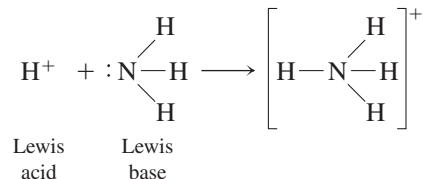
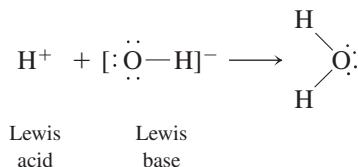


Note that Brønsted–Lowry acid–base reactions (proton donor–proton acceptor reactions) are encompassed by the Lewis model. For example, the reaction between a proton and an ammonia molecule, that is,

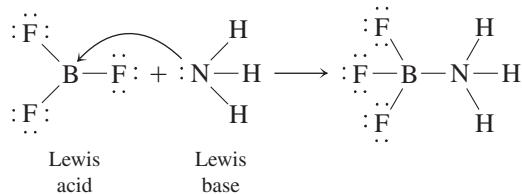


can be represented as a reaction between an electron-pair acceptor (H^+) and an electron-pair donor (NH_3). The same holds true for a reaction between a proton and a hydroxide ion:



The Lewis model encompasses the Brønsted–Lowry model, but the reverse is not true.

The real value of the Lewis model for acids and bases is that it covers many reactions that do not involve Brønsted–Lowry acids. For example, consider the gas-phase reaction between boron trifluoride and ammonia.



Here the electron-deficient BF_3 molecule (there are only six electrons around the boron) completes its octet by reacting with NH_3 , which has a lone pair of electrons. (see Fig. 14.12.) In fact, as mentioned in Chapter 8, the electron deficiency of boron trifluoride makes it very reactive toward any electron-pair donor. That is, it is a strong Lewis acid.

The hydration of a metal ion, such as Al^{3+} , also can be viewed as a Lewis acid–base reaction:

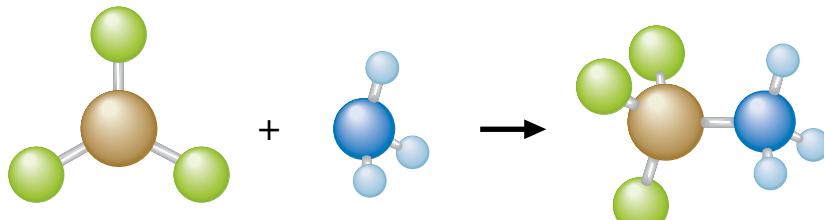
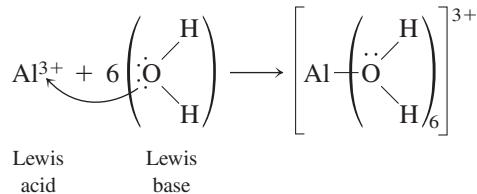
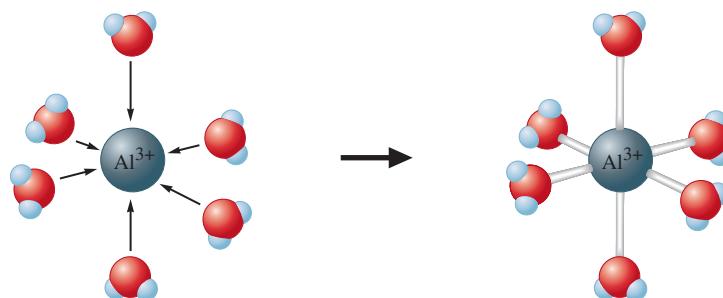


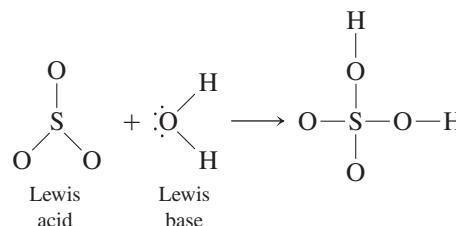
FIGURE 14.12

Reaction of BF_3 with NH_3 .

**FIGURE 14.13**The $\text{Al}(\text{H}_2\text{O})_6^{3+}$ ion.

Here the Al^{3+} ion accepts one electron pair from each of six water molecules to form $\text{Al}(\text{H}_2\text{O})_6^{3+}$ (see Fig. 14.13).

In addition, the reaction between a covalent oxide and water to form a Brønsted–Lowry acid can be defined as a Lewis acid–base reaction. An example is the reaction between sulfur trioxide and water:



Note that as the water molecule attaches to sulfur trioxide, a proton shift occurs to form sulfuric acid.

Sample Exercise 14.22

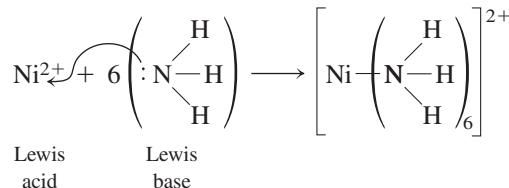
Lewis Acids and Bases

For each reaction, identify the Lewis acid and base.

- $\text{Ni}^{2+}(aq) + 6\text{NH}_3(aq) \longrightarrow \text{Ni}(\text{NH}_3)_6^{2+}(aq)$
- $\text{H}^+(aq) + \text{H}_2\text{O}(aq) \rightleftharpoons \text{H}_3\text{O}^+(aq)$

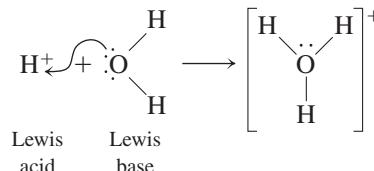
Solution

- Each NH_3 molecule donates an electron pair to the Ni^{2+} ion:



The nickel(II) ion is the Lewis acid, and ammonia is the Lewis base.

- The proton is the Lewis acid and the water molecule is the Lewis base:



See Exercises 14.119 and 14.120.



CHEMICAL IMPACT

Self-Destructing Paper

The New York City Public Library has 88 miles of bookshelves, and on 36 miles of these shelves the books are quietly disintegrating between their covers. In fact, an estimated 40% of the books in the major research collections in the United States will soon be too fragile to handle.

The problem results from the acidic paper widely used in printing books in the past century. Ironically, books from the eighteenth, seventeenth, sixteenth, and even fifteenth century are in much better shape. Gutenberg Bibles contain paper that is in remarkably good condition. In those days, paper was made by hand from linen or rags, but in the nineteenth century, the demand for cheap paper skyrocketed. Paper manufacturers found that paper could be made economically, by machine, using wood pulp. To size the paper (that is, fill in microscopic holes to lower absorption of moisture and prevent seeping or spreading of inks), alum $[Al_2(SO_4)_3]$ was added in large amounts.



A book ravaged by the decomposition of acidic paper.

Because the hydrated aluminum ion $[Al(H_2O)_6]^{3+}$ is an acid ($K_a \approx 10^{-5}$), paper manufactured using alum is quite acidic.

14.12 Strategy for Solving Acid–Base Problems: A Summary

In this chapter we have encountered many different situations involving aqueous solutions of acids and bases, and in the next chapter we will encounter still more. In solving for the equilibrium concentrations in these aqueous solutions, it is tempting to create a pigeonhole for each possible situation and to memorize the procedures necessary to deal with that particular case. This approach is just not practical and usually leads to frustration: Too many pigeonholes are required—there seems to be an infinite number of cases. But you can handle any case successfully by taking a systematic, patient, and thoughtful approach. When analyzing an acid–base equilibrium problem, do *not* ask yourself how a memorized solution can be used to solve the problem. Instead, ask this question: *What are the major species in the solution and what is their chemical behavior?*

The most important part of doing a complicated acid–base equilibrium problem is the analysis you do at the beginning of a problem.

What major species are present?

Does a reaction occur that can be assumed to go to completion?

What equilibrium dominates the solution?

Let the problem guide you. Be patient.

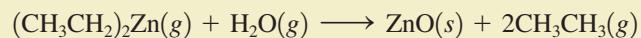
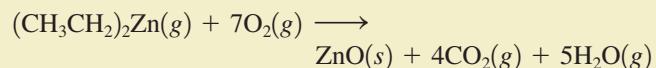
The following steps outline a general strategy for solving problems involving acid–base equilibria.

Over time this acidity causes the paper fibers to disintegrate; the pages of books fall apart when they are used.

One could transfer the contents of the threatened books to microfilm, but that would be a very slow and expensive process. Can the books be chemically treated to neutralize the acid and stop the deterioration? Yes. In fact, you know enough chemistry at this point to design the treatment patented in 1936 by Otto Schierholz. He dipped individual pages in solutions of alkaline earth bicarbonate salts $[\text{Mg}(\text{HCO}_3)_2, \text{Ca}(\text{HCO}_3)_2$, and so on]. The HCO_3^- ions present in these solutions react with the H^+ in the paper to give CO_2 and H_2O . This treatment works well and is used today to preserve especially important works, but it is slow and labor-intensive.

It would be much more economical if large numbers of books could be treated at one time without disturbing the bindings. However, soaking entire books in an aqueous solution is out of the question. A logical question then is: Are there gaseous bases that could be used to neutralize the acid? Certainly; the organic amines (general formula, RNH_2) are bases, and those with low molar masses are gases under normal conditions. Experiments in which books were treated using ammonia, butylamine ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$), and other amines have shown that the method works, but only for a short time. The amines do enter the paper and neutralize the acid, but being volatile, they gradually evaporate, leaving the paper in its original acidic condition.

A much more effective treatment involves diethylzinc [$(\text{CH}_3\text{CH}_2)_2\text{Zn}$], which boils at 117°C and 1 atm. Diethylzinc (DEZ) reacts with oxygen or water to produce ZnO as follows:



The solid zinc oxide produced in these reactions is deposited among the paper fibers, and being a basic oxide, it neutralizes the acid present as shown in the equation



One major problem is that DEZ ignites spontaneously on contact with air. Therefore, this treatment must be carried out in a chamber filled mainly with $\text{N}_2(g)$, where the amount of O_2 present can be rigorously controlled. The pressure in the chamber must be maintained well below one atmosphere both to lower the boiling point of DEZ and to remove excess moisture from the book's pages. Several major DEZ fires have slowed its implementation as a book preservative. However, the Library of Congress has designed a new DEZ treatment plant that includes a chamber large enough for approximately 9000 books to be treated at one time.

Solving Acid–Base Problems

- **1** List the major species in solution.
- **2** Look for reactions that can be assumed to go to completion—for example, a strong acid dissociating or H^+ reacting with OH^- .
- **3** For a reaction that can be assumed to go to completion:
 - Determine the concentration of the products.
 - Write down the major species in solution after the reaction.
- **4** Look at each major component of the solution and decide if it is an acid or a base.
- **5** Pick the equilibrium that will control the pH. Use known values of the dissociation constants for the various species to help decide on the dominant equilibrium.
 - Write the equation for the reaction and the equilibrium expression.
 - Compute the initial concentrations (assuming the dominant equilibrium has not yet occurred, that is, no acid dissociation, and so on).
 - Define x .
 - Compute the equilibrium concentrations in terms of x .
 - Substitute the concentrations into the equilibrium expression, and solve for x .
 - Check the validity of the approximation.
 - Calculate the pH and other concentrations as required.

Although these steps may seem somewhat cumbersome, especially for simpler problems, they will become increasingly helpful as the aqueous solutions become more complicated. If you develop the habit of approaching acid–base problems systematically, the more complex cases will be much easier to manage.

which leads to the equilibrium expression

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] \quad \text{or} \quad [\text{H}^+][\text{OH}^-] = K_w$$

- K_w is the ion-product constant for water
- At 25°C in pure water $[\text{H}^+] = [\text{OH}^-] = 1.0 \times 10^{-7}$, so $K_w = 1.0 \times 10^{-14}$
- Acidic solution: $[\text{H}^+] > [\text{OH}^-]$
- Basic solution: $[\text{OH}^-] > [\text{H}^+]$
- Neutral solution: $[\text{H}^+] = [\text{OH}^-]$

The pH scale

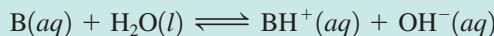
- $\text{pH} = -\log [\text{H}^+]$
- Since pH is a log scale, the pH changes by 1 for every 10-fold change in $[\text{H}^+]$
- The log scale is also used for $[\text{OH}^-]$ and for K_a values

$$\text{pOH} = -\log[\text{OH}^-]$$

$$\text{p}K_a = -\log K_a$$

Bases

- Strong bases are hydroxide salts, such as NaOH and KOH
- Weak bases react with water to produce OH^-



- The equilibrium constant for this reaction is called K_b where

$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$$

- In water a base B is always competing with OH^- for a proton (H^+), so K_b values tend to be very small, thus making B a weak base (compared to OH^-)

Polyprotic acids

- A polyprotic acid has more than one acidic proton
- Polyprotic acids dissociate one proton at a time
 - Each step has a characteristic K_a value
 - Typically for a weak polyprotic acid, $K_{a_1} > K_{a_2} > K_{a_3}$
- Sulfuric acid is unique
 - It is a strong acid in the first dissociation step (K_{a_1} is very large)
 - It is a weak acid in the second step

Acid–base properties of salts

- Can produce acidic, basic, or neutral solutions
- Salts that contain:
 - Cations of strong bases and anions of strong acids produce neutral solutions
 - Cations of strong bases and anions of weak acids produce basic solutions
 - Cations of weak bases and anions of strong acids produce acidic solutions
- Acidic solutions are produced by salts containing a highly charged metal cation—for example, Al^{3+} and Fe^{3+}

Effect of structure on acid–base properties

- Many substances that function as acids or bases contain the H—O—X grouping
 - Molecules in which the O—X bond is strong and covalent tend to behave as acids
 - As X becomes more electronegative, the acid becomes stronger
 - When the O—X bond is ionic, the substance behaves as a base, releasing OH^- ions in water

REVIEW QUESTIONS

- Define each of the following:
 - Arrhenius acid
 - Brønsted–Lowry acid
 - Lewis acid

Which of the definitions is most general? Write reactions to justify your answer.

- Define or illustrate the meaning of the following terms:

- K_a reaction
- K_a equilibrium constant
- K_b reaction
- K_b equilibrium constant
- conjugate acid–base pair

- Define or illustrate the meaning of the following terms:

- amphoteric
- K_w reaction
- K_w equilibrium constant
- pH
- pOH
- pK_w

Give the conditions for a neutral solution at 25°C, in terms of $[H^+]$, pH, and the relationship between $[H^+]$ and $[OH^-]$. Do the same for an acidic solution and for a basic solution. As a solution becomes more acidic, what happens to pH, pOH, $[H^+]$, and $[OH^-]$? As a solution becomes more basic, what happens to pH, pOH, $[H^+]$, and $[OH^-]$?

- How is acid strength related to the value of K_a ? What is the difference between strong acids versus weak acids (see Table 14.1)? As the strength of an acid increases, what happens to the strength of the conjugate base? How is base strength related to the value of K_b ? As the strength of a base increases, what happens to the strength of the conjugate acid?
- Two strategies are followed when solving for the pH of an acid in water. What is the strategy for calculating the pH of a strong acid in water? What major assumptions are made when solving strong acid problems? The best way to recognize strong acids is to memorize them. List the six common strong acids (the two not listed in the text are HBr and HI).

Most acids, by contrast, are weak acids. When solving for the pH of a weak acid in water, you must have the K_a value. List two places in this text that provide K_a values for weak acids. You can utilize these tables to help you recognize weak acids. What is the strategy for calculating the pH of a weak acid in water? What assumptions are generally made? What is the 5% rule? If the 5% rule fails, how do you calculate the pH of a weak acid in water?

- Two strategies are also followed when solving for the pH of a base in water. What is the strategy for calculating the pH of a strong base in water? List the strong bases mentioned in the text that should be committed to memory. Why is calculating the pH of $Ca(OH)_2$ solutions a little more difficult than calculating the pH of NaOH solutions?

Most bases are weak bases. The presence of what element most commonly results in basic properties for an organic compound? What is present on this element in compounds that allows it to accept a proton?

Table 14.3 and Appendix 5 of the text list K_b values for some weak bases. What strategy is used to solve for the pH of a weak base in water? What assumptions are made when solving for the pH of weak base solutions? If the 5% rule fails, how do you calculate the pH of a weak base in water?

