpoons H_{2(g)} + F_{2(g)}$

A 1.0 L reaction vessel contained 0.045 mol of $F_{2(g)}$ at equilibrium. What was the initial amount of HF in the reaction vessel?

13. A chemist was studying the following reaction.

$SO_{2(g)} + NO_{2(g)} \rightleftharpoons NO_{(g)} + SO_{3(g)}$

In a 1.0 L container, the chemist added 1.7×10^{-1} mol of $SO_{2(g)}$ to 1.1×10^{-1} mol of $NO_{2(g)}$. The value of K_c for the reaction at a certain temperature is 4.8. What is the equilibrium concentration of $SO_{3(g)}$ at this temperature?

14. Phosgene, $COCl_{2(g)}$, is an extremely toxic gas. It was used during World War I. Today it is used to manufacture pesticides, pharmaceuticals, dyes, and polymers. It is prepared by mixing carbon monoxide and chlorine gas.

$CO_{(g)} + Cl_{2(g)} \rightleftharpoons COCl_{2(g)}$

Continued ...

Continued ...

0.055 mol of $CO_{(g)}$ and 0.072 mol of $Cl_{2(g)}$ are placed in a 5.0 L container. At 870 K, the equilibrium constant is 0.20. What are the equilibrium concentrations of the mixture at 870 K?

15. Hydrogen bromide decomposes at 700 K.

$2HBr_{(g)} \rightleftharpoons H_{2(g)} + Br_{2(g)} \quad K_c = 4.2 \times 10^{-9}$

0.090 mol of HBr is placed in a 2.0 L reaction vessel and heated to 700 K. What is the equilibrium concentration of each gas?

Qualitatively Interpreting the Equilibrium Constant

The Sample Problem on page 344 showed how to calculate the amounts of gases at equilibrium for the following reaction.

$$CO_{(g)} + H_2O_{(g)} \rightleftharpoons H_{2(g)} + CO_{2(g)}$$

Recall that the equilibrium constant for this reaction was 8.3 at 700 K. 1.0 mol of $CO_{(g)}$ and 1.0 mol of $H_2O_{(g)}$ were put in a 5.0 L container. At equilibrium, 0.48 mol of $H_{2(g)}$ and 0.48 mol of $CO_{2(g)}$ were present. The starting amounts were in stoichiometric ratios. Consequently, if the reaction had gone to completion, there would have been no limiting reactant. You would have expected 1.0 mol of both $H_{2(g)}$ and $CO_{2(g)}$. Thus, you can calculate the percent yield of the reaction as follows:

$$\begin{aligned}\text{Percent yield} &= \frac{\text{Equilibrium } [H_2] \times 100\%}{\text{Maximum } [H_2]} \\ &= \frac{0.48 \times 100\%}{1.0} \\ &= 48\%\end{aligned}$$

This value indicates the extent of the reaction. It is linked to the size of K_c. As you know, the equilibrium expression is always written with the product terms over the reactant terms. Therefore, a large K_c means that the concentration of products is larger than the concentration of reactants at equilibrium. When referring to a reaction with a large K_c, chemists often say that the position of equilibrium lies to the right, or that it favours the products. Similarly, if K_c is small, the concentration of reactants is larger than the concentration of products. Chemists say that the position of equilibrium lies to the left, or that it favours reactants. Thus, the following general statements are true:

- *When $K > 1$, products are favoured.* The equilibrium lies far to the right. Reactions where K is greater than 10^{10} are usually regarded as going to completion.
- *When $K \approx 1$, there are approximately equal concentrations of reactants and products at equilibrium.*
- *When $K < 1$, reactants are favoured.* The equilibrium lies far to the left. Reactions in which K is smaller than 10^{-10} are usually regarded as not taking place at all.

Notice that the subscript "c" has been left off K in these general statements. This reflects the fact that there are other equilibrium constants that these statements apply to, not just equilibrium constants involving concentrations. You will learn about other types of equilibrium constants in the next two chapters. For the rest of this chapter, though, you will continue to see the subscript "c" used.

In the Sample Problem and Practice Problems below, you will consider how temperature affects the extent of a reaction. Keep in mind that the size of K_c is not related to the time that a reaction takes to achieve equilibrium. Very large values of K_c may be associated with reactions that take place extremely slowly. The time that a reaction takes to reach equilibrium depends on the rate of the reaction. This is determined by the size of the activation energy.

Sample Problem

Temperature and the Extent of a Reaction

Problem

Consider the reaction of carbon monoxide and chlorine to form phosgene, $COCl_{2(g)}$.

$$CO_{(g)} + Cl_{2(g)} \rightleftharpoons COCl_{2(g)}$$

At 870 K, the value of K_c is 0.20. At 370 K, the value of K_c is 4.6×10^7. Based on only the values of K_c, is the production of $COCl_{2(g)}$ more favourable at the higher or lower temperature?

What Is Required?

You need to choose the temperature that favours the greater concentration of product.

What Is Given?

$K_c = 0.2$ at 870 K

$K_c = 4.6 \times 10^7$ at 370 K

Plan Your Strategy

Phosgene is a product in the chemical equation. A greater concentration of product corresponds to a larger value of K_c.

Act on Your Strategy

The value of K_c is larger at 370 K. The position of equilibrium lies far to the right. It favours the formation of $COCl_2$ at the lower temperature.

Check Your Solution

The problem asked you to choose the temperature for a larger concentration of the product. K_c is expressed as a fraction with product terms in the numerator. Therefore, the larger value of K_c corresponds to the larger concentration of product.

CONCEPT CHECK

Does a small value of K_c indicate a slow reaction? Use an example to justify your answer.

Practice Problems

16. For the reaction $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$, the value of K_c is 25.0 at 1100 K and 8.0×10^2 at room temperature, 300 K. Which temperature favours the dissociation of $HI_{(g)}$ into its component gases?

17. Three reactions, and their equilibrium constants, are given below.

I. $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ $\quad K_c = 4.7 \times 10^{-31}$

II. $2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$ $\quad K_c = 1.8 \times 10^{-6}$

III. $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ $\quad K_c = 0.025$

Continued ...

Continued ...

Arrange these reactions in the order of their tendency to form products.

18. Identify each reaction as essentially going to completion or not taking place.

(a) $N_{2(g)} + 3Cl_{2(g)} \rightleftharpoons 2NCl_{3(g)}$ $K_c = 3.0 \times 10^{11}$

(b) $2CH_{4(g)} \rightleftharpoons C_2H_{6(g)} + H_{2(g)}$ $K_c = 9.5 \times 10^{-13}$

(c) $2NO_{(g)} + 2CO_{(g)} \rightleftharpoons N_{2(g)} + 2CO_{2(g)}$ $K_c = 2.2 \times 10^{59}$

19. Most metal ions combine with other ions in solution. For example, in aqueous ammonia, silver(I) ions are at equilibrium with different complex ions.

$[Ag(H_2O)_2]^+_{(aq)} + 2NH_{3(aq)} \rightleftharpoons [Ag(NH_3)_2]^+_{(aq)} + 2H_2O_{(\ell)}$

At room temperature, K_c for this reaction is 1×10^7. Which of the two silver complex ions is more stable? Explain your reasoning.

20. Consider the following reaction.

$H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)}$ $K_c = 2.4 \times 10^{33}$ at 25°C

$HCl_{(g)}$ is placed in a reaction vessel. To what extent do you expect the equilibrium mixture to dissociate into $H_{2(g)}$ and $Cl_{2(g)}$?

The Meaning of a Small Equilibrium Constant

Understanding the meaning of a small equilibrium constant can sometimes help to simplify a calculation that would otherwise involve a quadratic equation. When K_c is small compared with the initial concentration, the value of the initial concentration minus x is approximately equal to the initial concentration. Thus, you can ignore x. Of course, if the initial concentration of a substance is zero, any equilibrium concentration of the substance, no matter how small, is significant. In general, values of K_c are not measured with accuracy better than 5%. Therefore, making the approximation is justified if the calculation error you introduce is less than 5%.

To help you decide whether or not the approximation is justified, divide the initial concentration by the value of K_c. If the answer is greater than 500, the approximation is justified. If the answer is between 100 and 500, it may be justified. If the answer is less than 100, it is not justified. The equilibrium expression must be solved in full.

Sample Problem

Using the Approximation Method

Problem

The atmosphere contains large amounts of oxygen and nitrogen. The two gases do not react, however, at ordinary temperatures. They do react at high temperatures, such as the temperatures produced by a lightning flash or a running car engine. In fact, nitrogen oxides from exhaust gases are a serious pollution problem.

A chemist is studying the following equilibrium reaction.

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

The chemist puts 0.085 mol of $N_{2(g)}$ and 0.038 mol of $O_{2(g)}$ in a 1.0 L rigid cylinder. At the temperature of the exhaust gases from a particular engine, the value of K_c is 4.2×10^{-8}. What is the concentration of $NO_{(g)}$ in the mixture at equilibrium?

What Is Required?

You need to find the concentration of NO at equilibrium.

What Is Given?

You have the balanced chemical equation. You know the value of K_c and the following concentrations: $[N_2] = 0.085$ mol/L and $[O_2] = 0.038$ mol/L.

Plan Your Strategy

Step 1 Divide the smallest initial concentration by K_c to determine whether you can ignore the change in concentration.

Step 2 Set up an ICE table. Let x represent the change in $[N_2]$ and $[O_2]$.

Step 3 Write the equilibrium expression. Substitute the equilibrium concentrations into the equilibrium expression. Solve the equilibrium expression for x.

Step 4 Calculate [NO] at equilibrium.

Act on Your Strategy

Step 1

$$\frac{\text{Smallest initial concentration}}{K_c} = \frac{0.038}{4.2 \times 10^{-8}}$$
$$= 9.0 \times 10^5$$

Because this is well above 500, you can ignore the changes in $[N_2]$ and $[O_2]$.