7. Table 14.4 lists the stepwise K_a values for some polyprotic acids. What is the difference between a monoprotic acid, a diprotic acid, and a triprotic acid? Most polyprotic acids are weak acids; the major exception is H_2SO_4 . To solve for the pH of a solution of H_2SO_4 , you must solve a strong acid problem as well as a weak acid problem. Explain. Write out the reactions that refer to K_{a_1} and K_{a_2} for H_2SO_4 .

For H_3PO_4 , $K_{a_1} = 7.5 \times 10^{-3}$, $K_{a_2} = 6.2 \times 10^{-8}$, and $K_{a_3} = 4.8 \times 10^{-13}$. Write out the reactions that refer to the K_{a_1} , K_{a_2} , and K_{a_3} equilibrium constants. What are the three acids in a solution of H_3PO_4 ? Which acid is strongest? What are the three conjugate bases in a solution of H_3PO_4 ? Which conjugate base is strongest? Summarize the strategy for calculating the pH of a polyprotic acid in water.

8. For conjugate acid–base pairs, how are K_a and K_b related? Consider the reaction of acetic acid in water



where $K_a = 1.8 \times 10^{-5}$.

- Which two bases are competing for the proton?
- Which is the stronger base?
- In light of your answer to part b, why do we classify the acetate ion (CH_3CO_2^-) as a weak base? Use an appropriate reaction to justify your answer.

In general, as base strength increases, conjugate acid strength decreases. Explain why the conjugate acid of the weak base NH_3 is a weak acid.

To summarize, the conjugate base of a weak acid is a weak base and the conjugate acid of a weak base is a weak acid (weak gives you weak). Assuming K_a for a monoprotic strong acid is 1×10^6 , calculate K_b for the conjugate base of this strong acid. Why do conjugate bases of strong acids have no basic properties in water? List the conjugate bases of the six common strong acids. To tie it all together, some instructors have students think of Li^+ , K^+ , Rb^+ , Cs^+ , Ca^{2+} , Sr^{2+} , and Ba^{2+} as the conjugate acids of the strong bases LiOH , KOH , RbOH , CsOH , $\text{Ca}(\text{OH})_2$, $\text{Sr}(\text{OH})_2$, and $\text{Ba}(\text{OH})_2$. Although not technically correct, the conjugate acid strength of these cations is similar to the conjugate base strength of the strong acids. That is, these cations have no acidic properties in water; similarly, the conjugate bases of strong acids have no basic properties (strong gives you worthless). Fill in the blanks with the correct response. The conjugate base of a weak acid is a _____ base. The conjugate acid of a weak base is a _____ acid. The conjugate base of a strong acid is a _____ base. The conjugate acid of a strong base is a _____ acid. (Hint: Weak gives you weak and strong gives you worthless.)

9. What is a salt? List some anions that behave as weak bases in water. List some anions that have no basic properties in water. List some cations that behave as weak acids in water. List some cations that have no acidic properties in water. Using these lists, give some formulas for salts that have only weak base properties in water. What strategy would you use to solve for the pH of these basic salt solutions? Identify some salts that have only weak acid properties in water. What strategy would you use to solve for the pH of these acidic salt solutions? Identify some salts that have no acidic or basic properties in water (produce neutral solutions). When a salt contains both a weak acid ion and a weak base ion, how do you predict whether the solution pH is acidic, basic, or neutral?

10. For oxyacids, how does acid strength depend on
- the strength of the bond to the acidic hydrogen atom?
 - the electronegativity of the element bonded to the oxygen atom that bears the acidic hydrogen?
 - the number of oxygen atoms?

How does the strength of a conjugate base depend on these factors?

What type of solution forms when a nonmetal oxide dissolves in water?

Give an example of such an oxide. What type of solution forms when a metal oxide dissolves in water? Give an example of such an oxide.

Active Learning Questions

These questions are designed to be used by groups of students in class. The questions allow students to explore their understanding of concepts through discussion and peer teaching. The real value of these questions is the learning that occurs while students talk to each other about chemical concepts.

- Consider two beakers of pure water at different temperatures. How do their pH values compare? Which is more acidic? more basic? Explain.
- Differentiate between the terms *strength* and *concentration* as they apply to acids and bases. When is HCl strong? Weak? Concentrated? Dilute? Answer the same questions for ammonia. Is the conjugate base of a weak acid a strong base?
- Sketch two graphs: (a) percent dissociation for weak acid HA versus the initial concentration of HA ($[HA]_0$) and (b) H^+ concentration versus $[HA]_0$. Explain both.
- Consider a solution prepared by mixing a weak acid HA and HCl. What are the major species? Explain what is occurring in solution. How would you calculate the pH? What if you added NaA to this solution? Then added NaOH?
- Explain why salts can be acidic, basic, or neutral, and show examples. Do this without specific numbers.
- Consider two separate aqueous solutions: one of a weak acid HA and one of HCl. Assuming you started with 10 molecules of each:
 - Draw a picture of what each solution looks like at equilibrium.
 - What are the major species in each beaker?
 - From your pictures, calculate the K_a values of each acid.
 - Order the following from the strongest to the weakest base: H_2O , A^- , Cl^- . Explain your order.
- You are asked to calculate the H^+ concentration in a solution of $NaOH(aq)$. Because sodium hydroxide is a base, can we say there is no H^+ , since having H^+ would imply that the solution is acidic?
- Consider a solution prepared by mixing a weak acid HA, HCl, and NaA. Which of the following statements best describes what happens?

- The H^+ from the HCl reacts completely with the A^- from the NaA. Then the HA dissociates somewhat.
 - The H^+ from the HCl reacts somewhat with the A^- from the NaA to make HA, while the HA is dissociating. Eventually you have equal amounts of everything.
 - The H^+ from the HCl reacts somewhat with the A^- from the NaA to make HA while the HA is dissociating. Eventually all the reactions have equal rates.
 - The H^+ from the HCl reacts completely with the A^- from the NaA. Then the HA dissociates somewhat until “too much” H^+ and A^- are formed, so the H^+ and A^- react to form HA, and so on. Eventually equilibrium is reached.
- Justify your choice, and for choices you did not pick, explain what is wrong with them.
- Consider a solution formed by mixing 100.0 mL of 0.10 M HA ($K_a = 1.0 \times 10^{-6}$), 100.00 mL of 0.10 M NaA, and 100.0 mL of 0.10 M HCl. In calculating the pH for the final solution, you would make some assumptions about the order in which various reactions occur to simplify the calculations. State these assumptions. Does it matter whether the reactions actually occur in the assumed order? Explain.
 - A certain sodium compound is dissolved in water to liberate Na^+ ions and a certain negative ion. What evidence would you look for to determine whether the anion is behaving as an acid or a base? How could you tell whether the anion is a strong base? Explain how the anion could behave simultaneously as an acid and a base.
 - Acids and bases can be thought of as chemical opposites (acids are proton donors, and bases are proton acceptors). Therefore, one might think that $K_a = 1/K_b$. Why isn’t this the case? What is the relationship between K_a and K_b ? Prove it with a derivation.
 - Consider two solutions of the salts $NaX(aq)$ and $NaY(aq)$ at equal concentrations. What would you need to know to determine which solution has the higher pH? Explain how you would decide (perhaps even provide a sample calculation).
 - What is meant by *pH*? True or false: A strong acid solution always has a lower pH than a weak acid solution. Explain.
 - Why is the pH of water at 25°C equal to 7.00?
 - Can the pH of a solution be negative? Explain.

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide*.

Questions

16. Why is H_3O^+ the strongest acid and OH^- the strongest base that can exist in significant amounts in aqueous solutions?
17. How many significant figures are there in the numbers: 10.78, 6.78, 0.78? If these were pH values, to how many significant figures can you express the $[\text{H}^+]$? Explain any discrepancies between your answers to the two questions.
18. In terms of orbitals and electron arrangements, what must be present for a molecule or an ion to act as a Lewis acid? What must be present for a molecule or an ion to act as a Lewis base?
19. Give three example solutions that fit each of the following descriptions.
 - a. A strong electrolyte solution that is very acidic.
 - b. A strong electrolyte solution that is slightly acidic.
 - c. A strong electrolyte solution that is very basic.
 - d. A strong electrolyte solution that is slightly basic.
 - e. A strong electrolyte solution that is neutral.
20. Derive an expression for the relationship between pK_a and pK_b for a conjugate acid–base pair. ($pK = -\log K$)
21. Consider the following statements. Write out an example reaction and K expression that is associated with each statement.
 - a. The autoionization of water.
 - b. An acid reacts with water to produce the conjugate base of the acid and the hydronium ion.
 - c. A base reacts with water to produce the conjugate acid of the base and the hydroxide ion.
22. Which of the following statements is(are) true? Correct the false statements.
 - a. When a base is dissolved in water, the lowest possible pH of the solution is 7.0.
 - b. When an acid is dissolved in water, the lowest possible pH is 0.
 - c. A strong acid solution will have a lower pH than a weak acid solution.
 - d. A 0.0010 M $\text{Ba}(\text{OH})_2$ solution has a pOH that is twice the pOH value of a 0.0010 M KOH solution.
23. Consider the following mathematical expressions.
 - a. $[\text{H}^+] = [\text{HA}]_0$
 - b. $[\text{H}^+] = (K_a \times [\text{HA}]_0)^{1/2}$
 - c. $[\text{OH}^-] = 2[\text{B}]_0$
 - d. $[\text{OH}^-] = (K_b \times [\text{B}]_0)^{1/2}$

For each expression, give three solutions where the mathematical expression would give a good approximation for the $[\text{H}^+]$ or $[\text{OH}^-]$. $[\text{Ha}_0]$ and $[\text{B}]$ represent initial concentrations of an acid or a base.
24. Consider a 0.10 M H_2CO_3 solution and a 0.10 M H_2SO_4 solution. Without doing any detailed calculations, choose one of the following statements that best describes the $[\text{H}^+]$ of each solution and explain your answer.
 - a. The $[\text{H}^+]$ is less than 0.10 M.
 - b. The $[\text{H}^+]$ is 0.10 M.

c. The $[\text{H}^+]$ is between 0.10 M and 0.20 M.

d. The $[\text{H}^+]$ is 0.20 M.

25. Of the hydrogen halides, only HF is a weak acid. Give a possible explanation.
26. Explain why the following are done, both of which are related to acid/base chemistry.
 - a. Power plants burning coal with high sulfur content use scrubbers to help eliminate sulfur emissions.
 - b. A gardener mixes lime (CaO) into the soil of his garden.

Exercises

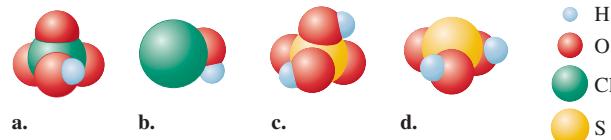
In this section similar exercises are paired.

Nature of Acids and Bases

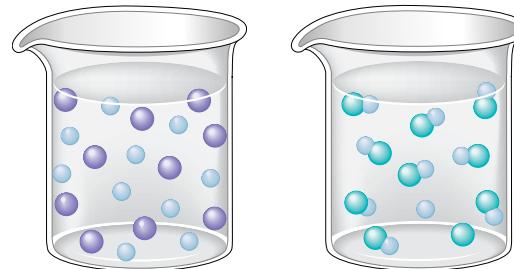
27. Write balanced equations that describe the following reactions.
 - a. the dissociation of perchloric acid in water
 - b. the dissociation of propanoic acid ($\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$) in water
 - c. the dissociation of ammonium ion in water
28. Write the dissociation reaction and the corresponding K_a equilibrium expression for each of the following acids in water.
 - a. HCN
 - b. HOC_6H_5
 - c. $\text{C}_6\text{H}_5\text{NH}_3^+$

29. For each of the following aqueous reactions, identify the acid, the base, the conjugate base, and the conjugate acid.
 - a. $\text{H}_2\text{O} + \text{H}_2\text{CO}_3 \rightleftharpoons \text{H}_3\text{O}^+ + \text{HCO}_3^-$
 - b. $\text{C}_5\text{H}_5\text{NH}^+ + \text{H}_2\text{O} \rightleftharpoons \text{C}_5\text{H}_5\text{N} + \text{H}_3\text{O}^+$
 - c. $\text{HCO}_3^- + \text{C}_5\text{H}_5\text{NH}^+ \rightleftharpoons \text{H}_2\text{CO}_3 + \text{C}_5\text{H}_5\text{N}$
30. For each of the following aqueous reactions, identify the acid, the base, the conjugate base, and the conjugate acid.
 - a. $\text{Al}(\text{H}_2\text{O})_6^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Al}(\text{H}_2\text{O})_5(\text{OH})^{2+}$
 - b. $\text{H}_2\text{O} + \text{HONH}_3^+ \rightleftharpoons \text{HONH}_2 + \text{H}_3\text{O}^+$
 - c. $\text{HOCl} + \text{C}_6\text{H}_5\text{NH}_2 \rightleftharpoons \text{OCl}^- + \text{C}_6\text{H}_5\text{NH}_3^+$

31. Classify each of the following as a strong acid or a weak acid.



32. Consider the following illustrations:

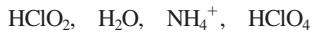


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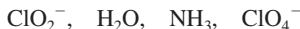
Which beaker best illustrates what happens when the following acids are dissolved in water?

- a. HNO_2
- b. HNO_3
- c. HCl
- d. HF
- e. $\text{HC}_2\text{H}_3\text{O}_2$

33. Use Table 14.2 to order the following from the strongest to the weakest acid.



34. Use Table 14.2 to order the following from the strongest to the weakest base.



35. You may need Table 14.2 to answer the following questions.

- a. Which is the stronger acid, HCl or H_2O ?
- b. Which is the stronger acid, H_2O or HNO_2 ?
- c. Which is the stronger acid, HCN or HOCH_2H_5 ?

36. You may need Table 14.2 to answer the following questions.

- a. Which is the stronger base, Cl^- or H_2O ?
- b. Which is the stronger base, H_2O or NO_2^- ?
- c. Which is the stronger base, CN^- or OC_6H_5^- ?

Autoionization of Water and the pH Scale

37. Calculate the $[\text{OH}^-]$ of each of the following solutions at 25°C . Identify each solution as neutral, acidic, or basic.

- a. $[\text{H}^+] = 1.0 \times 10^{-7} \text{ M}$
- b. $[\text{H}^+] = 8.3 \times 10^{-16} \text{ M}$
- c. $[\text{H}^+] = 12 \text{ M}$
- d. $[\text{H}^+] = 5.4 \times 10^{-5} \text{ M}$

38. Calculate the $[\text{H}^+]$ of each of the following solutions at 25°C . Identify each solution as neutral, acidic, or basic.

- a. $[\text{OH}^-] = 1.5 \text{ M}$
- b. $[\text{OH}^-] = 3.6 \times 10^{-15} \text{ M}$
- c. $[\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$
- d. $[\text{OH}^-] = 7.3 \times 10^{-4} \text{ M}$

39. Values of K_w as a function of temperature are as follows:

Temperature ($^\circ\text{C}$)	K_w
0	1.14×10^{-15}
25	1.00×10^{-14}
35	2.09×10^{-14}
40.	2.92×10^{-14}
50.	5.47×10^{-14}

- a. Is the autoionization of water exothermic or endothermic?
- b. Calculate $[\text{H}^+]$ and $[\text{OH}^-]$ in a neutral solution at 50°C .

40. At 40°C the value of K_w is 2.92×10^{-14} .

- a. Calculate the $[\text{H}^+]$ and $[\text{OH}^-]$ in pure water at 40°C .
- b. What is the pH of pure water at 40°C ?
- c. If the hydroxide ion concentration in a solution is 0.10 M , what is the pH at 40°C ?

41. Calculate the pH and pOH of the solutions in Exercises 37 and 38.

42. Calculate $[\text{H}^+]$ and $[\text{OH}^-]$ for each solution at 25°C . Identify each solution as neutral, acidic, or basic.