Step 2

Concentration (mol/L)	$N_{2(g)}$	+	$O_{2(g)}$	$\rightleftharpoons$	$2NO_{(g)}$
Initial	0.085		0.038		0
Change	$-x$		$-x$		$+2x$
Equilibrium	$0.085 - x \approx 0.085$		$0.038 - x \approx 0.038$		$2x$

Step 3

$$K_c = \frac{[NO]^2}{[N_2][O_2]}$$
$$4.2 \times 10^{-8} = \frac{(2x)^2}{0.085 \times 0.038}$$
$$= \frac{4x^2}{0.003\,23}$$
$$x = \sqrt{3.39 \times 10^{-11}}$$
$$= 5.82 \times 10^{-6}$$

Step 4 $[NO] = 2x$

Therefore, the concentration of $NO_{(g)}$ at equilibrium is 1.2×10^{-5} mol/L.

Continued ...

Continued ...

Check Your Solution

First, check your assumption that x is negligible compared with the initial concentrations. Your assumption is valid because, using the rules for subtracting measured quantities, $0.038 - (5.8 \times 10^{-6}) = 0.038$. Next, check the equilibrium values:

$$\frac{(1.2 \times 10^{-5})^2}{0.0085 \times 0.038} = 4.5 \times 10^{-8}$$

This is equal to the equilibrium constant, within rounding errors in the calculation.

Practice Problems

21. The following equation represents the equilibrium reaction for the dissociation of phosgene gas.

$COCl_{2(g)} \rightleftharpoons CO_{(g)} + Cl_{2(g)}$

At 100°C, the value of K_c for this reaction is 2.2×10^{-8}. The initial concentration of $COCl_{2(g)}$ in a closed container at 100°C is 1.5 mol/L. What are the equilibrium concentrations of $CO_{(g)}$ and $Cl_{2(g)}$?

22. Hydrogen sulfide is a poisonous gas with a characteristic, offensive odour. It dissociates at 1400°C, with K_c equal to 2.4×10^{-4}.

$H_2S_{(g)} \rightleftharpoons 2H_{2(g)} + S_{2(g)}$

4.0 mol of H_2S is placed in a 3.0 L container. What is the equilibrium concentration of $H_{2(g)}$ at 1400°C?

23. At a certain temperature, the value of K_c for the following reaction is 3.3×10^{-12}.

$2NCl_{3(g)} \rightleftharpoons N_{2(g)} + 3Cl_{2(g)}$

A certain amount of nitrogen trichloride, $NCl_{3(g)}$, is put in a 1.0 L reaction vessel at this temperature. At equilibrium, 4.6×10^{-4} mol of $N_{2(g)}$ is present. What amount of $NCl_{3(g)}$ was put in the reaction vessel?

24. At a certain temperature, the value of K_c for the following reaction is 4.2×10^{-8}.

$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$

0.45 mol of $N_{2(g)}$ and 0.26 mol of $O_{2(g)}$ are put in a 6.0 L reaction vessel. What is the equilibrium concentration of $NO_{(g)}$ at this temperature?

25. At a particular temperature, K_c for the decomposition of carbon dioxide gas is 2.0×10^{-6}.

$2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)}$

3.0 mol of CO_2 is put in a 5.0 L container. Calculate the equilibrium concentration of each gas.

Section Summary

In this section, you learned that the equilibrium constant, K_c, is a ratio of product concentrations to reactant concentrations. You used concentrations to find K, and you used K to find concentrations. You also used an ICE table to track and summarize the initial, change, and equilibrium quantities in a reaction. You found that the value of K_c is small for reactions that reach equilibrium with a high concentration of reactants, and the value of K_c is large for reactions that reach equilibrium with a low concentration of reactants. In the next section, you will learn how to determine whether or not a reaction is at equilibrium, and, if it is not, in which direction it will go to achieve equilibrium.

Section Review

1. K/U Write equilibrium expressions for each homogeneous reaction.
   - (a) $SbCl_{5(g)} \rightleftharpoons SbCl_{3(g)} + Cl_{2(g)}$
   - (b) $2H_{2(g)} + 2NO_{(g)} \rightleftharpoons N_{2(g)} + 2H_2O_{(g)}$
   - (c) $2H_2S_{(g)} + CH_{4(g)} \rightleftharpoons 4H_{2(g)} + CS_{2(g)}$
2. I When 1.0 mol of ammonia gas is injected into a 0.50 L flask, the following reaction proceeds to equilibrium.

   $2NH_{3(g)} \rightleftharpoons N_{2(g)} + 3H_{2(g)}$

   At equilibrium, 0.30 mol of hydrogen gas is present.
   - (a) Calculate the equilibrium concentrations of $N_{2(g)}$ and $NH_{3(g)}$.
   - (b) What is the value of K_c?
3. I At a certain temperature, K_c for the following reaction between sulfur dioxide and nitrogen dioxide is 4.8.

   $SO_{2(g)} + NO_{2(g)} \rightleftharpoons NO_{(g)} + SO_{3(g)}$

   $SO_{2(g)}$ and $NO_{2(g)}$ have the same initial concentration: 0.36 mol/L. What amount of $SO_{3(g)}$ is present in a 5.0 L container at equilibrium?
4. I Phosphorus trichloride reacts with chlorine to form phosphorus pentachloride.

   $PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)}$

   0.75 mol of PCl_3 and 0.75 mol of Cl_2 are placed in a 8.0 L reaction vessel at 500 K. What is the equilibrium concentration of the mixture? The value of K_c at 500 K is 49.
5. MC Hydrogen gas has several advantages and disadvantages as a potential fuel. Hydrogen can be obtained by the thermal decomposition of water at high temperatures.

   $2H_2O_{(g)} \rightleftharpoons 2H_{2(g)} + O_{2(g)} \quad K_c = 7.3 \times 10^{-18}$ at 1000°C
   - (a) The initial concentration of water in a reaction vessel is 0.055 mol/L. What is the equilibrium concentration of $H_{2(g)}$ at 1000°C?
   - (b) Comment on the practicality of the thermal decomposition of water to obtain $H_{2(g)}$.

7.4 Predicting the Direction of a Reaction

Section Preview/ Specific Expectations

In this section, you will

- **explain** how to use Le Châtelier's principle to predict the direction in which a chemical system at equilibrium will shift when concentration changes
- **apply** Le Châtelier's principle to **make** and **test** predictions about how different factors affect a chemical system at equilibrium
- **communicate** your understanding of the following terms: *reaction quotient (Q_c), Le Châtelier's principle, common ion effect*

So far in this chapter, you have worked with reactions that have reached equilibrium. What if a reaction has not yet reached equilibrium, however? How can you predict the direction in which the reaction must proceed to reach equilibrium? To do this, you substitute the concentrations of reactants and products into an expression that is identical to the equilibrium expression. Because these concentrations may not be the concentrations that the equilibrium system would have, the expression is given a different name: the reaction quotient. The **reaction quotient**, $\boldsymbol{Q_c}$, is an expression that is identical to the equilibrium constant expression, *but* its value is calculated using concentrations that are not necessarily those at equilibrium.

The Relationship Between the Equilibrium Constant and the Reaction Quotient

Recall the general reaction $aP + bQ \rightleftharpoons cR + dS$. The reaction quotient expression for this reaction is

$$Q_c = \frac{[R]^c[S]^d}{[P]^a[Q]^b}$$

You can calculate a value for Q_c by substituting the concentration of each substance into this expression. If the value of Q_c is equal to K_c, the system must be at equilibrium. If Q_c is greater than K_c, the numerator must be very large. The concentrations of the chemicals on the right side of the equation must be more than their concentrations at equilibrium. In this situation, the system attains equilibrium by moving to the left. Conversely, if Q_c is less than K_c, the system attains equilibrium by moving to the right. Figure 7.8 summarizes these relationships between Q_c and K_c.

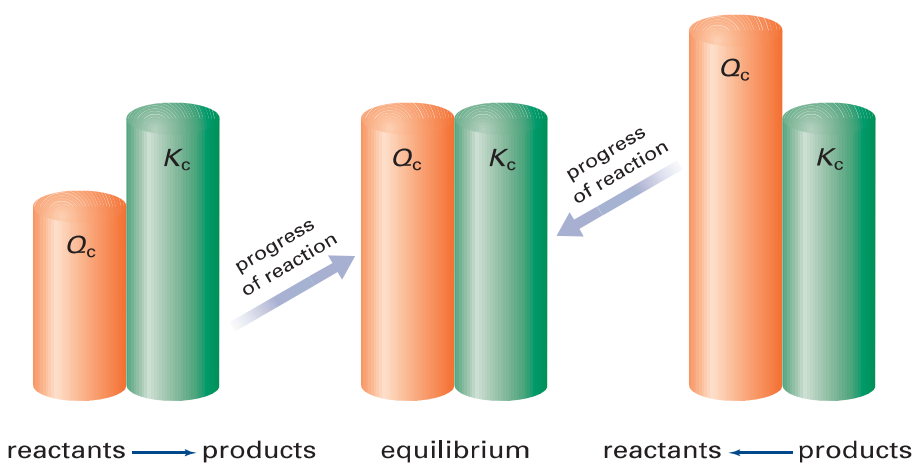


Figure 7.8 **This diagram shows how Q_c and K_c determine reaction direction. When $Q_c < K_c$, the system attains equilibrium by moving to the right, favouring products. When $Q_c = K_c$, the system is at equilibrium. When $Q_c > K_c$, the system attains equilibrium by moving to the left, favouring reactants.**

The next Sample Problem shows you how to calculate Q_c and interpret its value.

Sample Problem

Determining the Direction of Shift to Attain Equilibrium

Problem

Ammonia is one of the world's most important chemicals, in terms of the quantity manufactured. Some ammonia is processed into nitric acid and various polymers. Roughly 80% of ammonia is used to make fertilizers, such as ammonium nitrate. In the Haber process for manufacturing ammonia, nitrogen and hydrogen combine in the presence of a catalyst.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

At 500°C, the value of K_c for this reaction is 0.40. The following concentrations of gases are present in a container at 500°C: $[N_{2(g)}] = 0.10$ mol/L, $[H_{2(g)}] = 0.30$ mol/L, and $[NH_{3(g)}] = 0.20$ mol/L. Is this mixture of gases at equilibrium? If not, in which direction will the reaction go to reach equilibrium?

What Is Required?

You need to calculate Q_c and interpret its value.

What Is Given?