- a. pH = 7.40 (the normal pH of blood)
- b. pH = 15.3

- c. pH = -1.0
- d. pH = 3.20
- e. pOH = 5.0
- f. pOH = 9.60

43. Fill in the missing information in the following table.

	pH	pOH	$[\text{H}^+]$	$[\text{OH}^-]$	Acidic, Basic, or Neutral?
Solution a	6.88	—	—	—	—
Solution b	—	—	—	$8.4 \times 10^{-14} \text{ M}$	—
Solution c	—	3.11	—	—	—
Solution d	—	—	$1.0 \times 10^{-7} \text{ M}$	—	—

44. Fill in the missing information in the following table.

	pH	pOH	$[\text{H}^+]$	$[\text{OH}^-]$	Acidic, Basic, or Neutral?
Solution a	9.63	—	—	—	—
Solution b	—	—	—	$3.9 \times 10^{-6} \text{ M}$	—
Solution c	—	—	0.027 M	—	—
Solution d	—	12.2	—	—	—

45. The pH of a sample of gastric juice in a person's stomach is 2.1. Calculate the pOH, $[\text{H}^+]$, and $[\text{OH}^-]$ for this sample. Is gastric juice acidic or basic?

46. The pOH of a sample of baking soda dissolved in water is 5.74 at 25°C . Calculate the pH, $[\text{H}^+]$, and $[\text{OH}^-]$ for this sample. Is the solution acidic or basic?

Solutions of Acids

47. What are the major species present in 0.250 M solutions of each of the following acids? Calculate the pH of each of these solutions.

- a. HClO_4
- b. HNO_3

48. Calculate the pH of each of the following solutions of a strong acid in water.

- a. 0.10 M HCl
- b. 5.0 M HCl
- c. $1.0 \times 10^{-11} \text{ M HCl}$

49. A solution is prepared by adding 50.0 mL of 0.050 M HCl to 150.0 mL of 0.10 M HNO_3 . Calculate the concentrations of all species in this solution.

50. A solution is prepared by mixing 90.0 mL of 5.00 M HCl and 30.0 mL of 8.00 M HNO_3 . Water is then added until the final volume is 1.00 L. Calculate $[\text{H}^+]$, $[\text{OH}^-]$, and the pH for this solution.

- 51.** How would you prepare 1600 mL of a pH = 1.50 solution using concentrated (12 M) HCl?
- 52.** What mass of HNO₃ is present in 250.0 mL of a nitric acid solution having a pH = 5.10?
- 53.** What are the major species present in 0.250 M solutions of each of the following acids? Calculate the pH of each of these solutions.
- HNO₂
 - CH₃CO₂H (HC₂H₃O₂)
- 54.** What are the major species present in 0.250 M solutions of each of the following acids? Calculate the pH of each of these solutions.
- HOC₆H₅
 - HCN
- 55.** A 0.0560-g sample of acetic acid is added to enough water to make 50.00 mL of solution. Calculate [H⁺], [CH₃COO⁻], [CH₃COOH], and the pH at equilibrium. K_a for acetic acid is 1.8×10^{-5} .
- 56.** For propanoic acid (HC₃H₅O₂, K_a = 1.3×10^{-5}), determine the concentration of all species present, the pH, and the percent dissociation of a 0.100 M solution.
- 57.** Calculate the concentration of all species present and the pH of a 0.020 M HF solution.
- 58.** Calculate the pH of a 0.20 M solution of iodic acid (HIO₃, K_a = 0.17).
- 59.** Monochloroacetic acid, HC₂H₂ClO₂, is a skin irritant that is used in “chemical peels” intended to remove the top layer of dead skin from the face and ultimately improve the complexion. The value of K_a for monochloroacetic acid is 1.35×10^{-3} . Calculate the pH of a 0.10 M solution of monochloroacetic acid.
- 60.** A typical aspirin tablet contains 325 mg of acetylsalicylic acid, HC₉H₇O₄. Calculate the pH of a solution that is prepared by dissolving two aspirin tablets in one cup (237 mL) of solution. Assume the aspirin tablets are pure acetylsalicylic acid, K_a = 3.3×10^{-4} .
- 61.** Calculate the pH of each of the following.
- a solution containing 0.10 M HCl and 0.10 M HOCl
 - a solution containing 0.050 M HNO₃ and 0.50 M HC₂H₃O₂.
- 62.** Calculate the pH of a solution that contains 1.0 M HF and 1.0 M HOC₆H₅. Also calculate the concentration of OC₆H₅⁻ in this solution at equilibrium.
- 63.** Calculate the percent dissociation of the acid in each of the following solutions.
- 0.50 M acetic acid
 - 0.050 M acetic acid
 - 0.0050 M acetic acid
 - Use Le Châtelier’s principle to explain why percent dissociation increases as the concentration of a weak acid decreases.
 - Even though the percent dissociation increases from solutions a to c, the [H⁺] decreases. Explain.
- 64.** Using the K_a values in Table 14.2, calculate the percent dissociation in a 0.20 M solution of each of the following acids.
- nitric acid (HNO₃)
 - nitrous acid (HNO₂)
 - phenol (HOC₆H₅)
- d.** How is percent dissociation of an acid related to the K_a value for the acid (assuming equal initial concentrations of acids)?
- 65.** A 0.15 M solution of a weak acid is 3.0% dissociated. Calculate K_a.
- 66.** An acid HX is 25% dissociated in water. If the equilibrium concentration of HX is 0.30 M, calculate the K_a value for HX.
- 67.** The pH of a 1.00×10^{-2} M solution of cyanic acid (HOCN) is 2.77 at 25°C. Calculate K_a for HOCN from this result.
- 68.** Trichloroacetic acid (CCl₃CO₂H) is a corrosive acid that is used to precipitate proteins. The pH of a 0.050 M solution of trichloroacetic acid is the same as the pH of a 0.040 M HClO₄ solution. Calculate K_a for trichloroacetic acid.
- 69.** A solution of formic acid (HCOOH, K_a = 1.8×10^{-4}) has a pH of 2.70. Calculate the initial concentration of formic acid in this solution.
- 70.** One mole of a weak acid HA was dissolved in 2.0 L of solution. After the system had come to equilibrium, the concentration of HA was found to be 0.45 M. Calculate K_a for HA.

Solutions of Bases

- 71.** Write the reaction and the corresponding K_b equilibrium expression for each of the following substances acting as bases in water.
- NH₃
 - C₅H₅N
- 72.** Write the reaction and the corresponding K_b equilibrium expression for each of the following substances acting as bases in water.
- aniline, C₆H₅NH₂
 - dimethylamine, (CH₃)₂NH
- 73.** Use Table 14.3 to help order the following bases from strongest to weakest.
- NO₃⁻, H₂O, NH₃, C₅H₅N
- 74.** Use Table 14.3 to help order the following acids from strongest to weakest.
- HNO₃, H₂O, NH₄⁺, C₅H₅NH⁺
- 75.** Use Table 14.3 to help answer the following questions.
- Which is the stronger base, ClO₄⁻ or C₆H₅NH₂?
 - Which is the stronger base, H₂O or C₆H₅NH₂?
 - Which is the stronger base, OH⁻ or C₆H₅NH₂?
 - Which is the stronger base, C₆H₅NH₂ or CH₃NH₂?
- 76.** Use Table 14.3 to help answer the following questions.
- Which is the stronger acid, HClO₄ or C₆H₅NH₃⁺?
 - Which is the stronger acid, H₂O or C₆H₅NH₃⁺?
 - Which is the stronger acid, C₆H₅NH₃⁺ or CH₃NH₃⁺?
- 77.** Calculate the pH of the following solutions.
- 0.10 M NaOH
 - 1.0×10^{-10} M NaOH
 - 2.0 M NaOH
- 78.** Calculate [OH⁻], pOH, and pH for each of the following.
- 0.00040 M Ca(OH)₂
 - a solution containing 25 g of KOH per liter
 - a solution containing 150.0 g of NaOH per liter

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- 79.** What are the major species present in 0.015 M solutions of each of the following bases?
 a. KOH b. Ba(OH)₂

What is [OH⁻] and the pH of each of these solutions?

- 80.** What are the major species present in the following mixtures of bases?
 a. 0.050 M NaOH and 0.050 M LiOH
 b. 0.0010 M Ca(OH)₂ and 0.020 M RbOH

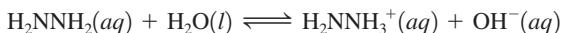
What is [OH⁻] and the pH of each of these solutions?

- 81.** What mass of KOH is necessary to prepare 800.0 mL of a solution having a pH = 11.56?

- 82.** Calculate the concentration of an aqueous Sr(OH)₂ that has pH = 10.50.

- 83.** What are the major species present in a 0.150 M NH₃ solution? Calculate the [OH⁻] and the pH of this solution.

- 84.** For the reaction of hydrazine (N₂H₄) in water,



K_b is 3.0×10^{-6} . Calculate the concentrations of all species and the pH of a 2.0 M solution of hydrazine in water.

- 85.** Calculate [OH⁻], [H⁺], and the pH of 0.20 M solutions of each of the following amines.

- a. triethylamine [(C₂H₅)₃N, $K_b = 4.0 \times 10^{-4}$]
 b. hydroxylamine (HONH₂, $K_b = 1.1 \times 10^{-8}$)

- 86.** Calculate [OH⁻], [H⁺], and the pH of 0.20 M solutions of each of the following amines (the K_b values are found in Table 14.3).
 a. aniline b. methylamine

- 87.** Calculate the pH of a 0.20 M C₂H₅NH₂ solution ($K_b = 5.6 \times 10^{-4}$).

- 88.** Calculate the pH of a 0.050 M (C₂H₅)₂NH solution ($K_b = 1.3 \times 10^{-3}$).

- 89.** Calculate the percent ionization in each of the following solutions.
 a. 0.10 M NH₃ b. 0.010 M NH₃

- 90.** Calculate the percentage of pyridine (C₅H₅N) that forms pyridinium ion, C₅H₅NH⁺, in a 0.10 M aqueous solution of pyridine ($K_b = 1.7 \times 10^{-9}$).

- 91.** Codeine (C₁₈H₂₁NO₃) is a derivative of morphine that is used as an analgesic, narcotic, or antitussive. It was once commonly used in cough syrups but is now available only by prescription because of its addictive properties. If the pH of a 1.7×10^{-3} M solution of codeine is 9.59, calculate K_b .

- 92.** Calculate the mass of HONH₂ required to dissolve in enough water to make 250.0 mL of solution having a pH of 10.00. ($K_b = 1.1 \times 10^{-8}$.)

Polyprotic Acids

- 93.** Write out the stepwise K_a reactions for the diprotic acid H₂SO₃.
- 94.** Write out the stepwise K_a reactions for citric acid (H₃C₆H₅O₇), a triprotic acid.

- 95.** Using the K_a values in Table 14.4 and only the first dissociation step, calculate the pH of 0.10 M solutions of each of the following polyprotic acids.
 a. H₃PO₄ b. H₂CO₃

- 96.** Arsenic acid (H₃AsO₄) is a triprotic acid with $K_{a_1} = 5 \times 10^{-3}$, $K_{a_2} = 8 \times 10^{-8}$, and $K_{a_3} = 6 \times 10^{-10}$. Calculate [H⁺], [OH⁻], [H₃AsO₄], [H₂AsO₄⁻], [HAsO₄²⁻], and [AsO₄³⁻] in a 0.20 M arsenic acid solution.

- 97.** Calculate the pH of a 2.0 M H₂SO₄ solution.

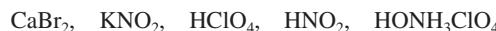
- 98.** Calculate the pH of a 5.0×10^{-3} M solution of H₂SO₄.

Acid–Base Properties of Salts

- 99.** Arrange the following 0.10 M solutions in order of most acidic to most basic.



- 100.** Arrange the following 0.10 M solutions in order from most acidic to most basic. See Appendix 5 for K_a and K_b values.



- 101.** Given that the K_a value for acetic acid is 1.8×10^{-5} and the K_a value for hypochlorous acid is 3.5×10^{-8} , which is the stronger base, OCl⁻ or C₂H₃O₂⁻?

- 102.** The K_b values for ammonia and methylamine are 1.8×10^{-5} and 4.4×10^{-4} , respectively. Which is the stronger acid, NH₄⁺ or CH₃NH₃⁺?

- 103.** Sodium azide (NaN₃) is sometimes added to water to kill bacteria. Calculate the concentration of all species in a 0.010 M solution of NaN₃. The K_a value for hydrazoic acid (HN₃) is 1.9×10^{-5} .

- 104.** Calculate the concentrations of all species present in a 0.25 M solution of ethylammonium chloride (C₂H₅NH₃Cl).

- 105.** Calculate the pH of each of the following solutions.

- a. 0.10 M CH₃NH₃Cl b. 0.050 M NaCN

- 106.** Calculate the pH of each of the following solutions.

- a. 0.12 M KNO₂ c. 0.40 M NH₄ClO₄
 b. 0.45 M NaOCl

- 107.** An unknown salt is either NaCN, NaC₂H₃O₂, NaF, NaCl, or NaOCl. When 0.100 mol of the salt is dissolved in 1.00 L of solution, the pH of the solution is 8.07. What is the identity of the salt?

- 108.** Consider a solution of an unknown salt having the general formula BHCl, where B is one of the weak bases in Table 14.3. A 0.10 M solution of the unknown salt has a pH of 5.82. What is the actual formula of the salt?

- 109.** Calculate the pH of a 0.050 M Al(NO₃)₃ solution. The K_a value for Al(H₂O)₆³⁺ is 1.4×10^{-5} .

- 110.** Calculate the pH of a 0.10 M CoCl₃ solution. The K_a value for Co(H₂O)₆³⁺ is 1.0×10^{-5} .

- 111.** Are solutions of the following salts acidic, basic, or neutral? For those that are not neutral, write balanced chemical equations for the reactions causing the solution to be acidic or basic. The relevant K_a and K_b values are found in Tables 14.2 and 14.3.

- a. NaNO₃ c. C₅H₅NHClO₄ e. KCl
 b. NaNO₂ d. NH₄NO₂ f. NH₄OCl

- 112.** Are solutions of the following salts acidic, basic, or neutral? For those that are not neutral, write balanced equations for the

reactions causing the solution to be acidic or basic. The relevant K_a and K_b values are found in Tables 14.2 and 14.3.

- | | | |
|--|--------------------------------------|--------------------------------------|
| a. KCl | c. $\text{CH}_3\text{NH}_3\text{Cl}$ | e. NH_4F |
| b. $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ | d. KF | f. $\text{CH}_3\text{NH}_3\text{CN}$ |

Relationships Between Structure and Strengths of Acids and Bases

113. Place the species in each of the following groups in order of increasing acid strength. Explain the order you chose for each group.

- | | |
|-------------------------------------|--|
| a. HIO_3 , HBrO_3 | c. HOCl, HOI |
| b. HNO_2 , HNO_3 | d. H_3PO_4 , H_3PO_3 |

114. Place the species in each of the following groups in order of increasing base strength. Give your reasoning in each case.

- | | | |
|---------------------------------------|--------------------------------------|-----------------------------------|
| a. IO_3^- , BrO_3^- | b. NO_2^- , NO_3^- | c. OCl^- , OI^- |
|---------------------------------------|--------------------------------------|-----------------------------------|

115. Place the species in each of the following groups in order of increasing acid strength.

- | |
|--|
| a. H_2O , H_2S , H_2Se (bond energies: H—O, 467 kJ/mol; H—S, 363 kJ/mol; H—Se, 276 kJ/mol) |
| b. $\text{CH}_3\text{CO}_2\text{H}$, $\text{FCH}_2\text{CO}_2\text{H}$, $\text{F}_2\text{CHCO}_2\text{H}$, $\text{F}_3\text{CCO}_2\text{H}$ |
| c. NH_4^+ , HONH_3^+ |
| d. NH_4^+ , PH_4^+ (bond energies: N—H, 391 kJ/mol; P—H, 322 kJ/mol) |

Give reasons for the orders you chose.

116. Using your results from Exercise 115, place the species in each of the following groups in order of increasing base strength.

- | | | |
|---|----------------------------------|------------------------------------|
| a. OH^- , SH^- , SeH^- | b. NH_3 , PH_3 | c. NH_3 , HONH_2 |
|---|----------------------------------|------------------------------------|

117. Will the following oxides give acidic, basic, or neutral solutions when dissolved in water? Write reactions to justify your answers.

- | | | |
|--------|--------------------|----------------------|
| a. CaO | b. SO ₂ | c. Cl ₂ O |
|--------|--------------------|----------------------|

118. Will the following oxides give acidic, basic, or neutral solutions when dissolved in water? Write reactions to justify your answers.

- | | | |
|----------------------|--------------------|--------|
| a. Li ₂ O | b. CO ₂ | c. SrO |
|----------------------|--------------------|--------|

Lewis Acids and Bases

119. Identify the Lewis acid and the Lewis base in each of the following reactions.

- | |
|--|
| a. $\text{B}(\text{OH})_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{B}(\text{OH})_4^-(aq) + \text{H}^+(aq)$ |
| b. $\text{Ag}^+(aq) + 2\text{NH}_3(aq) \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+(aq)$ |
| c. $\text{BF}_3(g) + \text{F}^-(aq) \rightleftharpoons \text{BF}_4^-(aq)$ |

120. Identify the Lewis acid and the Lewis base in each of the following reactions.

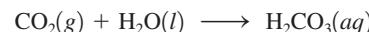
- | |
|--|
| a. $\text{Fe}^{3+}(aq) + 6\text{H}_2\text{O}(l) \rightleftharpoons \text{Fe}(\text{H}_2\text{O})_6^{3+}(aq)$ |
| b. $\text{H}_2\text{O}(l) + \text{CN}^-(aq) \rightleftharpoons \text{HCN}(aq) + \text{OH}^-(aq)$ |
| c. $\text{HgI}_2(s) + 2\text{I}^-(aq) \rightleftharpoons \text{HgI}_4^{2-}(aq)$ |

121. Aluminum hydroxide is an amphoteric substance. It can act as either a Brønsted–Lowry base or a Lewis acid. Write a reaction showing $\text{Al}(\text{OH})_3$ acting as a base toward H^+ and as an acid toward OH^- .

122. Zinc hydroxide is an amphoteric substance. Write equations that describe $\text{Zn}(\text{OH})_2$ acting as a Brønsted–Lowry base toward H^+ and as a Lewis acid toward OH^- .

123. Would you expect Fe^{3+} or Fe^{2+} to be the stronger Lewis acid? Explain.

124. Use the Lewis acid–base model to explain the following reaction.



Additional Exercises

125. A 10.0-mL sample of an HCl solution has a pH of 2.000. What volume of water must be added to change the pH to 4.000?

126. Which of the following represent conjugate acid–base pairs? For those pairs that are not conjugates, write the correct conjugate acid or base for each species in the pair.

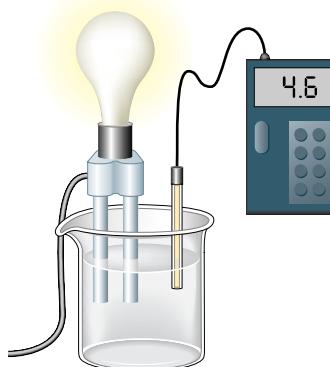
- | | |
|---|---|
| a. H_2O , OH^- | c. H_3PO_4 , H_2PO_4^- |
| b. H_2SO_4 , SO_4^{2-} | d. $\text{HC}_2\text{H}_3\text{O}_2$, $\text{C}_2\text{H}_3\text{O}_2^-$ |

127. A solution is made by adding 50.0 mL of 0.200 M acetic acid ($K_a = 1.8 \times 10^{-5}$) to 50.0 mL of 1.00×10^{-3} M HCl.

- a. Calculate the pH of the solution.
- b. Calculate the acetate ion concentration.

128. You have 100.0 g of saccharin, a sugar substitute, and you want to prepare a pH = 5.75 solution. What volume of solution can be prepared? For saccharin, $\text{HC}_7\text{H}_4\text{NSO}_3$, $pK_a = 11.70$ ($pK_a = -\log K_a$).

129. A solution is tested for pH and conductivity as pictured below:



The solution contains one of the following substances: HCl, NaOH, NH_4Cl , HCN, NH₃, HF, or NaCN. If the solute concentration is about 1.0 M, what is the identity of the solute?

130. A 0.25-g sample of lime (CaO) is dissolved in enough water to make 1500 mL of solution. Calculate the pH of the solution.

131. At 25°C, a saturated solution of benzoic acid ($K_a = 6.4 \times 10^{-5}$) has a pH of 2.80. Calculate the water solubility of benzoic acid in moles per liter.

132. Calculate the pH and $[\text{S}^{2-}]$ in a 0.10 M H_2S solution. Assume $K_{a_1} = 1.0 \times 10^{-7}$; $K_{a_2} = 1.0 \times 10^{-19}$.

133. A typical vitamin C tablet (containing pure ascorbic acid, $\text{H}_2\text{C}_6\text{H}_6\text{O}_6$) weighs 500. mg. One vitamin C tablet is dissolved in enough water to make 200.0 mL of solution. Calculate the pH of this solution. Ascorbic acid is a diprotic acid.

134. Calculate the pH of an aqueous solution containing 1.0×10^{-2} M HCl, 1.0×10^{-2} M H_2SO_4 , and 1.0×10^{-2} M HCN.

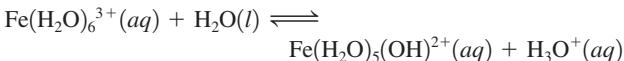
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135. Acrylic acid ($\text{CH}_2=\text{CHCO}_2\text{H}$) is a precursor for many important plastics. K_a for acrylic acid is 5.6×10^{-5} .

- Calculate the pH of a 0.10 M solution of acrylic acid.
- Calculate the percent dissociation of a 0.10 M solution of acrylic acid.
- Calculate the pH of a 0.050 M solution of sodium acrylate ($\text{NaC}_3\text{H}_3\text{O}_2$).

136. A 0.20 M sodium chlorobenzoate ($\text{NaC}_7\text{H}_4\text{ClO}_2$) solution has a pH of 8.65. Calculate the pH of a 0.20 M chlorobenzoic acid ($\text{HC}_7\text{H}_4\text{ClO}_2$) solution.

137. The equilibrium constant K_a for the reaction



is 6.0×10^{-3} .

- Calculate the pH of a 0.10 M solution of $\text{Fe}(\text{H}_2\text{O})_6^{3+}$.
- Will a 1.0 M solution of iron(II) nitrate have a higher or lower pH than a 1.0 M solution of iron(III) nitrate? Explain.

138. Rank the following 0.10 M solutions in order of increasing pH.

- HI , HF , NaF , NaI
- NH_4Br , HBr , KBr , NH_3
- $\text{C}_6\text{H}_5\text{NH}_3\text{NO}_3$, NaNO_3 , NaOH , HOC_6H_5 , KOC_6H_5 , $\text{C}_6\text{H}_5\text{NH}_2$, HNO_3

139. Is an aqueous solution of NaHSO_4 acidic, basic, or neutral? What reaction occurs with water? Calculate the pH of a 0.10 M solution of NaHSO_4 .

140. Calculate $[\text{CO}_3^{2-}]$ in a 0.010 M solution of CO_2 in water (H_2CO_3). If all the CO_3^{2-} in this solution comes from the reaction



what percentage of the H^+ ions in the solution is a result of the dissociation of HCO_3^- ? When acid is added to a solution of sodium hydrogen carbonate (NaHCO_3), vigorous bubbling occurs. How is this reaction related to the existence of carbonic acid (H_2CO_3) molecules in aqueous solution?

141. Hemoglobin (abbreviated Hb) is a protein that is responsible for the transport of oxygen in the blood of mammals. Each hemoglobin molecule contains four iron atoms that are the binding sites for O_2 molecules. The oxygen binding is pH dependent. The relevant equilibrium reaction is



Use Le Châtelier's principle to answer the following.

- What form of hemoglobin, HbH_4^{4+} or $\text{Hb}(\text{O}_2)_4$, is favored in the lungs? What form is favored in the cells?
- When a person hyperventilates, the concentration of CO_2 in the blood is decreased. How does this affect the oxygen-binding equilibrium? How does breathing into a paper bag help to counteract this effect?
- When a person has suffered a cardiac arrest, injection of a sodium bicarbonate solution is given. Why is this necessary?

142. Calculate the value for the equilibrium constant for each of the following aqueous reactions.

- $\text{NH}_3 + \text{H}_3\text{O}^+ \rightleftharpoons \text{NH}_4^+ + \text{H}_2\text{O}$
- $\text{NO}_2^- + \text{H}_3\text{O}^+ \rightleftharpoons \text{HNO}_2 + \text{H}_2\text{O}$
- $\text{NH}_4^+ + \text{OH}^- \rightleftharpoons \text{NH}_3 + \text{H}_2\text{O}$
- $\text{HNO}_2 + \text{OH}^- \rightleftharpoons \text{H}_2\text{O} + \text{NO}_2^-$

143. Students are often surprised to learn that organic acids, such as acetic acid, contain $-\text{OH}$ groups. Actually, all oxyacids contain hydroxyl groups. Sulfuric acid, usually written as H_2SO_4 , has the structural formula $\text{SO}_2(\text{OH})_2$, where S is the central atom. Identify the acids whose structural formulas are shown below. Why do they behave as acids, while NaOH and KOH are bases?

- $\text{SO}(\text{OH})_2$
- $\text{ClO}_2(\text{OH})$
- $\text{HPO}(\text{OH})_2$

Challenge Problems

144. The pH of $1.0 \times 10^{-8}\text{ M}$ hydrochloric acid is not 8.00. The correct pH can be calculated by considering the relationship between the molarities of the three principal ions in the solution (H^+ , Cl^- , and OH^-). These molarities can be calculated from algebraic equations that can be derived from the considerations given below.

- The solution is electrically neutral.
- The hydrochloric acid can be assumed to be 100% ionized.
- The product of the molarities of the hydronium ions and the hydroxide ions must equal K_w .

Calculate the pH of a $1.0 \times 10^{-8}\text{ M}$ HCl solution.

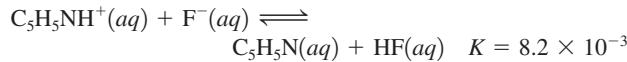
145. Calculate the pH of a $1.0 \times 10^{-7}\text{ M}$ solution of NaOH in water.

146. Calculate $[\text{OH}^-]$ in a $3.0 \times 10^{-7}\text{ M}$ solution of $\text{Ca}(\text{OH})_2$.

147. Consider 50.0 mL of a solution of weak acid $\text{HA} = K_a(1.00 \times 10^{-6})$, which has a pH of 4.000. What volume of water must be added to make the pH = 5.000?

148. Making use of the assumptions we ordinarily make in calculating the pH of an aqueous solution of a weak acid, calculate the pH of a $1.0 \times 10^{-6}\text{ M}$ solution of hypobromous acid (HBrO , $K_a = 2 \times 10^{-9}$). What is wrong with your answer? Why is it wrong? Without trying to solve the problem, tell what has to be included to solve the problem correctly.

149. Calculate the pH of a 0.200 M solution of $\text{C}_5\text{H}_5\text{NHF}$. Hint: $\text{C}_5\text{H}_5\text{NHF}$ is a salt composed of $\text{C}_5\text{H}_5\text{NH}^+$ and F^- ions. The principal equilibrium in this solution is the best acid reacting with the best base; the reaction for the principal equilibrium is



150. Determine the pH of a 0.50 M solution of NH_4OCl . See Exercise 149.

151. Calculate $[\text{OH}^-]$ in a solution obtained by adding 0.0100 mol of solid NaOH to 1.00 L of 15.0 M NH_3 .

152. What mass of $\text{NaOH}(s)$ must be added to 1.0 L of 0.050 M NH_3 to ensure that the percent ionization of NH_3 is no greater than 0.0010%? Assume no volume change on addition of NaOH.

153. A certain acid, HA, has a vapor density of 5.11 g/L when in the gas phase at a temperature of 25°C and a pressure of 1.00 atm. When 1.50 g of this acid is dissolved in enough water to make 100.0 mL of solution, the pH is found to be 1.80. Calculate K_a for the acid.

154. Calculate the mass of sodium hydroxide that must be added to 1.00 L of 1.00 M $\text{HC}_2\text{H}_3\text{O}_2$ to double the pH of the solution (assume that the NaOH does not change the volume of the solution).

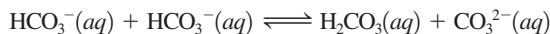
155. Consider the species PO_4^{3-} , HPO_4^{2-} , and H_2PO_4^- . Each ion can act as a base in water. Determine the K_b value for each of these species. Which species is the strongest base?

156. Calculate the pH of a 0.10 M solution of sodium phosphate. See Exercise 155.

157. Will 0.10 M solutions of the following salts be acidic, basic, or neutral? See Appendix 5 for K_a values.

- ammonium bicarbonate
- sodium dihydrogen phosphate
- sodium hydrogen phosphate
- ammonium dihydrogen phosphate
- ammonium formate

158. a. The principal equilibrium in a solution of NaHCO_3 is



Calculate the value of the equilibrium constant for this reaction.

- b.** At equilibrium, what is the relationship between $[\text{H}_2\text{CO}_3]$ and $[\text{CO}_3^{2-}]$?
- c.** Using the equilibrium

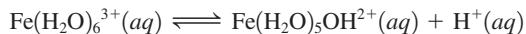


derive an expression for the pH of the solution in terms of K_{a_1} and K_{a_2} using the result from part b.

- d.** What is the pH of a solution of NaHCO_3 ?

159. A 0.100-g sample of the weak acid HA (molar mass = 100.0 g/mol) is dissolved in 500.0 g of water. The freezing point of the resulting solution is -0.0056°C . Calculate the value of K_a for this acid. Assume molarity equals molarity in this solution.

160. A sample containing 0.0500 mol of $\text{Fe}_2(\text{SO}_4)_3$ is dissolved in enough water to make 1.00 L of solution. This solution contains hydrated SO_4^{2-} and $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ ions. The latter behaves as an acid:



- a.** Calculate the expected osmotic pressure of this solution at 25°C if the above dissociation is negligible.
- b.** The actual osmotic pressure of the solution is 6.73 atm at 25°C . Calculate K_a for the dissociation reaction of $\text{Fe}(\text{H}_2\text{O})_6^{3+}$. (To do this calculation, you must assume that none of the ions goes through the semipermeable membrane. Actually, this is not a great assumption for the tiny H^+ ion.)

Integrative Problems

These problems require the integration of multiple concepts to find the solutions.

161. A 2.14-g sample of sodium hypoiodite is dissolved in water to make 1.25 L of solution. The solution pH is 11.32. What is K_b for the hypoiodite ion?

162. Isocyanic acid (HNCO) can be prepared by heating sodium cyanate in the presence of solid oxalic acid according to the equation



Upon isolating pure $\text{HNCO}(l)$, an aqueous solution of HNCO can be prepared by dissolving the liquid HNCO in water. What is the pH of a 100.-mL solution of HNCO prepared from the reaction of 10.0 g each of NaOCN and $\text{H}_2\text{C}_2\text{O}_4$, assuming all of the HNCO produced is dissolved in solution? (K_a of $\text{HNCO} = 1.2 \times 10^{-4}$.)

163. Papaverine hydrochloride (abbreviated papH^+Cl^- ; molar mass = 378.85 g/mol) is a drug that belongs to a group of medicines called vasodilators, which cause blood vessels to expand, thereby increasing blood flow. This drug is the conjugate acid of the weak base papaverine (abbreviated pap; $K_b = 8.33 \times 10^{-9}$ at 35.0°C). Calculate the pH of a 30.0 mg/mL aqueous dose of papH^+Cl^- prepared at 35.0°C . K_w at 35.0°C is 2.1×10^{-14} .

Marathon Problems*

These problems are designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

164. Captain Kirk, of the Starship *Enterprise*, has been told by his superiors that only a chemist can be trusted with the combination to the safe containing the dilithium crystals that power the ship. The combination is the pH of solution A, described below, followed by the pH of solution C. (Example: If the pH of solution A is 3.47 and that of solution C is 8.15, then the combination to the safe is 3-47-8-15.) The chemist must determine the combination using only the information below (all solutions are at 25°C):

Solution A is 50.0 mL of a 0.100 M solution of the weak monoprotic acid HX.

Solution B is a 0.0500 M solution of the salt NaX. It has a pH of 10.02.

Solution C is made by adding 15.0 mL of 0.250 M KOH to solution A.

What is the combination to the safe?

165. For the following, mix equal volumes of one solution from Group I with one solution from Group II to achieve the indicated pH. Calculate the pH of each solution.