You have the balanced chemical equation. You know that the value of K_c is 0.40. You also know the concentrations of the gases: $[N_2] = 0.10$ mol/L, $[H_2] = 0.30$ mol/L, and $[NH_3] = 0.20$ mol/L.

Plan Your Strategy

Write the expression for Q_c, and then calculate its value. Compare the value of Q_c with the value of K_c. Decide whether the system is at equilibrium and, if not, in which direction the reaction will go.

Act on Your Strategy

$$Q_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$= \frac{(0.20)^2}{(0.10)(0.30)^3}$$

$$= 14.8$$

$$\therefore Q_c > 0.40$$

The system is not at equilibrium. The reaction will proceed by moving to the left.

Check Your Solution

Check your calculation of Q_c. (Errors in evaluating fractions with exponents are common.) The value of K_c is less than one, so you would expect the numerator to be less than the denominator. This is difficult to evaluate without a calculator, however, because of the powers.

Practice Problems

26. The following reaction takes place inside a cylinder with a movable piston.

$2NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$

At room temperature, the equilibrium concentrations inside the cylinder are $[NO_2] = 0.0206$ mol/L and $[N_2O_4] = 0.0724$ mol/L.

(a) Calculate the value of K_c.

(b) Calculate the concentration of each gas at the moment that the piston is used to halve the volume of the reacting mixture. Assume that the temperature remains constant.

(c) Determine the value of Q_c when the volume is halved.

(d) Predict the direction in which the reaction will proceed to re-establish equilibrium.

27. Ethyl acetate is an ester that can be synthesized by reacting ethanoic acid (acetic acid) with ethanol. At room temperature, the equilibrium constant for this reaction is 2.2.

$CH_3COOH_{(\ell)} + CH_3CH_2OH_{(\ell)} \rightleftharpoons CH_3COOCH_2CH_{3(l)} + H_2O_{(\ell)}$

Various samples were analyzed. The concentrations are given in the table below. Decide whether each sample is at equilibrium. If it is not at equilibrium, predict the direction in which the reaction will proceed to establish equilibrium.

Sample	$[CH_3COOH]$ (mol/L)	$[CH_3CH_2OH]$ (mol/L)	$[CH_3COOCH_2CH_3]$ (mol/L)	$[H_2O]$ (mol/L)
(a)	0.10	0.10	0.10	0.10
(b)	0.084	0.13	0.16	0.28
(c)	0.14	0.21	0.33	0.20
(d)	0.063	0.11	0.15	0.17

28. In the past, methanol was obtained by heating wood without allowing the wood to burn. The products were collected, and methanol (sometimes called "wood alcohol") was separated by distillation. Today methanol is manufactured by reacting carbon monoxide with hydrogen gas.

$CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(g)}$

At 210°C, K_c for this reaction is 14.5. A gaseous mixture at 210°C contains the following concentrations of gases: $[CO] = 0.25$ mol/L, $[H_2] = 0.15$ mol/L, and $[CH_3OH] = 0.36$ mol/L. What will be the direction of the reaction if the gaseous mixture reaches equilibrium?

Le Châtelier's Principle

What happens to a system at equilibrium if the concentration of one of the reacting chemicals is changed? This question has practical importance, because many manufacturing processes are continual. Products are removed and more reactants are added without stopping the process. For example, consider the Haber process that was mentioned in the previous Sample Problem.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

At 500°C, K_c is 0.40. The gases have the following concentrations: $[N_2] = 0.10$ mol/L, $[H_2] = 0.10$ mol/L, and $[NH_3] = 0.0063$ mol/L. (You can check this by calculating Q_c and making sure that it is equal to K_c.)

Ammonia can be removed from the equilibrium mixture by cooling because ammonia liquefies at a higher temperature than either nitrogen or hydrogen. What happens to an equilibrium mixture if some ammonia is removed? To find out, you need to calculate Q_c.

$$Q_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

If ammonia is removed from the equilibrium mixture, the numerator will decrease, so Q_c will be smaller than K_c. When $Q_c < K_c$, the system attains equilibrium by moving to the right. Why? The system must respond to the removal of ammonia by forming more ammonia. Similarly, if nitrogen, hydrogen, or both were added, the system would re-establish equilibrium by shifting to the right. As long as the temperature remains constant, the re-established equilibrium will have the same K_c as the original equilibrium.

A French chemist, Henri Le Châtelier, experimented with various chemical equilibrium systems. (See Figure 7.9.) In 1888, Le Châtelier summarized his work on changes to equilibrium systems in a general statement called **Le Châtelier's principle**. It may be stated as follows: *A dynamic equilibrium tends to respond so as to relieve the effect of any change in the conditions that affect the equilibrium.*

Le Châtelier's principle predicts the way that an equilibrium system responds to change. For example, when the concentration of a substance in a reaction mixture is changed, Le Châtelier's principle qualitatively predicts what you can show quantitatively by evaluating the reaction quotient. If products are removed from an equilibrium system, more products must be formed to relieve the change. This is just as you would predict, because Q_c will be less than K_c.

Le Châtelier's principle also predicts what will happen when other changes are made to an equilibrium system. For example, you can use Le Châtelier's principle to predict the effects of changing the volume of a cylinder that contains a mixture of gases, or the effects of changing the temperature of an equilibrium system. In the next investigation, you will use Le Châtelier's principle to predict the effects of making various changes to different equilibrium systems. The Chemistry Bulletin that follows the investigation considers applications of Le Châtelier's principle to areas outside of chemistry. Afterward, you will continue your studies of Le Châtelier's principle and equilibrium systems in chemistry.

Figure 7.9 **Henri Le Châtelier (1850–1936) specialized in mining engineering. He studied the thermodynamics involved in heating ores to obtain metals. His results led to important advances in the understanding of equilibrium systems.**

Electronic Learning Partner

Your Chemistry 12 Electronic Learning Partner can help you reinforce your understanding of Le Châtelier's principle.

Investigation 7-B

SKILL FOCUS

- Predicting
- Performing and recording
- Analyzing and interpreting

Perturbing Equilibrium

In this investigation, you will use Le Châtelier's principle to predict the effect of changing one factor in each system at equilibrium. Then you will test your prediction using a colour change or the appearance (or disappearance) of a precipitate.

Question

How can Le Châtelier's principle qualitatively predict the effect of a change in a chemical equilibrium?

Predictions

Your teacher will give you a table that lists four equilibrium systems and the changes you will make to each system. In the appropriate column, record your predictions for each test. If you predict that the change will cause the system to re-attain equilibrium by shifting toward the reactants, record "left." If you predict that the system will re-establish equilibrium by shifting toward the products, record "right."

Safety Precautions

- Potassium chromate and barium chloride are toxic.
- Hydrochloric acid and sodium hydroxide are corrosive. Wash any spills on your skin or clothing with plenty of cool water. Inform your teacher immediately.

Materials

Part 1

3 test tubes
0.1 mol/L $K_2CrO_{4(aq)}$
1 mol/L $HCl_{(aq)}$
1 mol/L $NaOH_{(aq)}$
1 mol/L $Fe(NO_3)_{3(aq)}$
1 mol/L $BaCl_{2(aq)}$

Part 2

25 mL beaker
2 test tubes
test tube rack
scoopula
0.01 mol/L $NH_{3(aq)}$
6.0 mol/L $HCl_{(aq)}$
phenolphthalein solution
$NH_4Cl_{(s)}$

Part 3

4 small test tubes
$CoCl_{2(s)}$
ethanol
concentrated $HCl_{(aq)}$ in a dropper bottle
0.1 mol/L $AgNO_{3(aq)}$ in a dropper bottle
distilled water in a dropper bottle
25 mL or 50 mL beaker
test tube rack
test tube holder
hot-water bath (prepared by your teacher)
cold-water bath (prepared by your teacher)

Part 4

small piece of copper
concentrated nitric acid
test tube
test tube rack
one-hole stopper
glass delivery tube
short length of rubber tubing
syringe with a cap or rubber stopper to seal the tip
$NO_{2(g)}/N_2O_{4(g)}$ tubes
boiling water
ice water

Procedure

Part 1 The Chromate/Dichromate Equilibrium

Equilibrium System

$$H^+_{(aq)} + 2CrO_4^{2-}{}_{(aq)} \rightleftharpoons Cr_2O_7^{2-}{}_{(aq)} + OH^-_{(aq)}$$

yellowish orange

1. Pour about 5 mL of 0.1 mol/L $K_2CrO_{4(aq)}$ into each of three test tubes. You will use test tube 1 as a colour reference.
2. Add 5 drops of $HCl_{(aq)}$ to test tube 2. Record any colour change.
3. Add 5 drops of $NaOH_{(aq)}$ to test tube 2. Record what happens.
4. Finally, add 5 drops of $Fe(NO_3)_{3(aq)}$ to test tube 2. A precipitate of $Fe(OH)_{3(s)}$ should form. Note the colour of the solution above the precipitate.
5. Add 5 drops of $BaCl_{2(aq)}$ to test tube 3. A precipitate of $BaCrO_{4(s)}$ should form. Record the colour of the solution above the precipitate.
6. Dispose of the chemicals as instructed by your teacher.

Part 2 Changes to a Base Equilibrium System

Safety Precautions

Ammonia and hydrochloric acid are corrosive. Wash any spills on your skin or clothing with plenty of cool water. Inform your teacher immediately.

Equilibrium System

$$NH_{3(aq)} + H_2O_{(\ell)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-_{(aq)}$$

1. Pour about 10 mL of $NH_{3(aq)}$ into a small beaker. Place the beaker on a sheet of white paper. Add 2 drops of phenolphthalein indicator.
2. Divide the solution equally into two small test tubes. To one of the test tubes, add a few small crystals of $NH_4Cl_{(s)}$ on the end of a scoopula. Record your observations.
3. To the other test tube, add a few drops of $HCl_{(aq)}$ until you see a change. Again note the colour change. (The H^+ ions combine with the OH^- ions, removing them from the equilibrium mixture.)
4. Dispose of the chemicals as instructed by your teacher.

Part 3 Concentration and Temperature Changes

Safety Precautions

- Concentrated hydrochloric acid is hazardous to your eyes, skin, and clothing. Treat spills with baking powder and copious amounts of cool water. Inform your teacher immediately.
- Ethanol is flammable. Keep samples of ethanol and the supply bottle away from open flames.