Group I: 0.20 M NH_4Cl , 0.20 M HCl, 0.20 M $\text{C}_6\text{H}_5\text{NH}_3\text{Cl}$, 0.20 M $(\text{C}_2\text{H}_5)_3\text{NHCl}$

Group II: 0.20 M KOI, 0.20 M NaCN, 0.20 M KOCl, 0.20 M NaNO_2

- the solution with the lowest pH
- the solution with the highest pH
- the solution with the pH closest to 7.00



Get help understanding core concepts and visualizing molecular-level interactions, and practice problem solving, by visiting the Online Study Center at college.hmco.com/PIC/zumdahl7e.

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15 Applications of Aqueous Equilibria

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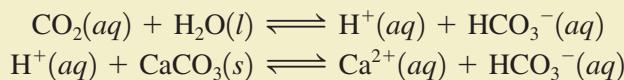


Stalactites are formed when carbonate minerals dissolve in ground water acidified by carbon dioxide and then solidify when the water evaporates.

M

uch important chemistry, including almost all the chemistry of the natural world, occurs in aqueous solution. We have already introduced one very significant class of aqueous equilibria, acid–base reactions. In this chapter we consider more applications of acid–base chemistry and introduce two additional types of aqueous equilibria, those involving the solubility of salts and those involving the formation of complex ions.

The interplay of acid–base, solubility, and complex ion equilibria is often important in natural processes, such as the weathering of minerals, the uptake of nutrients by plants, and tooth decay. For example, limestone (CaCO_3) will dissolve in water made acidic by dissolved carbon dioxide:



This two-step process and its reverse account for the formation of limestone caves and the stalactites and stalagmites found therein. In the forward direction of the process, the acidic water (containing carbon dioxide) dissolves the underground limestone deposits, thereby forming a cavern. The reverse process occurs as the water drips from the ceiling of the cave, and the carbon dioxide is lost to the air. This causes solid calcium carbonate to form, producing stalactites on the ceiling and stalagmites where the drops hit the cave floor.

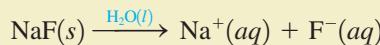
Before we consider the other types of aqueous equilibria, we will deal with acid–base equilibria in more detail.

Acid–Base Equilibria

15.1 Solutions of Acids or Bases Containing a Common Ion

In Chapter 14 we were concerned with calculating the equilibrium concentrations of species (particularly H^+ ions) in solutions containing an acid or a base. In this section we discuss solutions that contain not only the weak acid HA but also its salt NaA. Although this appears to be a new type of problem, we will see that this case can be handled rather easily using the procedures developed in Chapter 14.

Suppose we have a solution containing the weak acid hydrofluoric acid (HF , $K_a = 7.2 \times 10^{-4}$) and its salt sodium fluoride (NaF). Recall that when a salt dissolves in water, it breaks up completely into its ions—it is a strong electrolyte:



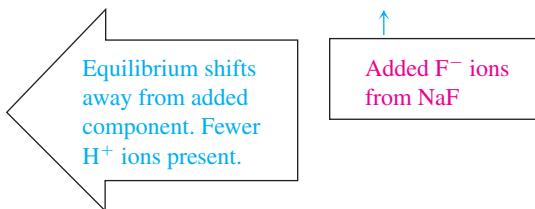
Since hydrofluoric acid is a weak acid and only slightly dissociated, the major species in the solution are HF , Na^+ , F^- , and H_2O . The **common ion** in this solution is F^- , since it is produced by both hydrofluoric acid and sodium fluoride. What effect does the presence of the dissolved sodium fluoride have on the dissociation equilibrium of hydrofluoric acid?

To answer this question, we compare the extent of dissociation of hydrofluoric acid in two different solutions, the first containing 1.0 M HF and the second containing 1.0 M HF

and 1.0 M NaF. By Le Châtelier's principle, we would expect the dissociation equilibrium for HF



in the second solution to be *driven to the left by the presence of F⁻ ions from the NaF*. Thus the extent of dissociation of HF will be *less* in the presence of dissolved NaF:



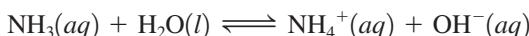
The common ion effect is an application of Le Châtelier's principle.

The shift in equilibrium position that occurs because of the addition of an ion already involved in the equilibrium reaction is called the **common ion effect**. This effect makes a solution of NaF and HF less acidic than a solution of HF alone.

The common ion effect is quite general. For example, solid NH₄Cl added to a 1.0 M NH₃ solution produces additional ammonium ions:



and this causes the position of the ammonia–water equilibrium to shift to the left:



This reduces the equilibrium concentration of OH⁻ ions.

The common ion effect is also important in solutions of polyprotic acids. The production of protons by the first dissociation step greatly inhibits the succeeding dissociation steps, which, of course, also produce protons, the common ion in this case. We will see later in this chapter that the common ion effect is also important in dealing with the solubility of salts.

Equilibrium Calculations

The procedures for finding the pH of a solution containing a weak acid or base plus a common ion are very similar to the procedures, which we covered in Chapter 14, for solutions containing the acids or bases alone. For example, in the case of a weak acid, the only important difference is that the initial concentration of the anion A⁻ is not zero in a solution that also contains the salt NaA. Sample Exercise 15.1 illustrates a typical example using the same general approach we developed in Chapter 14.

Sample Exercise 15.1

Acidic Solutions Containing Common Ions

In Section 14.5 we found that the equilibrium concentration of H⁺ in a 1.0 M HF solution is 2.7×10^{-2} M, and the percent dissociation of HF is 2.7%. Calculate [H⁺] and the percent dissociation of HF in a solution containing 1.0 M HF ($K_a = 7.2 \times 10^{-4}$) and 1.0 M NaF.

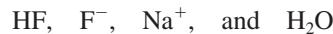
Major Species

	F ⁻
	Na ⁺
	HF
	H ₂ O

Solution

As the aqueous solutions we consider become more complex, it is more important than ever to be systematic and to *focus on the chemistry* occurring in the solution before thinking about mathematical procedures. The way to do this is *always* to write the major species first and consider the chemical properties of each one.

In a solution containing 1.0 M HF and 1.0 M NaF, the major species are



We know that Na⁺ ions have neither acidic nor basic properties and that water is a very weak acid (or base). Therefore, the important species are HF and F⁻, which participate in the acid dissociation equilibrium that controls [H⁺] in this solution. That is, the position of the equilibrium



will determine [H⁺] in the solution. The equilibrium expression is

$$K_a = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} = 7.2 \times 10^{-4}$$

The important concentrations are shown in the following table.

Initial Concentration (mol/L)	Equilibrium Concentration (mol/L)
[HF] ₀ = 1.0 (from dissolved HF)	[HF] = 1.0 - x
[F ⁻] ₀ = 1.0 (from dissolved NaF)	x mol/L HF dissociates [F ⁻] = 1.0 + x
[H ⁺] ₀ = 0 (neglect contribution from H ₂ O)	[H ⁺] = x

Note that [F⁻]₀ = 1.0 M because of the dissolved sodium fluoride and that at equilibrium [F⁻] > 1.0 M because when the acid dissociates it produces F⁻ as well as H⁺. Then

$$K_a = 7.2 \times 10^{-4} = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} = \frac{(x)(1.0 + x)}{1.0 - x} \approx \frac{(x)(1.0)}{1.0}$$

(since x is expected to be small).

Solving for x gives

$$x = \frac{1.0}{1.0} (7.2 \times 10^{-4}) = 7.2 \times 10^{-4}$$

Noting that x is small compared to 1.0, we conclude that this result is acceptable. Thus

$$[\text{H}^+] = x = 7.2 \times 10^{-4} \text{ M} \quad (\text{The pH is 3.14.})$$

The percent dissociation of HF in this solution is

$$\frac{[\text{H}^+]}{[\text{HF}]_0} \times 100 = \frac{7.2 \times 10^{-4} \text{ M}}{1.0 \text{ M}} \times 100 = 0.072\%$$

Compare these values for [H⁺] and percent dissociation of HF with those for a 1.0 M HF solution, where [H⁺] = 2.7 × 10⁻² M and the percent dissociation is 2.7%. The large difference shows clearly that the presence of the F⁻ ions from the dissolved NaF greatly inhibits the dissociation of HF. The position of the acid dissociation equilibrium has been shifted to the left by the presence of F⁻ ions from NaF.

See Exercises 15.25 and 15.26.

15.2 Buffered Solutions

The most important application of acid–base solutions containing a common ion is for buffering. A **buffered solution** is one that *resists a change in its pH* when either hydroxide ions or protons are added. The most important practical example of a buffered solution is our blood, which can absorb the acids and bases produced in biologic reactions without changing its pH. A constant pH for blood is vital because cells can survive only in a very narrow pH range.

A buffered solution may contain a *weak acid* and its salt (for example, HF and NaF) or a *weak base* and its salt (for example, NH₃ and NH₄Cl). By choosing the appropriate components, a solution can be buffered at virtually any pH.

In treating buffered solutions in this chapter, we will start by considering the equilibrium calculations. We will then use these results to show how buffering works. That is, we will answer the question: How does a buffered solution resist changes in pH when an acid or a base is added?

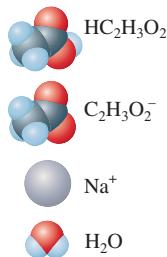
As you do the calculations associated with buffered solutions, keep in mind that these are merely solutions containing weak acids or bases, and the procedures required are the same ones we have already developed. Be sure to use the systematic approach introduced in Chapter 14.

The systematic approach developed in Chapter 14 for weak acids and bases applies to buffered solutions.

Sample Exercise 15.2

Notice as you do this problem that it is exactly like examples you have seen in Chapter 14.

Major Species

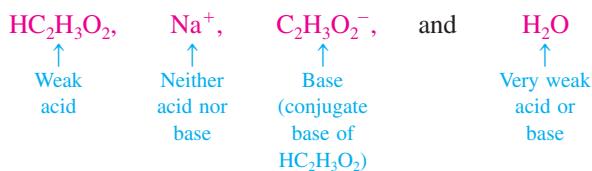


The pH of a Buffered Solution I

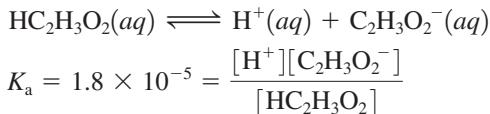
A buffered solution contains 0.50 M acetic acid (HC₂H₃O₂, $K_a = 1.8 \times 10^{-5}$) and 0.50 M sodium acetate (NaC₂H₃O₂). Calculate the pH of this solution.

Solution

The major species in the solution are



Examination of the solution components leads to the conclusion that the acetic acid dissociation equilibrium, which involves both HC₂H₃O₂ and C₂H₃O₂⁻, will control the pH of the solution:



The concentrations are as follows:



A digital pH meter shows the pH of the buffered solution to be 4.740.

Initial Concentration (mol/L)		Equilibrium Concentration (mol/L)
$[\text{HC}_2\text{H}_3\text{O}_2]_0 = 0.50$ $[\text{C}_2\text{H}_3\text{O}_2^-]_0 = 0.50$ $[\text{H}^+]_0 \approx 0$	$x \text{ mol/L of HC}_2\text{H}_3\text{O}_2 \xrightarrow{\text{dissociates to reach equilibrium}}$	$[\text{HC}_2\text{H}_3\text{O}_2] = 0.50 - x$ $[\text{C}_2\text{H}_3\text{O}_2^-] = 0.50 + x$ $[\text{H}^+] = x$

The corresponding ICE table is

	$\text{HC}_2\text{H}_3\text{O}_2(aq)$	\rightleftharpoons	$\text{H}^+(aq)$	+	$\text{C}_2\text{H}_3\text{O}_2^-(aq)$
Initial:	0.50		≈ 0		0.50
Change:	$-x$		$+x$		$+x$
Equilibrium:	$0.50 - x$		x		$0.50 + x$

Then

$$K_a = 1.8 \times 10^{-5} = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{(x)(0.50 + x)}{0.50 - x} \approx \frac{(x)(0.50)}{0.50}$$

and

$$x \approx 1.8 \times 10^{-5}$$

The approximations are valid (by the 5% rule), so

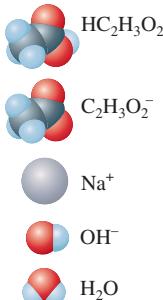
$$[\text{H}^+] = x = 1.8 \times 10^{-5} M \quad \text{and} \quad \text{pH} = 4.74$$

See Exercises 15.33 and 15.34.

Sample Exercise 15.3

pH Changes in Buffered Solutions

Major Species



Calculate the change in pH that occurs when 0.010 mol solid NaOH is added to 1.0 L of the buffered solution described in Sample Exercise 15.2. Compare this pH change with that which occurs when 0.010 mol solid NaOH is added to 1.0 L of water.

Solution

Since the added solid NaOH will completely dissociate, the major species in solution *before any reaction occurs* are $\text{HC}_2\text{H}_3\text{O}_2$, Na^+ , $\text{C}_2\text{H}_3\text{O}_2^-$, OH^- , and H_2O . Note that the solution contains a relatively large amount of the very strong base hydroxide ion, which has a great affinity for protons. The best source of protons is the acetic acid, and the reaction that will occur is

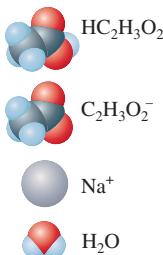


Although acetic acid is a weak acid, the hydroxide ion is such a strong base that the reaction above will *proceed essentially to completion* (until the OH^- ions are consumed).

The best approach to this problem involves two distinct steps: (1) assume that the reaction goes to completion, and carry out the stoichiometric calculations, and then (2) carry out the equilibrium calculations.

1. *The stoichiometry problem.* The stoichiometry for the reaction is shown below.

Major Species



	$\text{HC}_2\text{H}_3\text{O}_2$	+	OH^-	\longrightarrow	$\text{C}_2\text{H}_3\text{O}_2^-$	+	H_2O
Before reaction:	$1.0 \text{ L} \times 0.50 \text{ M}$ $= 0.50 \text{ mol}$		0.010 mol		$1.0 \text{ L} \times 0.50 \text{ M}$ $= 0.50 \text{ mol}$		
After reaction:	$0.50 - 0.010$ $= 0.49 \text{ mol}$		$0.010 - 0.010$ $= 0 \text{ mol}$		$0.50 + 0.010$ $= 0.51 \text{ mol}$		

Note that 0.010 mol $\text{HC}_2\text{H}_3\text{O}_2$ has been converted to 0.010 mol $\text{C}_2\text{H}_3\text{O}_2^-$ by the added OH^- .



(top) Pure water at pH 7.000. (bottom)
When 0.01 mol NaOH is added to 1.0 L of
pure water, the pH jumps to 12.000.

2. The equilibrium problem. After the reaction between OH^- and $\text{HC}_2\text{H}_3\text{O}_2$ is complete, the major species in solution are



The dominant equilibrium involves the dissociation of acetic acid.

This problem is then very similar to that in Sample Exercise 15.2. The only difference is that the addition of 0.010 mol OH^- has consumed some $\text{HC}_2\text{H}_3\text{O}_2$ and produced some $\text{C}_2\text{H}_3\text{O}_2^-$, yielding the following ICE table:

	$\text{HC}_2\text{H}_3\text{O}_2(aq)$	\rightleftharpoons	$\text{H}^+(aq)$	+	$\text{C}_2\text{H}_3\text{O}_2^-(aq)$
Initial:	0.49		0		0.51
Change:	$-x$		$+x$		$+x$
Equilibrium:	$0.49 - x$		x		$0.51 + x$

Note that the initial concentrations are defined after the reaction with OH^- is complete but before the system adjusts to equilibrium. Following the usual procedure gives

$$K_a = 1.8 \times 10^{-5} = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{(x)(0.51 + x)}{0.49 - x} \approx \frac{(x)(0.51)}{0.49}$$

and

$$x \approx 1.7 \times 10^{-5}$$

The approximations are valid (by the 5% rule), so

$$[\text{H}^+] = x = 1.7 \times 10^{-5} \quad \text{and} \quad \text{pH} = 4.76$$

The change in pH produced by the addition of 0.01 mol OH^- to this buffered solution is then

$$\begin{array}{ccc} 4.76 & - & 4.74 \\ \uparrow & & \uparrow \\ \text{New solution} & & \text{Original solution} \end{array} = +0.02$$

The pH increased by 0.02 pH units.

Now compare this with what happens when 0.01 mol solid NaOH is added to 1.0 L water to give 0.01 M NaOH. In this case $[\text{OH}^-] = 0.01 \text{ M}$ and

$$\begin{aligned} [\text{H}^+] &= \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-2}} = 1.0 \times 10^{-12} \\ \text{pH} &= 12.00 \end{aligned}$$

Thus the change in pH is

$$\begin{array}{ccc} 12.00 & - & 7.00 \\ \uparrow & & \uparrow \\ \text{New solution} & & \text{Pure water} \end{array} = +5.00$$

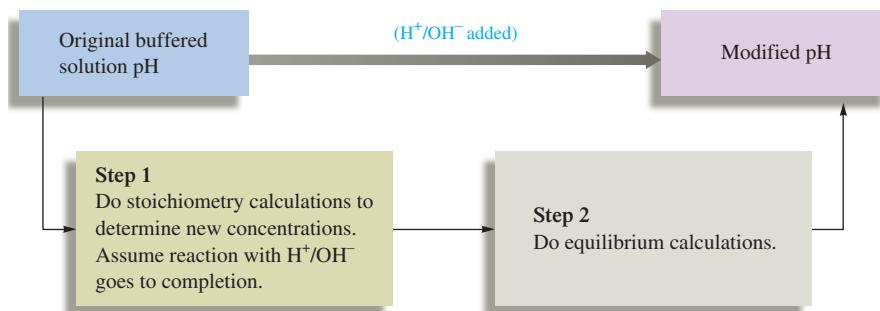
The increase is 5.00 pH units. Note how well the buffered solution resists a change in pH as compared with pure water.

See Exercises 15.35 and 15.36.

Sample Exercises 15.2 and 15.3 represent typical buffer problems that involve all the concepts that you need to know to handle buffered solutions containing weak acids. Pay special attention to the following points:

1. Buffered solutions are simply solutions of weak acids or bases containing a common ion. The pH calculations on buffered solutions require exactly the same procedures introduced in Chapter 14. *This is not a new type of problem.*

2. When a strong acid or base is added to a buffered solution, it is best to deal with the stoichiometry of the resulting reaction first. After the stoichiometric calculations are completed, then consider the equilibrium calculations. This procedure can be presented as follows:



Buffering: How Does It Work?

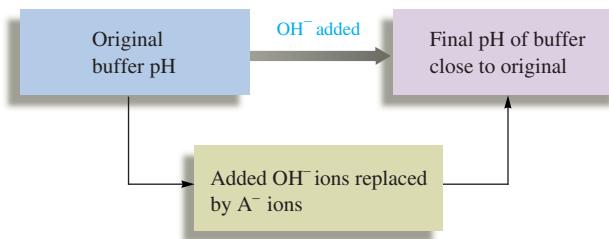


Visualization: Buffers

Sample Exercises 15.2 and 15.3 demonstrate the ability of a buffered solution to absorb hydroxide ions without a significant change in pH. *But how does a buffer work?* Suppose a buffered solution contains relatively large quantities of a weak acid HA and its conjugate base A⁻. When hydroxide ions are added to the solution, since the weak acid represents the best source of protons, the following reaction occurs:



The net result is that OH⁻ ions are not allowed to accumulate but are replaced by A⁻ ions.



The stability of the pH under these conditions can be understood by examining the equilibrium expression for the dissociation of HA:

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

or, rearranging,

$$[\text{H}^+] = K_a \frac{[\text{HA}]}{[\text{A}^-]}$$

In a buffered solution the pH is governed by the ratio [HA]/[A⁻].

In other words, the *equilibrium concentration of H⁺, and thus the pH, is determined by the ratio [HA]/[A⁻]*. When OH⁻ ions are added, HA is converted to A⁻, and the ratio [HA]/[A⁻] decreases. However, if the amounts of HA and A⁻ originally present are very large compared with the amount of OH⁻ added, the change in the [HA]/[A⁻] ratio will be small.

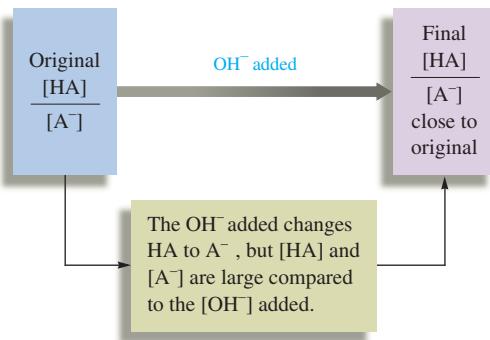
In Sample Exercises 15.2 and 15.3,

$$\frac{[\text{HA}]}{[\text{A}^-]} = \frac{0.50}{0.50} = 1.0 \quad \text{Initially}$$

$$\frac{[\text{HA}]}{[\text{A}^-]} = \frac{0.49}{0.51} = 0.96 \quad \text{After adding 0.01 mol/L OH}^-$$

The change in the ratio $[\text{HA}]/[\text{A}^-]$ is very small. Thus the $[\text{H}^+]$ and the pH remain essentially constant.

The essence of buffering, then, is that $[\text{HA}]$ and $[\text{A}^-]$ are large compared with the amount of OH^- added. Thus, when the OH^- is added, the concentrations of HA and A^- change, but only by small amounts. Under these conditions, the $[\text{HA}]/[\text{A}^-]$ ratio and thus the $[\text{H}^+]$ remain virtually constant.



Visualization: Adding an Acid to a Buffer

Similar reasoning applies when protons are added to a buffered solution of a weak acid and a salt of its conjugate base. Because the A^- ion has a high affinity for H^+ , the added H^+ ions react with A^- to form the weak acid:



and free H^+ ions do not accumulate. In this case there will be a net change of A^- to HA . However, if $[\text{A}^-]$ and $[\text{HA}]$ are large compared with the $[\text{H}^+]$ added, little change in the pH will occur.

The form of the acid dissociation equilibrium expression

$$[\text{H}^+] = K_a \frac{[\text{HA}]}{[\text{A}^-]} \quad (15.1)$$

is often useful for calculating $[\text{H}^+]$ in a buffered solution, since $[\text{HA}]$ and $[\text{A}^-]$ are known. For example, to calculate $[\text{H}^+]$ in a buffered solution containing 0.10 M HF ($K_a = 7.2 \times 10^{-4}$) and 0.30 M NaF, we simply substitute into Equation (15.1):

$$[\text{H}^+] = (7.2 \times 10^{-4}) \frac{0.10}{0.30} = 2.4 \times 10^{-4}\text{ M}$$

$\xrightarrow{\text{K}_a}$
 $\nwarrow [\text{F}^-]$

Another useful form of Equation (15.1) can be obtained by taking the negative log of both sides:

$$-\log[\text{H}^+] = -\log(K_a) - \log\left(\frac{[\text{HA}]}{[\text{A}^-]}\right)$$

That is,

$$\text{pH} = \text{p}K_a - \log\left(\frac{[\text{HA}]}{[\text{A}^-]}\right)$$

or, where inverting the log term reverses the sign:

$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right) = \text{p}K_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right) \quad (15.2)$$

This log form of the expression for K_a is called the **Henderson–Hasselbalch equation** and is useful for calculating the pH of solutions when the ratio $[\text{HA}]/[\text{A}^-]$ is known.

For a particular buffering system (conjugate acid–base pair), all solutions that have the same ratio $[\text{A}^-]/[\text{HA}]$ will have the same pH. For example, a buffered solution containing 5.0 M $\text{HC}_2\text{H}_3\text{O}_2$ and 3.0 M $\text{NaC}_2\text{H}_3\text{O}_2$ will have the same pH as one containing 0.050 M $\text{HC}_2\text{H}_3\text{O}_2$ and 0.030 M $\text{NaC}_2\text{H}_3\text{O}_2$. This can be shown as follows:

System	$[\text{A}^-]/[\text{HA}]$
5.0 M $\text{HC}_2\text{H}_3\text{O}_2$ and 3.0 M $\text{NaC}_2\text{H}_3\text{O}_2$	$\frac{3.0 \text{ M}}{5.0 \text{ M}} = 0.60$
0.050 M $\text{HC}_2\text{H}_3\text{O}_2$ and 0.030 M $\text{NaC}_2\text{H}_3\text{O}_2$	$\frac{0.030 \text{ M}}{0.050 \text{ M}} = 0.60$

Therefore,

$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}\right) = 4.74 + \log(0.60) = 4.74 - 0.22 = 4.52$$

Note that in using this equation we have assumed that the equilibrium concentrations of A^- and HA are equal to the initial concentrations. That is, we are assuming the validity of the approximations

$$[\text{A}^-] = [\text{A}^-]_0 + x \approx [\text{A}^-]_0 \quad \text{and} \quad [\text{HA}] = [\text{HA}]_0 - x \approx [\text{HA}]_0$$

where x is the amount of acid that dissociates. Since the initial concentrations of HA and A^- are relatively large in a buffered solution, this assumption is generally acceptable.

Sample Exercise 15.4

The pH of a Buffered Solution II

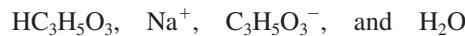
Major Species



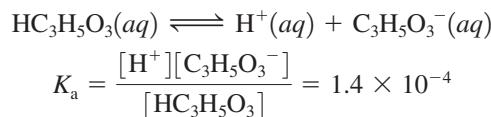
Calculate the pH of a solution containing 0.75 M lactic acid ($K_a = 1.4 \times 10^{-4}$) and 0.25 M sodium lactate. Lactic acid ($\text{HC}_3\text{H}_5\text{O}_3$) is a common constituent of biologic systems. For example, it is found in milk and is present in human muscle tissue during exertion.

Solution

The major species in solution are



Since Na^+ has no acid–base properties and H_2O is a weak acid or base, the pH will be controlled by the lactic acid dissociation equilibrium:



Since $[\text{HC}_3\text{H}_5\text{O}_3]_0$ and $[\text{C}_3\text{H}_5\text{O}_3^-]_0$ are relatively large,

$$[\text{HC}_3\text{H}_5\text{O}_3] \approx [\text{HC}_3\text{H}_5\text{O}_3]_0 = 0.75 \text{ M}$$

and

$$[\text{C}_3\text{H}_5\text{O}_3^-] \approx [\text{C}_3\text{H}_5\text{O}_3^-]_0 = 0.25 \text{ M}$$

Thus, using the rearranged K_a expression, we have

$$[\text{H}^+] = K_a \frac{[\text{HC}_3\text{H}_5\text{O}_3]}{[\text{C}_3\text{H}_5\text{O}_3^-]} = (1.4 \times 10^{-4}) \frac{(0.75 \text{ M})}{(0.25 \text{ M})} = 4.2 \times 10^{-4} \text{ M}$$

and

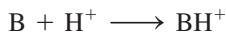
$$\text{pH} = -\log(4.2 \times 10^{-4}) = 3.38$$

Alternatively, we could use the Henderson–Hasselbalch equation:

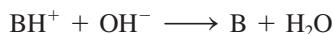
$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{C}_3\text{H}_5\text{O}_3^-]}{[\text{HC}_3\text{H}_5\text{O}_3]}\right) = 3.85 + \log\left(\frac{0.25 \text{ M}}{0.75 \text{ M}}\right) = 3.38$$

See Exercises 15.37 and 15.38.

Buffered solutions also can be formed from a weak base and the corresponding conjugate acid. In these solutions, the weak base B reacts with any H^+ added:



and the conjugate acid BH^+ reacts with any added OH^- :



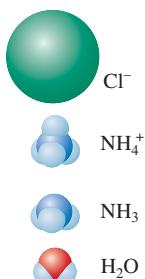
The approach needed to perform pH calculations for these systems is virtually identical to that used above. This makes sense because, as is true of all buffered solutions, a weak acid (BH^+) and a weak base (B) are present. A typical case is illustrated in Sample Exercise 15.5.

Sample Exercise 15.5

The pH of a Buffered Solution III

A buffered solution contains $0.25 \text{ M} \text{ NH}_3$ ($K_b = 1.8 \times 10^{-5}$) and $0.40 \text{ M} \text{ NH}_4\text{Cl}$. Calculate the pH of this solution.

Major Species

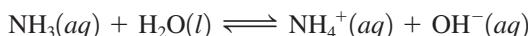


Solution

The major species in solution are



Since Cl^- is such a weak base and water is a weak acid or base, the important equilibrium is



$$\text{and } K_b = 1.8 \times 10^{-5} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

The appropriate ICE table is:

	$\text{NH}_3(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{NH}_4^+(aq)$	+	$\text{OH}^-(aq)$
Initial:	0.25		—		0.40		≈ 0
Change:	$-x$		—		$+x$		$+x$
Equilibrium:	$0.25 - x$		—		$0.40 + x$		x

Then

$$K_b = 1.8 \times 10^{-5} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(0.40 + x)(x)}{0.25 - x} \approx \frac{(0.40)(x)}{0.25}$$

and

$$x \approx 1.1 \times 10^{-5}$$

The approximations are valid (by the 5% rule), so

$$[\text{OH}^-] = x = 1.1 \times 10^{-5}$$

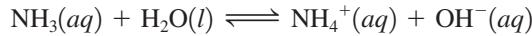
$$\text{pOH} = 4.95$$

$$\text{pH} = 14.00 - 4.95 = 9.05$$

This case is typical of a buffered solution in that the initial and equilibrium concentrations of buffering materials are essentially the same.

Alternative Solution

There is another way of looking at this problem. Since the solution contains relatively large quantities of both NH_4^+ and NH_3 , we can use the equilibrium



to calculate $[\text{OH}^-]$ and then calculate $[\text{H}^+]$ from K_w as we have just done. Or we can use the dissociation equilibrium for NH_4^+ , that is,



to calculate $[\text{H}^+]$ directly. Either choice will give the same answer, since the same equilibrium concentrations of NH_3 and NH_4^+ must satisfy both equilibria.

We can obtain the K_a value for NH_4^+ from the given K_b value for NH_3 , since $K_a \times K_b = K_w$:

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Then, using the Henderson–Hasselbalch equation, we have

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right) \\ &= 9.25 + \log\left(\frac{0.25 \text{ M}}{0.40 \text{ M}}\right) = 9.25 - 0.20 = 9.05 \end{aligned}$$

See Exercises 15.37 and 15.38.

Sample Exercise 15.6

Adding Strong Acid to a Buffered Solution I

Major Species



Cl^-



H^+



NH_4^+



NH_3



H_2O

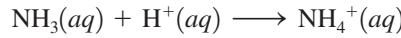
Calculate the pH of the solution that results when 0.10 mol gaseous HCl is added to 1.0 L of the buffered solution from Sample Exercise 15.5.

Solution

Before any reaction occurs, the solution contains the following major species:



What reaction can occur? We know that H^+ will not react with Cl^- to form HCl . In contrast to Cl^- , the NH_3 molecule has a great affinity for protons (this is demonstrated by the fact that NH_4^+ is such a weak acid [$K_a = 5.6 \times 10^{-10}$]). Thus NH_3 will react with H^+ to form NH_4^+ :



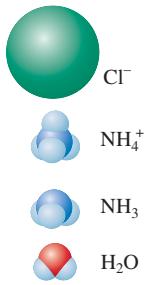
Since this reaction can be assumed to go essentially to completion to form the very weak acid NH_4^+ , we will do the stoichiometry calculations before we consider the equilibrium calculations. That is, we will let the reaction run to completion and then consider the equilibrium.

The stoichiometry calculations for this process are shown below.

Remember: Think about the chemistry first. Ask yourself if a reaction will occur among the major species.

	NH_3	+	H^+	→	NH_4^+
Before reaction:	$(1.0 \text{ L})(0.25 \text{ M})$ = 0.25 mol		0.10 mol ↑ Limiting reactant		$(1.0 \text{ L})(0.40 \text{ M})$ = 0.40 mol
After reaction:	0.25 – 0.10 = 0.15 mol		0		0.40 + 0.10 = 0.50 mol

Major Species



After the reaction goes to completion, the solution contains the major species

$$\text{NH}_3, \text{ NH}_4^+, \text{ Cl}^-, \text{ and } \text{H}_2\text{O}$$

and

$$[\text{NH}_3]_0 = \frac{0.15 \text{ mol}}{1.0 \text{ L}} = 0.15 \text{ M}$$

$$[\text{NH}_4^+]_0 = \frac{0.50 \text{ mol}}{1.0 \text{ L}} = 0.50 \text{ M}$$

We can use the Henderson–Hasselbalch equation, where

$$[\text{Base}] = [\text{NH}_3] \approx [\text{NH}_3]_0 = 0.15 \text{ M}$$

$$[\text{Acid}] = [\text{NH}_4^+] \approx [\text{NH}_4^+]_0 = 0.50 \text{ M}$$

Then

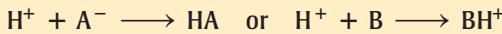
$$\begin{aligned} \text{pH} &= \text{p}K_a + \log\left(\frac{[\text{NH}_3]}{[\text{NH}_4^+]}\right) \\ &= 9.25 + \log\left(\frac{0.15 \text{ M}}{0.50 \text{ M}}\right) = 9.25 - 0.52 = 8.73 \end{aligned}$$

Note that the addition of HCl only slightly decreases the pH, as we would expect in a buffered solution.