Equilibrium System

$$Co(H_2O)_6^{2+}{}_{(aq)} + 4Cl^-_{(aq)} \rightleftharpoons CoCl_4^{2-}{}_{(aq)} + 6H_2O_{(\ell)}$$

pink **blue or purple**

$$\Delta H = +50 \text{ kJ/mol}$$

1. Measure about 15 mL of ethanol into a small beaker.
2. Record the colour of the $CoCl_2$. Dissolve a small amount (about half the size of a pea) in the beaker of ethanol. The solution should be blue or purple. If it is pink, add drops of concentrated $HCl_{(aq)}$ until the solution is blue-purple.
3. Divide the cobalt solution equally among the four small test tubes. Put one of the test tubes aside as a control.
4. To each of the other three test tubes, add 3 drops of distilled water, one drop at a time. Stir after you add each drop. Record any change in colour that occurs with each drop.
5. To one of the test tubes from step 4, add 5 drops of concentrated HCl, one drop at a time with stirring. Record the results.

6. Silver and chloride ions combine to form a precipitate of AgCl. To the third test tube, add $AgNO_{3(aq)}$, one drop at a time, until no more precipitate appears. Record the colour of the solution as the chloride ions precipitate.
7. Record the colour of the liquid mixture in the fourth test tube. Use a test tube holder to immerse this test tube in the hot-water bath. Record any colour change.
8. Place the test tube from step 7 in the cold-water bath. Record any colour change.
9. Dispose of the chemicals as instructed by your teacher.

Part 4 Investigating Gaseous Equilibria

CAUTION These are not student tests. Your teacher may demonstrate this equilibrium if a suitable fume hood is available for the first test, and if sealed tubes containing a mixture of nitrogen dioxide, $NO_{2(g)}$, and dinitrogen tetroxide, $N_2O_{4(g)}$, are available for the second test. If either or both tests are not demonstrated, refer to the photographs that show the changes.

Safety Precautions

- Concentrated nitric acid is highly corrosive and a strong oxidizing agent.
- Nitrogen dioxide and dinitrogen tetroxide are poisonous gases.

Equilibrium System

$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)} \quad \Delta H = +59\ kJ/mol$

colourless **brown**

1. Your teacher will use sealed tubes that contain a mixture of $N_2O_{4(g)}$ and $NO_{2(g)}$. One tube will be placed in boiling water, and a second tube will be placed in ice water. A third tube (if available) will remain at room temperature as a control. Compare and record the colour of the gas mixture at each temperature.
2. $NO_{2(g)}$ can be prepared by reacting copper with concentrated nitric acid. The gas is poisonous. The reaction, if your teacher performs it, *must* take place in a fume hood.
3. By using a one-hole stopper, glass delivery tube, and a short length of rubber tubing, some $NO_{2(g)}$ can be collected in a syringe. The syringe is then sealed by attaching a cap or by pushing the needle into a rubber stopper.
4. Observe what happens when the syringe plunger is pressed down sharply, changing the volume of the equilibrium mixture. You will observe an immediate change in colour. Then, if the plunger is held in a fixed position, the colour will change over a few seconds as the system re-establishes equilibrium. Carefully record these colour changes.

These three tubes contain a mixture of $NO_{2(g)}$ and $N_2O_{4(g)}$. The tube on the left is in an ice-water mixture. The centre tube is at room temperature. The tube on the right is in boiling water. Given that $NO_{2(g)}$ is brown, can you explain the shift in equilibrium? Think about Le Châtelier's principle and the enthalpy of the reaction between the two gases.

Analysis

1. Compare the predictions you made using Le Châtelier's principle with the observations you made in your tests. Account for any differences.

2. In which tests did you increase the concentration of a reactant or a product? Did your observations indicate a shift in equilibrium to form more or less of the reactant or product?

3. In which tests did you decrease the concentration of a reactant or product? Did your observations indicate a shift in equilibrium to form more or less of the reactant or product?

4. In two of the systems you studied, the enthalpy changes were given.

   $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)} \quad \Delta H = +59 \text{kJ/mol}$

   $Co(H_2O)_6^{2+}{}_{(aq)} + 4Cl^-{}_{(aq)} \rightleftharpoons CoCl_4^{2-}{}_{(aq)} + 6H_2O_{(\ell)}$

   $\Delta H = +50 \text{ kJ/mol}$

   (a) Are these systems endothermic or exothermic when read from left to right?

   (b) When heated, did these systems shift to the left or to the right? In terms of the energy change, was the observed shift in equilibrium toward the endothermic or exothermic side of the reaction?

   (c) Do you think the value of K_c changed or remained the same when the equilibrium mixture was heated? Explain your answer.

5. Think about the $N_2O_{4(g)}/NO_{2(g)}$ equilibrium.

   (a) How was the total pressure of the mixture affected when the plunger was pushed down?

   (b) How was the pressure of the mixture affected by the total number of gas molecules in the syringe?

   (c) Explain the observed shift in equilibrium when the plunger was pushed down. In your explanation, refer to Le Châtelier's principle and the total amount of gas in the syringe.

   (d) What would be the effect, if any, on the following equilibrium system if the volume was reduced? Explain.

   $2IBr_{(g)} \rightleftharpoons I_{2(g)} + Br_{2(g)}$

Conclusion

6. How did your results compare with your predictions? Discuss and resolve any discrepancies with your class.

The sealed syringe contains a mixture of $NO_{2(g)}$ and $N_2O_{4(g)}$. The photograph on the left shows an equilibrium mixture at atmospheric pressure. The middle photograph shows that the plunger has been pushed down, increasing the pressure. Two changes cause the darker appearance of the gas mixture. First, the concentration of gases is greater. Second, decreasing the volume heats the gas. This causes a shift toward $NO_{2(g)}$. The photograph on the right shows the result a few seconds after the plunger was pushed down. The gas has cooled back to room temperature. The colour of the mixture is less brown, indicating a shift toward $N_2O_{4(g)}$.

Chemistry Bulletin

Science | Technology | Society | Environment

Le Châtelier's Principle: Beyond Chemistry

How is Le Châtelier's principle related to predator-prey interactions in ecosystems?

Le Châtelier's principle is a general statement about how any system in equilibrium—not just a chemical system—responds to change. Le Châtelier principle concerns the conservation of energy or matter. There are corresponding laws in several other areas of science.

Heinrich Lenz studied the direction of the current that is induced in a conductor as a result of changing the magnetic field near it. You can think of this as the change in a system in electromagnetic equilibrium. Lenz published his law in 1834. It states that when a conductor interacts with a magnetic field, there must be an induced current that opposes the interaction, because of the law of conservation of energy. Lenz's law is used to explain the direction of the induced current in generators, transformers, inductors, and many other systems.

In geology, John Pratt and George Airy introduced the idea of isostacy in 1855. Earth's crust is in gravitational equilibrium in almost all places. The crust responds to changes in the load on it, however, by slowly moving vertically. Examples of how the load on Earth's crust can change include the weathering of mountain ranges and the melting of ice caps. Geologists estimate that the ice over parts of Scandinavia and northern Europe was well over 2 km thick during the last ice age. As a result of the ice melting and the removal of the weight pushing down on Earth's crust, the central part of Scandinavia has risen over 500 m. This uplift is continuing. Here gravitational potential energy is being conserved.

In ecology, ecosystems are really examples of steady state systems. Ecosystems involve a flow of energy in only one direction, from the Sun. Nevertheless, populations of plants and animals develop stable numbers that react to external changes, such as disease and variations in the weather. For example, if the number of carnivores in an ecosystem increases, more herbivores are eaten and the herbivore population decreases. The carnivores then have difficulty finding food. *Their* populations decrease due to competition, emigration, and starvation until a new balance, however delicate, is attained.

Le Châtelier's principle also applies to biology. Homeostasis is the tendency of a body system to remain in a state of equilibrium. Examples of homeostasis include the maintenance of body temperature (homeothermy) and the pH balance of blood.

In economics, the law of supply and demand is similar to Le Châtelier's principle. When the price of a commodity, such as the price of a kilogram of apples, is constant, the market for the commodity is at equilibrium. If the supply of the commodity falls, the equilibrium is changed. The market adjusts by increasing the price, which tends to increase the supply.

Making Connections

1. Identify and describe two other examples, in science or other fields, that illustrate Le Châtelier's principle.
2. Draw diagrams to show the above examples of Le Châtelier's principle in human physiology, ecology, and economics. Show how different conditions affect the equilibrium and how the systems react to establish a new equilibrium.

The Effect of Ions on Aqueous Equilibrium Systems

Many important equilibrium systems involve ions in aqueous solution. The **common ion effect** applies Le Châtelier's principle to ions in aqueous solution. As its name suggests, the common ion effect involves adding an ion to a solution in which the ion is already present in solution. It is really a concentration effect. The equilibrium shifts away from the added ion, as predicted by Le Châtelier's principle.

An aqueous solution that contains certain ions can be added to another solution to form a precipitate, if the ions have low solubility. For example, adding silver nitrate solution to test for $Cl^-_{(aq)}$ is effective due to the very low solubility of silver chloride. You can use the precipitation of an insoluble salt to remove almost all of a particular ion from a solution and, as a result, cause a shift in the position of equilibrium of the original solution. The common ion effect is important in the solubility of salts. The precipitation of insoluble salts is used to identify the presence of unknown ions. You will learn more about the common ion effect in Chapter 9.

The Effect of Temperature Changes on the Position of Equilibrium

As you know, the value of the equilibrium constant changes with temperature, because the rates of the forward and reverse reactions are affected. Le Châtelier's principle still holds, however. It can be used to predict the effect of temperature changes on a system when the sign of the enthalpy change for the reaction is known. For example, the dissociation of sulfur trioxide is endothermic.

$$2SO_{3(g)} \rightleftharpoons 2SO_{2(g)} + O_{2(g)} \quad \Delta H = 197 \text{ kJ}$$

As the reaction proceeds from left to right, energy is absorbed by the chemical system and converted to chemical potential energy. If an equilibrium mixture of these gases is heated, energy is added to the system. Le Châtelier's principle predicts a shift that will relieve the imposed change. Therefore, the shift will tend to remove the added energy. This will happen if the equilibrium shifts to the right, increasing the amount of $SO_{2(g)}$ and $O_{2(g)}$ formed. As a result, the value of K_c will increase. The shift in equilibrium is consistent (as it must be) with the law of conservation of energy.