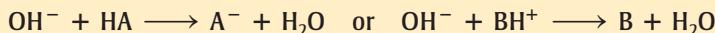
See Exercise 15.39.

Summary of the Most Important Characteristics of Buffered Solutions

- Buffered solutions contain relatively large concentrations of a weak acid and the corresponding weak base. They can involve a weak acid HA and the conjugate base A^- or a weak base B and the conjugate acid BH^+ .
- When H^+ is added to a buffered solution, it reacts essentially to completion with the weak base present:



- When OH^- is added to a buffered solution, it reacts essentially to completion with the weak acid present:



- The pH in the buffered solution is determined by the ratio of the concentrations of the weak acid and weak base. As long as this ratio remains virtually constant, the pH will remain virtually constant. This will be the case as long as the concentrations of the buffering materials (HA and A^- or B and BH^+) are large compared with the amounts of H^+ or OH^- added.

15.3 Buffering Capacity

A buffer with a large capacity contains large concentrations of the buffering components.

The **buffering capacity** of a buffered solution represents the amount of protons or hydroxide ions the buffer can absorb without a significant change in pH. A buffer with a large capacity contains large concentrations of buffering components and so can absorb a relatively large amount of protons or hydroxide ions and show little pH change. *The pH of a buffered solution is determined by the ratio $[\text{A}^-]/[\text{HA}]$. The capacity of a buffered solution is determined by the magnitudes of $[\text{HA}]$ and $[\text{A}^-]$.*

Sample Exercise 15.7

Adding Strong Acid to a Buffered Solution II

Calculate the change in pH that occurs when 0.010 mol gaseous HCl is added to 1.0 L of each of the following solutions:

Solution A: 5.00 M $\text{HC}_2\text{H}_3\text{O}_2$ and 5.00 M $\text{NaC}_2\text{H}_3\text{O}_2$

Solution B: 0.050 M $\text{HC}_2\text{H}_3\text{O}_2$ and 0.050 M $\text{NaC}_2\text{H}_3\text{O}_2$

For acetic acid, $K_a = 1.8 \times 10^{-5}$.

Solution

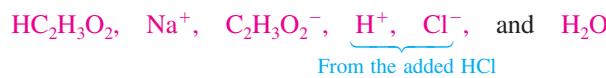
For both solutions the initial pH can be determined from the Henderson–Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}\right)$$

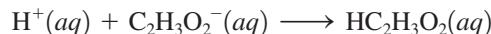
In each case, $[\text{C}_2\text{H}_3\text{O}_2^-] = [\text{HC}_2\text{H}_3\text{O}_2]$. Therefore, the initial pH for both A and B is

$$\text{pH} = \text{p}K_a + \log(1) = \text{p}K_a = -\log(1.8 \times 10^{-5}) = 4.74$$

After the addition of HCl to each of these solutions, the major species *before any reaction occurs* are



Will any reactions occur among these species? Note that we have a relatively large quantity of H^+ , which will readily react with any effective base. We know that Cl^- will not react with H^+ to form HCl in water. However, $\text{C}_2\text{H}_3\text{O}_2^-$ will react with H^+ to form the weak acid $\text{HC}_2\text{H}_3\text{O}_2$:

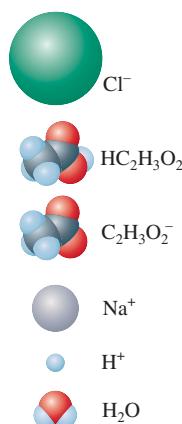


Because $\text{HC}_2\text{H}_3\text{O}_2$ is a weak acid, we assume that this reaction runs to completion; the 0.010 mol of added H^+ will convert 0.010 mol $\text{C}_2\text{H}_3\text{O}_2^-$ to 0.010 mol $\text{HC}_2\text{H}_3\text{O}_2$.

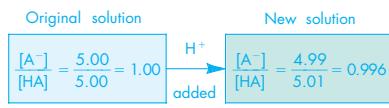
For solution A (since the solution volume is 1.0 L, the number of moles equals the molarity), the following calculations apply:

	H^+	+	$\text{C}_2\text{H}_3\text{O}_2^-$	→	$\text{HC}_2\text{H}_3\text{O}_2$
Before reaction:	0.010 M		5.00 M		5.00 M
After reaction:	0		4.99 M		5.01 M

Major Species



The new pH can be obtained by substituting the new concentrations into the Henderson–Hasselbalch equation:



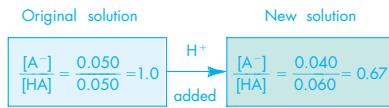
$$\begin{aligned}\text{pH} &= \text{p}K_a + \log\left(\frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}\right) \\ &= 4.74 + \log\left(\frac{4.99}{5.01}\right) = 4.74 - 0.0017 = 4.74\end{aligned}$$

There is virtually no change in pH for solution A when 0.010 mol gaseous HCl is added.

For solution B, the following calculations apply:

Before reaction:	H^+	+	$\text{C}_2\text{H}_3\text{O}_2^-$	\longrightarrow	$\text{HC}_2\text{H}_3\text{O}_2$
After reaction:	0.010 M		0.050 M		0.050 M
	0		0.040 M		0.060 M

The new pH is



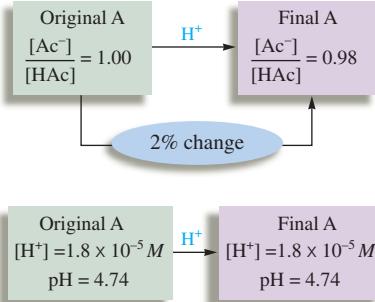
$$\begin{aligned}\text{pH} &= 4.74 + \log\left(\frac{0.040}{0.060}\right) \\ &= 4.74 - 0.18 = 4.56\end{aligned}$$

Although the pH change for solution B is small, a change did occur, which is in contrast to solution A.

These results show that solution A, which contains much larger quantities of buffering components, has a much higher buffering capacity than solution B.

See Exercises 15.39 and 15.40.

Solution A



We have seen that the pH of a buffered solution depends on the ratio of the concentrations of buffering components. When this ratio is least affected by added protons or hydroxide ions, the solution is the most resistant to a change in pH. To find the ratio that gives optimal buffering, let's suppose we have a buffered solution containing a large concentration of acetate ion and only a small concentration of acetic acid. Addition of protons to form acetic acid will produce a relatively large *percent* change in the concentration of acetic acid and so will produce a relatively large change in the ratio $[\text{C}_2\text{H}_3\text{O}_2^-]/[\text{HC}_2\text{H}_3\text{O}_2]$ (see Table 15.1). Similarly, if hydroxide ions are added to remove some acetic acid, the percent change in the concentration of acetic acid is again large. The same effects are seen if the initial concentration of acetic acid is large and that of acetate ion is small.

Solution B

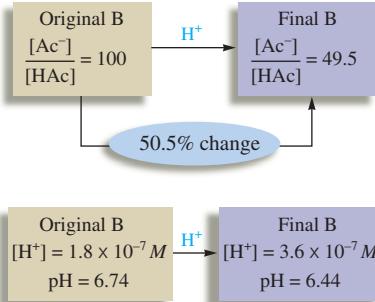


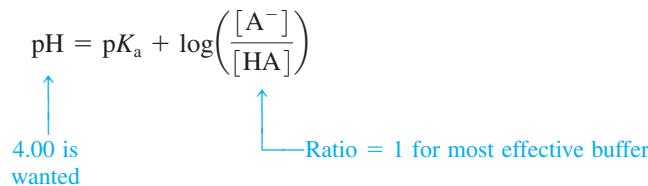
TABLE 15.1 Change in $[\text{C}_2\text{H}_3\text{O}_2^-]/[\text{HC}_2\text{H}_3\text{O}_2]$ for Two Solutions When 0.01 mol H^+ Is Added to 1.0 L of Each

Solution	$\left(\frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}\right)_{\text{orig}}$	$\left(\frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}\right)_{\text{new}}$	Percent Change
A	$\frac{1.00 \text{ M}}{1.00 \text{ M}} = 1.00$	$\frac{0.99 \text{ M}}{1.01 \text{ M}} = 0.98$	$1.00 \rightarrow 0.98$
B	$\frac{1.00 \text{ M}}{0.01 \text{ M}} = 100$	$\frac{0.99 \text{ M}}{0.02 \text{ M}} = 49.5$	$100 \rightarrow 49.5$

Because large changes in the ratio $[A^-]/[HA]$ will produce large changes in pH, we want to avoid this situation for the most effective buffering. This type of reasoning leads us to the general conclusion that optimal buffering occurs when $[HA]$ is equal to $[A^-]$. It is for this condition that the ratio $[A^-]/[HA]$ is most resistant to change when H^+ or OH^- is added to the buffered solution. This means that when choosing the buffering components for a specific application, we want $[A^-]/[HA]$ to equal 1. It follows that since

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) = pK_a + \log(1) = pK_a$$

the pK_a of the weak acid to be used in the buffer should be as close as possible to the desired pH. For example, suppose we need a buffered solution with a pH of 4.00. The most effective buffering will occur when $[HA]$ is equal to $[A^-]$. From the Henderson–Hasselbalch equation,



That is, $4.00 = pK_a + \log(1) = pK_a + 0$ and $pK_a = 4.00$

Thus the best choice of a weak acid is one that has $pK_a = 4.00$ or $K_a = 1.0 \times 10^{-4}$.

Sample Exercise 15.8

Preparing a Buffer

A chemist needs a solution buffered at pH 4.30 and can choose from the following acids (and their sodium salts):

- a. chloroacetic acid ($K_a = 1.35 \times 10^{-3}$)
- b. propanoic acid ($K_a = 1.3 \times 10^{-5}$)
- c. benzoic acid ($K_a = 6.4 \times 10^{-5}$)
- d. hypochlorous acid ($K_a = 3.5 \times 10^{-8}$)

Calculate the ratio $[HA]/[A^-]$ required for each system to yield a pH of 4.30. Which system will work best?

Solution

A pH of 4.30 corresponds to

$$[H^+] = 10^{-4.30} = \text{antilog}(-4.30) = 5.0 \times 10^{-5} M$$

Since K_a values rather than pK_a values are given for the various acids, we use Equation (15.1)

$$[H^+] = K_a \frac{[HA]}{[A^-]}$$

rather than the Henderson–Hasselbalch equation. We substitute the required $[H^+]$ and K_a for each acid into Equation (15.1) to calculate the ratio $[HA]/[A^-]$ needed in each case.

Acid	$[H^+] = K_a \frac{[HA]}{[A^-]}$	$\frac{[HA]}{[A^-]}$
a. Chloroacetic	$5.0 \times 10^{-5} = 1.35 \times 10^{-3} \left(\frac{[HA]}{[A^-]} \right)$	3.7×10^{-2}
b. Propanoic	$5.0 \times 10^{-5} = 1.3 \times 10^{-5} \left(\frac{[HA]}{[A^-]} \right)$	3.8
c. Benzoic	$5.0 \times 10^{-5} = 6.4 \times 10^{-5} \left(\frac{[HA]}{[A^-]} \right)$	0.78
d. Hypochlorous	$5.0 \times 10^{-5} = 3.5 \times 10^{-8} \left(\frac{[HA]}{[A^-]} \right)$	1.4×10^3

Since $[HA]/[A^-]$ for benzoic acid is closest to 1, the system of benzoic acid and its sodium salt will be the best choice among those given for buffering a solution at pH 4.3. This example demonstrates the principle that the optimal buffering system has a pK_a value close to the desired pH. The pK_a for benzoic acid is 4.19.

See Exercises 15.45 and 15.46.

15.4 Titrations and pH Curves

As we saw in Chapter 4, a titration is commonly used to determine the amount of acid or base in a solution. This process involves a solution of known concentration (the titrant) delivered from a buret into the unknown solution until the substance being analyzed is just consumed. The stoichiometric (equivalence) point is often signaled by the color change of an indicator. In this section we will discuss the pH changes that occur during an acid–base titration. We will use this information later to show how an appropriate indicator can be chosen for a particular titration.

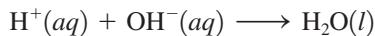
The progress of an acid–base titration is often monitored by plotting the pH of the solution being analyzed as a function of the amount of titrant added. Such a plot is called a **pH curve** or **titration curve**.



A setup used to do the pH titration of an acid or a base.

Strong Acid–Strong Base Titrations

The net ionic reaction for a strong acid–strong base titration is



To compute $[H^+]$ at a given point in the titration, we must determine the amount of H^+ that remains at that point and divide by the total volume of the solution. Before we proceed, we need to consider a new unit, which is especially convenient for titrations. Since titrations usually involve small quantities (burets are typically graduated in milliliters), the mole is inconveniently large. Therefore, we will use the **millimole** (abbreviated **mmol**), which, as the prefix indicates, is a thousandth of a mole:

$$1 \text{ mmol} = \frac{1 \text{ mol}}{1000} = 10^{-3} \text{ mol}$$

So far we have defined molarity only in terms of moles per liter. We can now define it in terms of *millimoles per milliliter*, as shown below:

$$1 \text{ millimole} = 1 \times 10^{-3} \text{ mol}$$

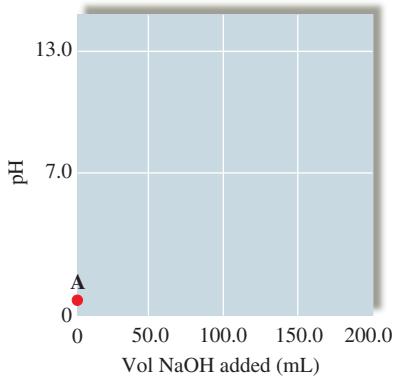
$$1 \text{ mL} = 1 \times 10^{-3} \text{ L}$$

$$\frac{\text{mmol}}{\text{mL}} = \frac{\text{mol}}{\text{L}} = M$$

$$\text{Molarity} = \frac{\text{mol solute}}{\text{L solution}} = \frac{\frac{\text{mol solute}}{1000}}{\frac{\text{L solution}}{1000}} = \frac{\text{mmol solute}}{\text{mL solution}}$$

A 1.0 M solution thus contains 1.0 mole of solute per liter of solution or, *equivalently*, 1.0 millimole of solute per milliliter of solution. Just as we obtain the number of moles of solute from the product of the volume in liters and the molarity, we obtain the number of millimoles of solute from the product of the volume in milliliters and the molarity:

$$\text{Number of mmol} = \text{volume (in mL)} \times \text{molarity}$$



CASE STUDY: Strong Acid–Strong Base Titration

We will illustrate the calculations involved in a strong acid–strong base titration by considering the titration of 50.0 mL of 0.200 M HNO_3 with 0.100 M NaOH . We will calculate the pH of the solution at selected points during the course of the titration, where specific volumes of 0.100 M NaOH have been added.