Suppose that the equilibrium of an endothermic reaction shifted to the left when the system was heated. From right to left, the reaction is exothermic. Thus, a shift to the left would release energy to the surroundings. This would make the mixture hotter. The equilibrium would shift still more to the left, releasing more and more energy. Clearly, this cannot happen without violating the law of conservation of energy.

The effect of temperature on the position of equilibrium can be summarized as follows:

- *Endothermic change* ($\Delta H > 0$): An increase in temperature shifts the equilibrium to the right, forming more products. The value of K_c increases. A decrease in temperature shifts the equilibrium to the left, forming more reactants. The value of K_c decreases.
- *Exothermic change* ($\Delta H < 0$): An increase in temperature shifts the equilibrium to the left, forming more reactants. The value of K_c decreases. A decrease in temperature shifts the equilibrium to the right, forming more products. The value of K_c increases.

CHEM FACT

Chickens have no sweat glands. When the temperature rises, they tend to breathe faster. This lowers the concentration of carbonate ions in their blood. Because eggshells are mostly calcium carbonate, faster-breathing chickens lay eggs with thinner shells. Rather than installing expensive air conditioning, chicken farmers can supply carbonated water for their chickens to drink when the temperature reaches "fowl" highs. How does this relate to Le Châtelier's principle?

The Effects of Volume and Pressure Changes on Equilibrium

When the volume of a mixture of gases decreases, the pressure of the gases must increase. Le Châtelier's principle predicts a shift in equilibrium to relieve this change. Therefore, the shift must tend to reduce the pressure of the gases. Molecules striking the walls of a container cause gas pressure, so a reduction in gas pressure at constant temperature must mean fewer gas molecules. Consider the following reaction again.

$$2SO_{3(g)} \rightleftharpoons 2SO_{2(g)} + O_{2(g)}$$

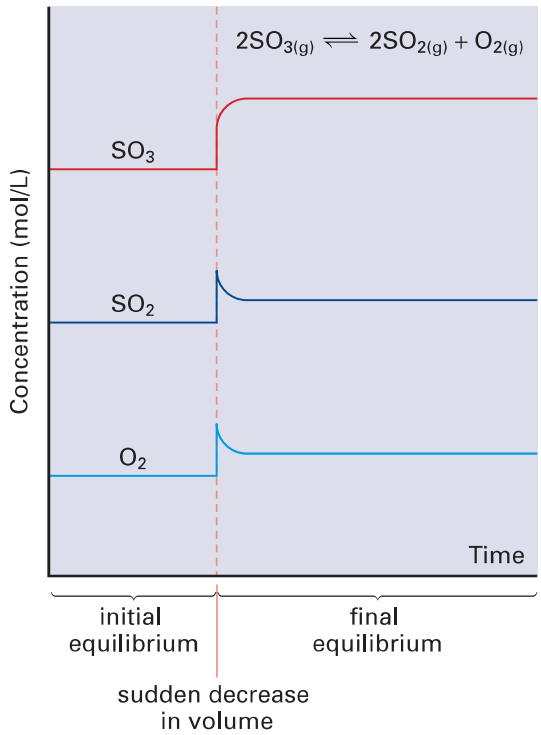


Figure 7.10 **Note the changes in the concentrations of the reacting gases. When the new equilibrium is established, the concentrations are different. Compare the concentrations of the gases in the first equilibrium and second equilibrium.**

There are two gas molecules on the left side of the equation. There are three gas molecules on the right side. Consequently, if the equilibrium shifts to the left, the pressure of the mixture will decrease. *Reducing the volume of an equilibrium mixture of gases, at constant temperature, causes a shift in equilibrium in the direction of fewer gas molecules.* What if there is the same number of gas molecules on both sides of the reaction equation? Changing the volume of the container, as shown in Figure 7.10, has no effect on the position of equilibrium. The value of K_c will be unchanged, as long as there is no change in temperature.

It is possible to increase the total pressure of gases in a rigid container by injecting more gas. If the injected gas reacts with the other gases in the equilibrium mixture, the effect is the same as increasing the concentration of a reactant. The equilibrium shifts to reduce the amount of added gas. If the injected gas does not react with the other gases (if an "inert" gas is added), there is no effect on the equilibrium. This is because the added gas is not part of the equilibrium system. Its addition causes no change in the volume of the container. Nitrogen (because of its low reactivity) and the noble gases are often used as inert gases. If the container expands when an inert gas is added, the effect is the same as increasing the volume and therefore decreasing the pressure of the reacting gases.

The Effect of a Catalyst on Equilibrium

A catalyst speeds up the *rate* of a reaction, either by allowing a different reaction mechanism or by providing additional mechanisms. The overall effect is to lower the activation energy, which increases the rate of reaction. The activation energy is lowered the same amount for the forward and reverse reactions, however. There is the same increase in reaction rates for both reactions. As a result, a catalyst does not affect the position of equilibrium. It only affects the time that is taken to achieve equilibrium.

Table 7.2 summarizes the effect of a catalyst, and other effects of changing conditions, on a system at equilibrium. The Sample Problem that follows provides an opportunity for you to use Le Châtelier's principle to predict the equilibrium shift in response to various conditions.

Table 7.2 The Effects of Changing Conditions on a System at Equilibrium

Type of reaction	Change to system	Effect on K_c	Direction of change
all reactions	increasing any reactant concentration, or decreasing any product concentration	no effect	toward products
	decreasing any reactant concentration, or increasing any product concentration	no effect	toward reactants
	using a catalyst	no effect	no change
exothermic	increasing temperature	decreases	toward reactants
	decreasing temperature	increases	toward products
endothermic	increasing temperature	increases	toward products
	decreasing temperature	decreases	toward reactants
equal number of reactant and product gas molecules	changing the volume of the container, or adding a non-reacting gas	no effect	no change
more gaseous product molecules than reactant gaseous molecules	decreasing the volume of the container at constant temperature	no effect	toward reactants
	increasing the volume of the container at constant temperature, or adding a non-reacting gas at contstant pressure	no effect	toward products
fewer gaseous product molecules than reactant gaseous molecules	decreasing the volume of the container at constant temperature	no effect	toward products
	increasing the volume of the container at constant temperature	no effect	toward reactants

Sample Problem

Using Le Châtelier's Principle

Problem

The following equilibrium takes place in a rigid container.

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)} \quad \Delta H = 56 \text{ kJ}$$

In which direction does the equilibrium shift as a result of each change?

(a) adding phosphorus pentachloride gas

(b) removing chlorine gas

(c) decreasing the temperature

(d) increasing the pressure by adding helium gas

(e) using a catalyst

What Is Required?

You need to determine whether each change causes the equilibrium to shift to the left or the right, or whether it has no effect.

What Is Given?

You have the balanced chemical equation. You know that the enthalpy change is 56 kJ. Therefore, the reaction is endothermic.

Continued ...

Continued ...

Plan Your Strategy

Identify the change. Then use the chemical equation to determine the shift in equilibrium that will minimize the change.

Act on Your Strategy

(a) $[PCl_5]$ increases. Therefore, the equilibrium must shift to minimize $[PCl_5]$. The reaction shifts to the right.

(b) $[Cl_2]$ is reduced. Therefore, the equilibrium must shift to increase $[Cl_2]$. The reaction shifts to the right.

(c) The temperature decreases. Therefore, the equilibrium must shift in the direction in which the reaction is exothermic. From left to right, the reaction is endothermic. Thus, the reaction must be exothermic from right to left. The reaction shifts to the left if the temperature is decreased.

(d) Helium does not react with any of the gases in the mixture. The position of equilibrium does not change.

(e) A catalyst has no effect on the position of equilibrium.

Check Your Solution

Check the changes. Any change that affects the equilibrium reaction must result in a shift that minimizes it.

Practice Problems

29. Consider the following reaction.

$H_{2(g)} + I_{2(g)} + 52\ kJ \rightleftharpoons 2HI_{(g)}$

In which direction does the equilibrium shift if there is an increase in temperature?

30. A decrease in the pressure of each equilibrium system below is caused by increasing the volume of the reaction container. In which direction does the equilibrium shift?

(a) $CO_{2(g)} + H_{2(g)} \rightleftharpoons CO_{(g)} + H_2O_{(g)}$

(b) $2NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$

(c) $2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)}$

(d) $CH_{4(g)} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + 4H_{2(g)}$

31. The following reaction is exothermic.

$2NO_{(g)} + 2H_{2(g)} \rightleftharpoons N_{2(g)} + 2H_2O_{(g)}$

In which direction does the equilibrium shift as a result of each change?

(a) removing the hydrogen gas

(b) increasing the pressure of gases in the reaction vessel by decreasing the volume

(c) increasing the pressure of gases in the reaction vessel by pumping in argon gas while keeping the volume of the vessel constant

(d) increasing the temperature

(e) using a catalyst

32. In question 31, which changes affect the value of K_c? Which changes do not affect the value of K_c?

33. Toluene, C_7H_8, is an important organic solvent. It is made industrially from methyl cyclohexane.

$$C_7H_{14(g)} \rightleftharpoons C_7H_{8(g)} + 3H_{2(g)}$$

The forward reaction is endothermic. State three different changes to an equilibrium mixture of these reacting gases that would shift the equilibrium toward greater production of toluene.

Applying Le Châtelier's Principle: Manufacturing Ammonia

Industrial processes must be run at optimal conditions to be economic. This means more than simply manipulating the reaction conditions to maximize the extent of the reaction. Business people, and the professionals they hire to advise them, must consider other factors as well. These factors include the rate of the reaction, safety, the location of the plant, the cost to build and operate the plant, the cost of acquiring reactant materials, the cost of transporting products, and the cost of hiring, educating, and maintaining plant workers.

The chapter introduction mentioned the importance of nitrogen to plants and animals. Despite nitrogen's abundance in the atmosphere, its low reactivity means that there is a limited supply in a form that organisms can use. In nature, bacteria and the energy of lightning supply the nitrates and other nitrogen compounds that plants need to survive. Humans use technology to produce these compounds for our extensive agricultural industry.

In this chapter, you learned about the Haber process for manufacturing ammonia. You used this process to help you understand various concepts related to equilibrium. As you can see in Figure 7.11, ammonia is a valuable industrial chemical. Its annual global production is well over 100 million tonnes. The vast majority of ammonia, roughly 80%, is used to make fertilizers. You will now examine how the equilibrium concepts you have been studying work together to provide society with a reliable, cost-effective supply of ammonia.

Before World War I, the main source of nitrates for human use was from large deposits of bird droppings in Peru and sodium nitrate from Chile. These sources were becoming scarce and expensive. Then Fritz Haber (1868–1934), a lecturer in a technical college in Germany, began to experiment with ways to manufacture ammonia. Haber knew that ammonia could be easily converted to nitrates and other useful nitrogen

Unit Issue Prep

To begin preparing for the Unit 4 Issue, make a simplified sketch of the carbon cycle,

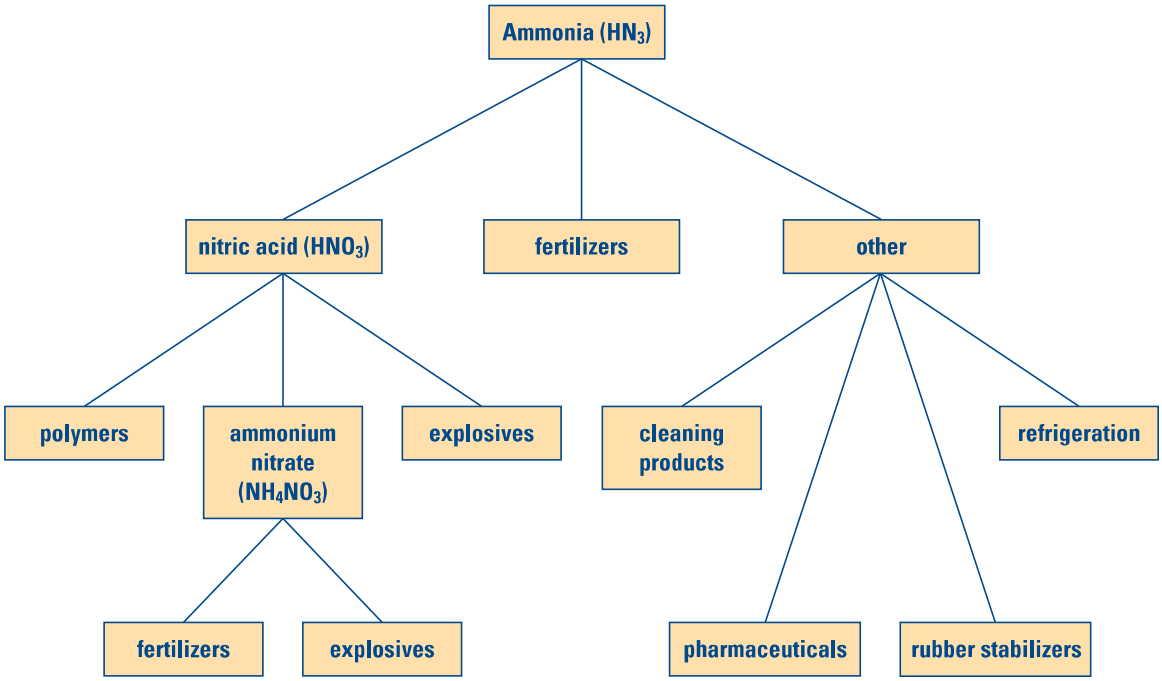


Figure 7.11 **Because ammonia is used to manufacture many essential products, it is one of the top five industrial chemicals in the world.**

compounds. What he needed was a method for producing large quantities of ammonia at minimal cost.

Haber experimented with the direct synthesis of ammonia.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \quad \Delta H^\circ = -92 \text{ kJ/mol}$$

Because the reaction is exothermic, heat is released as the reaction proceeds. Le Châtelier's principle predicts that the yield of ammonia is greater at lower temperatures. Just as in the contact process for manufacturing sulfuric acid, however, high yield is not the only important factor. The rate of reaction for ammonia synthesis is too slow at low temperatures.

Le Châtelier's principle also predicts that the yield of ammonia is greater at higher pressures. High-pressure plants are expensive to build and maintain, however. In fact, the first industrial plant that manufactured ammonia had its reaction vessel blow up. A German chemical engineer, Carl Bosch, solved this problem by designing a double-walled steel vessel that could operate at several hundred times atmospheric pressure. Modern plants operate at pressures in the range of 20 200 kPa to 30 400 kPa.

The gas mixture is kept pressurized in a condenser. (See Figure 7.12.) Ammonia is removed from the reaction vessel by cooling the gas mixture. Because of the hydrogen bonding between ammonia molecules, the gas condenses into a liquid while the nitrogen and hydrogen remain as gases. Nitrogen is removed to shift the equilibrium toward the production of more ammonia. Once the ammonia is removed, the gases are recycled back to the reaction vessel in a continuous operation.

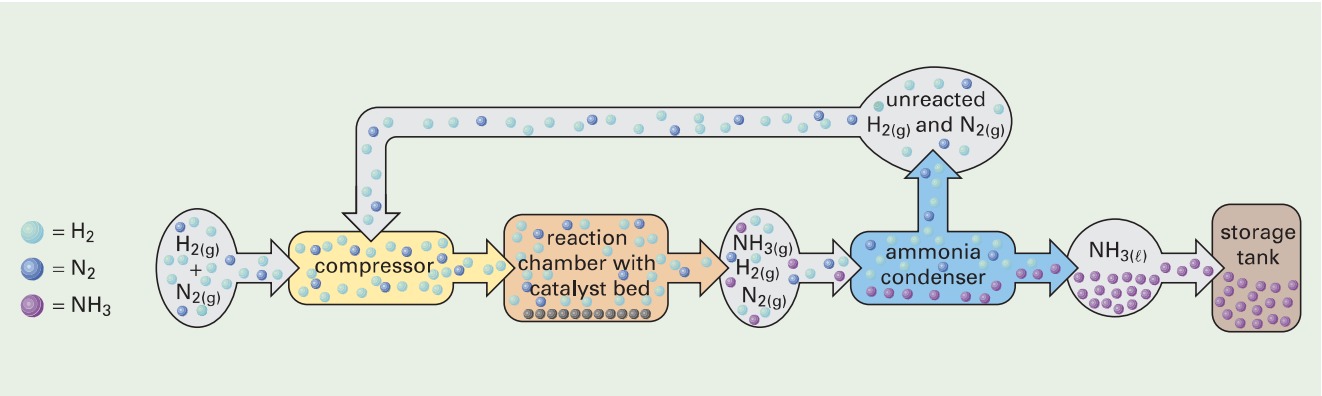


Figure 7.12 **This diagram shows the stages in the Haber-Bosch process for manufacturing ammonia. The catalyst is a mixture of MgO, Al_2O_3, and SiO_2, with embedded iron crystals.**

By manipulating the pressure and removing ammonia from the reaction vessel, Haber successfully increased the yield of ammonia. To increase the rate of the reaction, Haber needed to find a catalyst. A catalyst would allow the reaction to proceed at higher temperatures—a compromise between rate and yield. Some historians claim that Haber performed more than 6500 experiments trying to find a suitable catalyst. He finally chose an iron catalyst. This catalyst works well at the relatively moderate temperature of 400°C that is used for the reaction. It lasts about five years before losing its effectiveness.

Haber received the Nobel prize for Chemistry in 1918. Bosch received a Nobel prize in 1931 for his work on high pressure reactions. Today the Haber-Bosch process is used to manufacture virtually all the ammonia that is produced in the world. Plants are usually located near a source of natural gas, which is used to obtain the hydrogen gas.

$$CH_{4(g)} + H_2O_{(g)} \rightarrow CO_{(g)} + 3H_{2(g)}$$

The other raw material is air, which provides an inexhaustible supply of nitrogen gas.

CHEM FACT

During World War I, Haber helped to develop the technology for deploying phosgene, chlorine, and mustard gas as weapons of chemical warfare. His wife Clara, also a chemist, was disgusted by the use of science in war. When her husband refused to stop his support of the war effort, she committed suicide.

Section Summary

In this section, you learned that the expression for the reaction quotient is the same as the expression for the equilibrium constant. The concentrations that are used to solve these expressions may be different, however. When Q_c is less than K_c, the reaction proceeds to form more products. When Q_c is greater than K_c, the reaction proceeds to form more reactants. These changes continue until Q_c is equal to K_c. Le Châtelier's principle describes this tendency of a chemical system to return to equilibrium after a change moves it from equilibrium. The industrial process for manufacturing ammonia illustrates how chemical engineers apply Le Châtelier's principle to provide the most economical yield of a valuable chemical product.

K_c is only one of several equilibrium constants that chemists use to describe chemical systems. In the next chapter, you will learn how equilibrium applies to chemical systems that involve acids and bases.

Web LINK

www.mcgrawhill.ca/links/chemistry12

Sulfuric acid, methanol, and polystyrene are other industrially important chemicals that depend on equilibrium reactions for their production. Choose one of these chemicals, or another industrial chemical. Research methods that are used to produce it, as well as the products that are derived from it. To start your research, go to the web site above and click on **Web Links**. Prepare a report that outlines what you learned.

Section Review

1 I In which direction does the equilibrium shift as a result of the change to each homogeneous equilibrium system?

(a) Adding $Cl_{2(g)}$: $2Cl_{2(g)} + O_{2(g)} \rightleftharpoons 2Cl_2O_{(g)}$

(b) Removing $N_{2(g)}$: $2NO_{2(g)} \rightleftharpoons N_{2(g)} + 2O_{2(g)}$

(c) Using a catalyst: $CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$

(d) Decreasing the total volume of the reaction container: $2NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$

(e) Increasing the temperature: $CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)}$ $\Delta H = -230$ kJ

2 I For each reversible reaction, determine whether the forward reaction is favoured by high temperatures or low temperatures.

(a) $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ $\Delta H = +59$ kJ

(b) $2ICl_{(g)} \rightleftharpoons I_{2(g)} + Cl_{2(g)}$ $\Delta H = -35$ kJ

(c) $2CO_{2(g)} + 566\text{ kJ} \rightleftharpoons 2CO_{(g)} + O_{2(g)}$

(d) $2HF_{(g)} \rightleftharpoons H_{2(g)} + F_{2(g)}$ $\Delta H = -536$ kJ

3 I In each reaction, the volume of the reaction vessel is decreased. What is the effect (if any) on the position of equilibrium?

(a) $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$

(b) $4HCl_{(g)} + O_{2(g)} \rightleftharpoons 2Cl_{2(g)} + 2H_2O_{(g)}$

(c) $2H_2S_{(g)} + CH_{4(g)} \rightleftharpoons 4H_{2(g)} + CS_{2(g)}$

(d) $2CH_3COOH_{(aq)} + Ba(OH)_{2(aq)} \rightleftharpoons Ba(CH_3COO)_{2(aq)} + 2H_2O_{(\ell)}$

4 MC As you learned, the Haber process is used to produce ammonia.

(a) Write the chemical equation for the Haber process.

(b) Describe three changes that would increase the yield of ammonia, and explain why.

5 MC A key step in the production of sulfuric acid is the conversion of sulfur dioxide to sulfur trioxide. This step is exothermic.

(a) Write the chemical equation for this step, showing the sign of ΔH.

(b) Describe three changes that would increase the yield of sulfur trioxide.

(c) Explain why the reaction is carried out at a relatively high temperature.

(d) Why is a catalyst (vanadium pentoxide) used?

Careers in Chemistry

Anesthesiology: A Career in Pain Management

Laila Rafik Karwa

Dr. Laila Rafik Karwa is a specialist in pain. She prevents it, manages it, and alleviates it. She is an anesthesiologist.

Anesthesiologists are medical doctors who are responsible for inducing sleep before surgery, and for managing patients' pain before, during, and after surgery. Anesthesiologists are also involved in managing pain in patients who have severe illnesses, or acute or chronic pain. For example, Karwa's areas of interest include pediatric and obstetric anesthesia and acute pain management.

Anesthesiologists must have an intimate knowledge of the chemical and physical properties of gases. Many anesthetics are inhaled and are delivered to the bloodstream by diffusion. The speed at which diffusion occurs between the lungs, the blood, and other tissues of the body depends on a constant called the *partition coefficient*. This constant is a ratio that describes the equilibrium concentrations of a solute that is dissolved in two separate phases. The solute becomes separated (partitioned) between the two solvents in such a way that its concentration in one is directly proportional to its concentration in the other.

Gases diffuse from areas of high concentration to areas of low concentration. The speed at which diffusion occurs in the body depends on partition coefficients. The faster the concentration in the lung and brain tissues reaches the inhaled concentration of an anesthetic, the sooner a patient is induced.

Dr. Karwa enjoys the immediate gratification that comes with anesthesiology and the speed at which the anesthetics exact their effects. "What I like most about my job is the ability to let patients have their surgery being completely unaware of it, and to make them as pain-free as possible during and after surgery," she says. She chose medicine as a career because she was interested in biology and because she wanted to help other people with their health problems, after witnessing her father's struggles with rheumatic heart disease.

Dr. Karwa completed high school in Bombay, India, and later studied medicine at the University of Bombay. After medical school, she immigrated to Canada. She completed residency training in anesthesia at the University of Toronto and now works at St. Joseph's Health Science Centre as a staff anesthesiologist.

In Canada, students who are interested in a career as an anesthesiologist must complete two to three years of university before applying to medical school. Many medical schools in Canada require applicants to have taken courses in specific subjects in the biological and physical sciences, and to have some background in the humanities or social sciences. This education also helps students prepare for the Medical College Admissions Test (MCAT), which is required for application to most medical schools. The MCAT tests an applicant's aptitude for science, verbal reasoning, and writing. Most medical school programs in Canada are four years long.

Medical school graduates who decide to do specialty training in anesthesiology must complete a postgraduate residency program, which usually takes at least five years.

Making Career Connections

1. Although anesthesiologists tend to be associated with surgery, they also work outside the confines of the operating room. Research other locations where you might find an anesthesiologist.
2. Anesthetics are powerful medications. What risks to patients' health do anesthesiologists have to consider when they administer anesthetics?
3. Anesthetics are classified into three main groups: general, regional, and local. Research the criteria for this classification, and explain the distinctions.

CHAPTER 7 Review

Reflecting on Chapter 7

Summarize this chapter in the format of your choice. Here are a few ideas to use as guidelines:

- State the four conditions that apply to all equilibrium systems. Give examples to illustrate these conditions.
- Identify conditions that favour a reaction, and explain how they are related to equilibrium.
- Describe how enthalpy and entropy are related to chemical equilibrium.
- Compare the first and second laws of thermodynamics.
- Use experimental data to determine an equilibrium constant for concentration.
- Describe how to use an ICE table to solve problems that involve K_c.
- Compare Q_c and K_c to determine the direction of a chemical reaction.
- Explain the meaning of a small value of K_c.
- Use Le Châtelier's principle to predict the direction of a reaction.
- Outline the effects of changing conditions on a chemical system at equilibrium.
- Summarize the use of equilibrium and Le Châtelier's principle in industrial processes, such as the production of ammonia and sulfuric acid.

Reviewing Key Terms

For each of the following terms, write a sentence that shows your understanding of its meaning.

equilibrium
homogeneous equilibrium
heterogeneous equilibrium
favourable change
entropy (S)
second law of thermodynamics
free energy
law of chemical equilibrium
equilibrium constant (K_c)
ICE table
reaction quotient (Q_c)
Le Châtelier's principle
common ion effect

Knowledge/Understanding

1. Explain the difference between the rate of a reaction and the extent of a reaction.
2. At equilibrium, there is no overall change in the concentrations of reactants and products. Why, then, is this state described as dynamic?
3. For a reaction that goes to completion, is K_c very large or very small? Explain why.
4. In a chemical reaction, the change in enthalpy and the change in entropy are determined by the nature of the compounds involved.
   (a) What signs of ΔH and ΔS indicate that both factors contribute to a favourable reaction?
   (b) What signs of ΔH and ΔS indicate that both factors combine to make a reaction unfavourable?
5. Name the factors that can affect the equilibrium of a reaction.
6. Increasing temperature tends to increase the solubility of a solid in a liquid, but it tends to decrease the solubility of gases. Explain why.
7. The following reaction is at equilibrium. Which condition will produce a shift to the right: a decrease in volume or a decrease in temperature? Explain why.
   $H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)} + \text{heat}$
8. The following system is at equilibrium. Will an increase in pressure result in a shift to the left or to the right? How do you know?
   $2CO_{2(g)} \rightleftharpoons 2CO + O_{2(g)}$
9. Consider the following reaction.
   $CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)}$
   (a) The volume and temperature are kept constant, but the pressure on the system is increased. Explain how this affects the concentration of the reactants and products, and the direction in which the equilibrium shifts.
   (b) When equilibrium has been re-established, which substance(s) will show an increase in concentration?

Inquiry

10. The following equation represents the dissociation of hydrogen iodide gas. At 430°C, the value of K_c is 0.20.

$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{(g)}$

Some $HI_{(g)}$ is placed in a closed container at 430°C. Analysis at equilibrium shows that the concentration of $I_{2(g)}$ is 5.6×10^{-4} mol/L. What are the equilibrium concentrations of $H_{2(g)}$ and $HI_{(g)}$?

11. The oxidation of sulfur dioxide to sulfur trioxide is an important reaction. At 1000 K, the value of K_c is 3.6×10^{-3}.

$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

A closed flask originally contains 1.7 mol/L $SO_{2(g)}$ and 1.7 mol/L $O_{2(g)}$. What is $[SO_3]$ at equilibrium when the reaction vessel is maintained at 1000 K?

12. Ethanol and propanoic acid react to form the ester ethyl propanoate, which has the odour of bananas.

$CH_3CH_2OH_{(\ell)} + CH_3CH_2COOH_{(\ell)} \rightleftharpoons CH_3CH_2COOCH_2CH_3 + H_2O_{(\ell)}$

At 50°C, K_c for this reaction is 7.5. If 30.0 g of ethanol is mixed with 40.0 g of propanoic acid, what mass of ethyl propanoate will be present in the equilibrium mixture at 50°C?

Hint: Calculate the initial amounts of the reactants. Then solve the equilibrium equation using amounts instead of concentrations. The volume of the mixture does not affect the calculation.

13. 0.50 mol of $CO_{(g)}$ and 0.50 mol of $H_2O_{(g)}$ are placed in a 10 L container at 700 K. The following reaction occurs.

$CO_{(g)} + H_2O_{(g)} \rightleftharpoons H_{2(g)} + CO_{2(g)} \quad K_c = 8.3$

What is the concentration of each gas that is present at equilibrium?

14. Sulfur atoms combine to form molecules that have different numbers of atoms depending on the temperature. At about 1050°C, the following dissociation occurs.

$S_{8(g)} \rightleftharpoons 4S_{2(g)}$

The initial concentration of $S_{8(g)}$ in a flask is 9.2×10^{-3} mol/L, and the equilibrium concentration of the same gas is 2.3×10^{-3} mol/L. What is the value of K_c?

15. Perpetual motion machines seem to be a favourite project for inventors who do not understand the second law of thermodynamics. Design a simple machine that, once started, would recycle energy and, according to the first law of thermodynamics, should carry on forever. Why does the second law of thermodynamics rule out the possibility of ever making a perpetual motion machine?

16. Consider an equilibrium in which oxygen gas reacts with gaseous hydrogen chloride to form gaseous water and chlorine gas. At equilibrium, the gases have the following concentrations:

$[O_2] = 8.6 \times 10^{-2}$ mol/L,
$[HCl] = 2.7 \times 10^{-2}$ mol/L,
$[H_2O] = 7.8 \times 10^{-3}$ mol/L,
$[Cl_2] = 3.6 \times 10^{-3}$ mol/L.

(a) Write a balanced chemical equation for this reaction.

(b) Calculate the value of the equilibrium constant.

17. Sulfur trioxide gas reacts with gaseous hydrogen fluoride to produce gaseous sulfur hexafluoride and water vapour. The value of K_c is 6.3×10^{-3}.

(a) Write a balanced chemical equation for this reaction.

(b) 2.9 mol of sulfur trioxide is mixed with 9.1 mol of hydrogen fluoride in a 4.7 L flask. Set up an equation to determine the equilibrium concentration of sodium hexafluoride.

(c) Explain why you are likely unable to solve this equation.

18. The following results were collected for two experiments that involve the reaction, at 600°C, between gaseous sulfur dioxide and oxygen to form gaseous sulfur trioxide. Show that the value of K_c was the same in both experiments.

Experiment 1		Experiment 2	
Initial concentration (mol/L)	Equilibrium concentration (mol/L)	Initial concentration (mol/L)	Equilibrium concentration (mol/L)
$[SO_2] = 2.00$	$[SO_2] = 1.50$	$[SO_2] = 0.500$	$[SO_2] = 0.590$
$[O_2] = 1.50$	$[O_2] = 1.25$	$[O_2] = 0$	$[O_2] = 0.0450$
$[SO_3] = 3.00$	$[SO_3] = 3.50$	$[SO_3] = 0.350$	$[SO_3] = 0.260$

19. Write the chemical equation for the reversible reaction that has the following equilibrium expression.

$$K_c = \frac{[NO]^4[H_2O]^6}{[NH_3]^4[O_2]^5}$$

Assume that, at a certain temperature, [NO] and $[NH_3]$ are equal. Also assume that $[H_2O] = 2.0$ mol/L and $[O_2] = 3.0$ mol/L. What is the value of K_c at this temperature?

Communication

20. Discuss the following statements, which are attributed to the chemist Harry Bent:
    - The first law of thermodynamics says you cannot win, you can only break even.
    - The second law of thermodynamics says you cannot break even.

21. Equal amounts of hydrogen gas and iodine vapour are heated in a sealed flask.
    (a) Sketch a graph to show how $[H_{2(g)}]$ and $[HI_{(g)}]$ change over time.
    (b) Would you expect a graph of $[I_{2(g)}]$ and $[HI_{(g)}]$ to appear much different from your first graph? Explain why.
    (c) How does the value of Q_c change over time for this reaction?

22. A younger student in your school wants to grow a crystal of copper(II) sulfate. Write a short explanation that outlines how the student can use a small crystal and a saturated solution of copper(II) sulfate to grow a larger crystal.

Making Connections

23. The tendency of systems to reach a maximum state of entropy has been applied to the social sciences. Does the second law of thermodynamics help to explain the increase in garbage on the streets? Justify your answer.

24. At 25°C, the value of K_c for the reaction between nitrogen and oxygen is 4.7×10^{-31}:

    $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)} \quad K_c = 4.7 \times 10^{-31}$

    Assuming that air is composed of 80% nitrogen by volume and 20% oxygen by volume, estimate the concentration of nitric oxide to be expected in the atmosphere. Why is the actual [NO] usually greater?

25. One of the steps in the Ostwald process for the production of nitric acid involves the oxidation of ammonia.

    $4NH_{3(g)} + 5O_{2(g)} \rightleftharpoons 4NO_{(g)} + 6H_2O_{(g)} \quad \Delta H = -905$ kJ

    (a) State the reaction conditions that favour the production of nitrogen monoxide.
    (b) A rhodium/platinum alloy is used as a catalyst. What effect does the catalyst have on the rate of reaction? What effect does the catalyst have on the position of equilibrium?
    (c) Explain why the reaction temperature is relatively high, typically about 900°C.
    (d) A relatively low pressure of about 710 kPa is used. Suggest why.
    (e) In the next step of the Ostwald process, nitrogen monoxide is mixed with air to form nitrogen dioxide.

    $2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)} \quad \Delta H = -115$ kJ

    Why are the gases cooled for this reaction? What do you think happens to the heat that is extracted?
    (f) Finally, the nitrogen dioxide reacts with water to form nitric acid.

    $3NO_{2(g)} + H_2O_{(\ell)} \rightleftharpoons 2HNO_{3(aq)} + NO_{(g)}$

    What is done with the $NO_{(g)}$ that is formed? Name three uses of this product.

26. Polystyrene is one of our most useful polymers. Polystyrene resin is manufactured from styrene, which is made as follows:

    $C_6H_5CH_2CH_{3(g)} + 123\text{ kJ} \rightleftharpoons C_6H_5CHCH_{2(g)} + H_{2(g)}$

    (a) Predict the effects (if any) on this equilibrium if the following changes are made:
    - increasing the applied pressure
    - removing styrene
    - reducing the temperature
    - adding a catalyst
    - adding helium

27. (a) Based on your predictions in question 26, select the conditions that would maximize the equilibrium yield of styrene.
    (b) Why are the conditions you selected unlikely to be used by industry? What conditions must be used to maximize the yield of an industrial process?

(c) In practice, the pressure of the ethyl benzene is kept low. An inert substance—super-heated steam—is added to keep the total pressure of the mixture at atmospheric pressure. What advantage does this method have over running the reaction without the steam at a pressure that is less than atmospheric pressure?

(d) The super-heated steam supplies energy to the system. Why is this desirable? It also reacts with any carbon that is formed as a by-product at high temperatures, preventing the carbon from contaminating the catalyst. What products are formed as a result of the reaction between carbon and steam?

(e) What is the advantage of using super-heated steam at 600°C rather than ordinary steam at 100°C?

(f) In practice, an iron oxide catalyst is used. Explain why this is desirable.

(g) At 600°C, with an iron oxide catalyst, the conversion is only about 35% complete. The yield could be increased by raising the temperature. Suggest two plausible reasons why this is not done.

(h) The ethyl benzene that has not reacted is separated from the styrene by fractional distillation. The boiling point of ethyl benzene is 136°C, and the boiling point of styrene is 146°C. The styrene, of course, is used to make polystyrene. What is done with the ethyl benzene?

Answers to Practice Problems and Short Answers to Section Review Questions

Practice Problems: **1.** $K_c = \frac{[CH_3COOCH_2CH_3][H_2O]}{CH_3CH_2OH][CH_3COOH]}$ **2.** $K_c = \frac{[NO]^2}{[N_2][O_2]}$ **3.** $K_c = \frac{[H_2O]^2}{[H_2]^2[O_2]}$ **4.** $K_c = \frac{[Fe^{2+}]^2[I_2]}{[Fe^{3+}]^2[I^-]^2}$ **5.** $K_c = \frac{[NO]^4[H_2O]^6}{[NH_3]^4[O_2]^5}$ **6.** 1.9×10^{-2} **7.** 1.2×10^2 **8.** 0.013 **9.** 2.4×10^{-4} **10.** 0.15 **11.** $[I_2] = [Cl_2] = 0.015$ mol/L; $[ICl] = 14$ mol/L **12.** HF = 0.11 mol **13.** $[SO_3] = 0.089$ mol/L **14.** $[CO] = 0.011$ mol/L; $[Cl_2] = 0.014$ mol/L; $[COCl_2] = 3.1 \times 10^{-5}$ mol/L **15.** $[HBr] = 0.045$ mol/L; $[H_2] = [Br_2] = 2.9 \times 10^{-6}$ mol/L **16.** 1100 K **17.** III, II, I **18.(a)** completion **(b)** no reaction **(c)** completion **19.** $Ag(NH_3)_2]^+_{(aq)}$ **20.** essentially no dissociation **21.** $[CO] = [Cl_2] = 1.8 \times 10^{-4}$ mol/L **22.** $[H_2] = 8.6 \times 10^{-2}$ mol/L **23.** 6.1×10^{-5} mol **24.** $[NO] = 1.2 \times 10^{-5}$ mol/L **25.** $[CO_2] = 0.59$ mol/L; $[CO] = 1.1 \times 10^{-2}$ mol/L; $[O_2] = 5.6 \times 10^{-3}$ mol/L **26.(a)** $K_c = 171$ **(b)** $[NO_2] = 0.0412$ mol/L; $[N_2O_4] = 0.145$ mol/L **(c)** $Q_c = 85.3$ **(d)** right **27.(a)** right **(b)** left **(c)** at equilibrium **(d)** left **28.** left **29.** right **30.(a)** no change **(b)** left **(c)** right **(d)** right **31.(a)** left **(b)** right **(c)** no change **(d)** left **(e)** no change **32.** Only (d) changes the value of K_c. **33.** adding methyl cyclohexane; removing toluene; decreasing the pressure; increasing the temperature

Section Review: 7.2: **3.(a)** increases **(b)** decreases **(c)** increases **(d)** decreases **(e)** increases **4.(a)** + **(b)** − **(c)** − **(d)** − **(e)** +

7.3: **1.(a)** $\frac{[SbCl_3][Cl_2]}{[SbCl_5]}$ **(b)** $\frac{[N_2][H_2O]^2}{[H_2]^2[NO]^2}$ **(c)** $\frac{[H_2]^4[CS_2]}{[H_2S]^2[CH_4]}$ **2.(a)** $[N_2] = 0.20$ mol/L; $[NH_3] = 1.6$ mol/L **(b)** $K_c = 0.017$ **3.** 1.2 mol **4.** $[PCl_3] = [Cl] = 0.035$ mol/L; $[PCl_5] = 0.059$ mol/L **5.(a)** $[H_2] = 3.5 \times 10^{-7}$ mol/L **(b)** an impractical method **7.4:** **1.(a)** right **(b)** right **(c)** unchanged **(d)** right **(e)** left **2.(a)** high temperatures **(b)** low temperatures **(c)** high temperatures **(d)** low temperatures **3.(a)** unchanged **(b)** right **(c)** left **(d)** unchanged (because liquid volumes are largely unaffected by pressure changes) **4.(a)** $N_2 + 3H_2 \rightleftharpoons 2NH_3$ **(b)** adding N_2 or H_2; removing NH_3; increasing the pressure; lowering the temperature (because the reaction is exothermic)