A. No NaOH has been added.

Since HNO_3 is a strong acid (is completely dissociated), the solution contains the major species

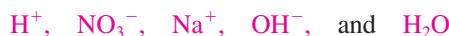


and the pH is determined by the H^+ from the nitric acid. Since 0.200 M HNO_3 contains 0.200 M H^+ ,

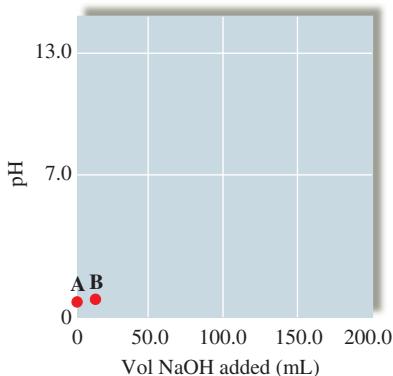
$$[\text{H}^+] = 0.200\text{ M} \quad \text{and} \quad \text{pH} = 0.699$$

B. 10.0 mL of 0.100 M NaOH has been added.

In the mixed solution *before any reaction occurs*, the major species are

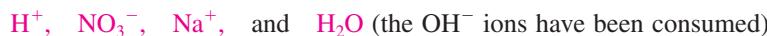


Note that large quantities of both H^+ and OH^- are present. The 1.00 mmol ($10.0\text{ mL} \times 0.100\text{ M}$) of added OH^- will react with 1.00 mmol H^+ to form water:



	H^+	+	OH^-	\longrightarrow	H_2O
Before reaction:	$50.0\text{ mL} \times 0.200\text{ M}$ $= 10.0\text{ mmol}$		$10.0\text{ mL} \times 0.100\text{ M}$ $= 1.00\text{ mmol}$		
After reaction:	$10.0 - 1.00$ $= 9.0\text{ mmol}$		$1.00 - 1.00$ $= 0$		

After the reaction, the solution contains



and the pH will be determined by the H^+ remaining:

$$[\text{H}^+] = \frac{\text{mmol H}^+ \text{ left}}{\text{volume of solution (mL)}} = \frac{9.0 \text{ mmol}}{(50.0 + 10.0) \text{ mL}} = 0.15 \text{ M}$$

↗
 Original volume of
 HNO_3 solution

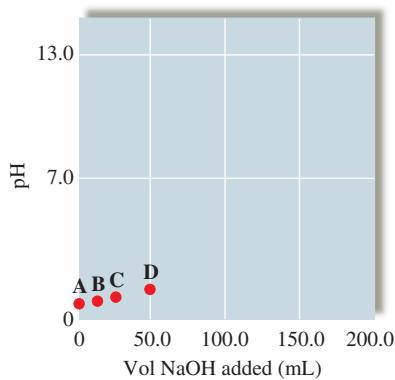
↙
 Volume of
 NaOH added

$$\text{pH} = -\log(0.15) = 0.82$$

The final solution volume is the sum of the original volume of HNO_3 and the volume of added NaOH .

C. 20.0 mL (total) of 0.100 M NaOH has been added.

We consider this point from the perspective that a total of 20.0 mL NaOH has been added to the *original* solution, rather than that 10.0 mL has been added to the solution from point B. It is best to go back to the original solution each time so that a mistake made at an earlier point does not show up in each succeeding calculation. As before, the added OH⁻ will react with H⁺ to form water:



	H ⁺	+	OH ⁻	→	H ₂ O
Before reaction:	50.0 mL × 0.200 M = 10.0 mmol		20.0 mL × 0.100 M = 2.00 mmol		
After reaction:	10.0 – 2.00 = 8.00 mmol		2.00 – 2.00 = 0 mmol		

After the reaction

$$[\text{H}^+] = \frac{8.00 \text{ mmol}}{(50.0 + 20.0) \text{ mL}} = 0.11 \text{ M}$$

$$\text{pH} = 0.942$$

D. 50.0 mL (total) of 0.100 M NaOH has been added.

Proceeding exactly as for points B and C, the pH is found to be 1.301.

E. 100.0 mL (total) of 0.100 M NaOH has been added.

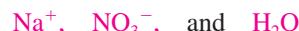
At this point the amount of NaOH that has been added is

$$100.0 \text{ mL} \times 0.100 \text{ M} = 10.0 \text{ mmol}$$

The original amount of nitric acid was

$$50.0 \text{ mL} \times 0.200 \text{ M} = 10.0 \text{ mmol}$$

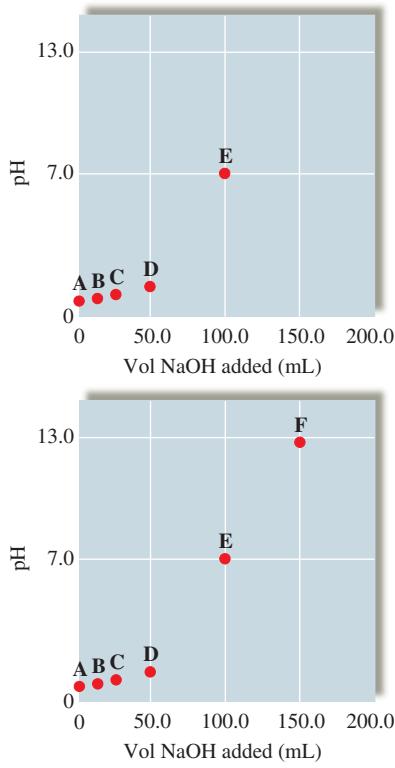
Enough OH⁻ has been added to react exactly with the H⁺ from the nitric acid. This is the **stoichiometric point**, or **equivalence point**, of the titration. At this point the major species in solution are



Since Na⁺ has no acid or base properties and NO₃⁻ is the anion of the strong acid HNO₃ and is therefore a very weak base, neither NO₃⁻ nor Na⁺ affects the pH, and the solution is neutral (the pH is 7.00).

F. 150.0 mL (total) of 0.100 M NaOH has been added.

The stoichiometric calculations for the titration reaction are as follows:



	H ⁺	+	OH ⁻	→	H ₂ O
Before reaction:	50.0 mL × 0.200 M = 10.0 mmol		150.0 mL × 0.100 M = 15.0 mmol		
After reaction:	10.0 – 10.0 = 0 mmol		15.0 – 10.0 = 5.0 mmol		
			↑ Excess OH ⁻ added		

Now OH^- is *in excess* and will determine the pH:

$$[\text{OH}^-] = \frac{\text{mmol OH}^- \text{ in excess}}{\text{volume (mL)}} = \frac{5.0 \text{ mmol}}{(50.0 + 150.0) \text{ mL}} = \frac{5.0 \text{ mmol}}{200.0 \text{ mL}} = 0.025 \text{ M}$$

Since $[\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$,

$$[\text{H}^+] = \frac{1.0 \times 10^{-14}}{2.5 \times 10^{-2}} = 4.0 \times 10^{-13} \text{ M} \quad \text{and} \quad \text{pH} = 12.40$$

G. 200.0 mL (total) of 0.100 M NaOH has been added.

Proceeding as for point F, the pH is found to be 12.60.

The results of these calculations are summarized by the pH curve shown in Fig. 15.1. Note that the pH changes very gradually until the titration is close to the equivalence point, where a dramatic change occurs. This behavior is due to the fact that early in the titration there is a relatively large amount of H^+ in the solution, and the addition of a given amount of OH^- thus produces a small change in pH. However, near the equivalence point $[\text{H}^+]$ is relatively small, and the addition of a small amount of OH^- produces a large change.

The pH curve in Fig. 15.1, typical of the titration of a strong acid with a strong base, has the following characteristics:

Before the equivalence point, $[\text{H}^+]$ (and hence the pH) can be calculated by dividing the number of millimoles of H^+ remaining by the total volume of the solution in milliliters.

At the equivalence point, the pH is 7.00.

After the equivalence point, $[\text{OH}^-]$ can be calculated by dividing the number of millimoles of excess OH^- by the total volume of the solution. Then $[\text{H}^+]$ is obtained from K_w .

The titration of a strong base with a strong acid requires reasoning very similar to that used above, except, of course, that OH^- is in excess before the equivalence point and H^+ is in excess after the equivalence point. The pH curve for the titration of 100.0 mL of 0.50 M NaOH with 1.0 M HCl is shown in Fig. 15.2.

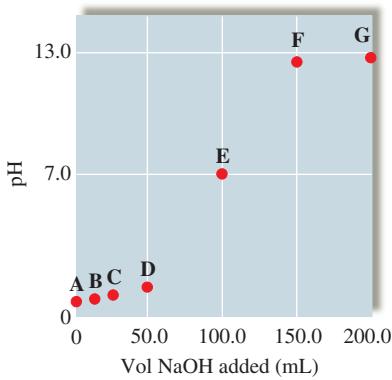


FIGURE 15.1

The pH curve for the titration of 50.0 mL of 0.200 M HNO_3 with 0.100 M NaOH. Note that the equivalence point occurs at 100.0 mL of NaOH added, the point where exactly enough OH^- has been added to react with all the H^+ originally present. The pH of 7 at the equivalence point is characteristic of a strong acid–strong base titration.

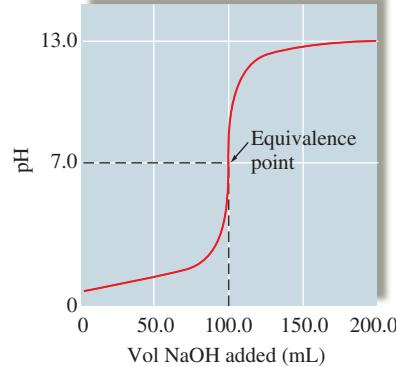


FIGURE 15.2

The pH curve for the titration of 100.0 mL of 0.50 M NaOH with 1.0 M HCl. The equivalence point occurs at 50.00 mL of HCl added, since at this point 5.0 mmol H^+ has been added to react with the original 5.0 mmol OH^- .

Titrations of Weak Acids with Strong Bases

We have seen that since strong acids and strong bases are completely dissociated, the calculations to obtain the pH curves for titrations involving the two are quite straightforward. However, when the acid being titrated is a weak acid, there is a major difference: To calculate $[H^+]$ after a certain amount of strong base has been added, we must deal with the weak acid dissociation equilibrium. We have dealt with this same situation earlier in this chapter when we treated buffered solutions. Calculation of the pH curve for a titration of a weak acid with a strong base really amounts to a series of buffer problems. In performing these calculations it is very important to remember that even though the acid is weak, it *reacts essentially to completion* with hydroxide ion, a very strong base.

Calculating the pH curve for a weak acid–strong base titration involves a two-step procedure.

- 1 **A stoichiometry problem.** The reaction of hydroxide ion with the weak acid is assumed to run to completion, and the concentrations of the acid *remaining* and the conjugate base *formed* are determined.
- 2 **An equilibrium problem.** The position of the weak acid equilibrium is determined, and the pH is calculated.

It is *essential* to do these steps *separately*. Note that the procedures necessary to do these calculations have all been used before.

CASE STUDY: Weak Acid–Strong Base Titration

As an illustration, we will consider the titration of 50.0 mL of 0.10 M acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$, $K_a = 1.8 \times 10^{-5}$) with 0.10 M NaOH. As before, we will calculate the pH at various points representing volumes of added NaOH.

A. No NaOH has been added.

This is a typical weak acid calculation of the type introduced in Chapter 14. The pH is 2.87. (Check this yourself.)

B. 10.0 mL of 0.10 M NaOH has been added.

The major species in the mixed solution *before any reaction takes place* are



The strong base OH^- will react with the strongest proton donor, which in this case is $\text{HC}_2\text{H}_3\text{O}_2$.

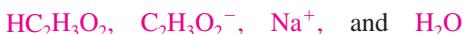
The Stoichiometry Problem

You are again doing exactly the same type of calculation already considered in Chapter 14.

	OH^-	+	$\text{HC}_2\text{H}_3\text{O}_2$	→	$\text{C}_2\text{H}_3\text{O}_2^-$	+	H_2O
Before reaction:	$10 \text{ mL} \times 0.10 \text{ M}$ = 1.0 mmol		$50.0 \text{ mL} \times 0.10 \text{ M}$ = 5.0 mmol		0 mmol		
After reaction:	$1.0 - 1.0$ = 0 mmol ↑ Limiting reactant		$5.0 - 1.0$ = 4.0 mmol		1.0 mmol ↑ Formed by the reaction		

The Equilibrium Problem

We examine the major components left in the solution *after the reaction takes place* to decide on the dominant equilibrium. The major species are



Since $\text{HC}_2\text{H}_3\text{O}_2$ is a much stronger acid than H_2O , and since $\text{C}_2\text{H}_3\text{O}_2^-$ is the conjugate base of $\text{HC}_2\text{H}_3\text{O}_2$, the pH will be determined by the position of the acetic acid dissociation equilibrium:



where

$$K_a = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}$$

We follow the usual steps to complete the equilibrium calculations:

Initial Concentration			Equilibrium Concentration
$[\text{HC}_2\text{H}_3\text{O}_2]_0 = \frac{4.0 \text{ mmol}}{(50.0 + 10.0) \text{ mL}} = \frac{4.0}{60.0}$			$[\text{HC}_2\text{H}_3\text{O}_2] = \frac{4.0}{60.0} - x$
$[\text{C}_2\text{H}_3\text{O}_2^-]_0 = \frac{1.0 \text{ mmol}}{(50.0 + 10.0) \text{ mL}} = \frac{1.0}{60.0}$	$x \text{ mmol/mL}$ $\xrightarrow{\text{HC}_2\text{H}_3\text{O}_2 \text{ dissociates}}$		$[\text{C}_2\text{H}_3\text{O}_2^-] = \frac{1.0}{60.0} + x$
$[\text{H}^+]_0 \approx 0$			$[\text{H}^+] = x$

The initial concentrations are defined after the reaction with OH^- has gone to completion but before any dissociation of $\text{HC}_2\text{H}_3\text{O}_2$ occurs.

The appropriate ICE table is

	$\text{HC}_2\text{H}_3\text{O}_2(aq)$	\rightleftharpoons	$\text{H}^+(aq)$	+	$\text{C}_2\text{H}_3\text{O}_2^-(aq)$
I nitial:	$\frac{4.0}{60.0}$		≈ 0		$\frac{1.0}{60.0}$
C hange:	$-x$		$+x$		$+x$
E quilibrium:	$\frac{4.0}{60.0} - x$		x		$\frac{1.0}{60.0} + x$

Therefore,

$$1.8 \times 10^{-5} = K_a = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{x \left(\frac{1.0}{60.0} + x \right)}{\frac{4.0}{60.0} - x} \approx \frac{x \left(\frac{1.0}{60.0} \right)}{\frac{4.0}{60.0}} = \left(\frac{1.0}{4.0} \right) x$$

$$x = \left(\frac{4.0}{1.0} \right) (1.8 \times 10^{-5}) = 7.2 \times 10^{-5} = [\text{H}^+] \quad \text{and} \quad \text{pH} = 4.14$$

Note that the approximations made are well within the 5% rule.

C. 25.0 mL (total) of 0.10 M NaOH has been added.

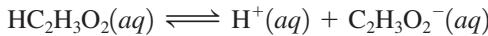
The procedure here is very similar to that used at point B and will only be summarized briefly. The stoichiometry problem is summarized as follows:

	OH^-	+	$\text{HC}_2\text{H}_3\text{O}_2$	\longrightarrow	$\text{C}_2\text{H}_3\text{O}_2^-$	+	H_2O
Before reaction:	$25.0 \text{ mL} \times 0.10 \text{ M}$		$50.0 \text{ mL} \times 0.10 \text{ M}$		0 mmol		
	$= 2.5 \text{ mmol}$		$= 5.0 \text{ mmol}$				
After reaction:	$2.5 - 2.5 = 0$		$5.0 - 2.5 = 2.5$		2.5 mmol		

After the reaction, the major species in solution are



The equilibrium that will control the pH is



and the pertinent concentrations are as follows:

Initial Concentration		Equilibrium Concentration
$[\text{HC}_2\text{H}_3\text{O}_2]_0 = \frac{2.5 \text{ mmol}}{(50.0 + 25.0) \text{ mL}}$		$[\text{HC}_2\text{H}_3\text{O}_2] = \frac{2.5}{75.0} - x$
$[\text{C}_2\text{H}_3\text{O}_2^-]_0 = \frac{2.5 \text{ mmol}}{(50.0 + 25.0) \text{ mL}}$	$\xrightarrow[\text{dissociates}]{\text{HC}_2\text{H}_3\text{O}_2}$	$[\text{C}_2\text{H}_3\text{O}_2^-] = \frac{2.5}{75.0} + x$
$[\text{H}^+]_0 \approx 0$		$[\text{H}^+] = x$

The corresponding ICE table is

	$\text{HC}_2\text{H}_3\text{O}_2(aq)$	\rightleftharpoons	$\text{H}^+(aq)$	+	$\text{C}_2\text{H}_3\text{O}_2^-(aq)$
I nitial:	$\frac{2.5}{75.0}$		≈ 0		$\frac{2.5}{75.0}$
C hange:	$-x$		$+x$		$+x$
E quilibrium:	$\frac{2.5}{75.0} - x$		x		$\frac{2.5}{75.0} + x$

Therefore,

$$1.8 \times 10^{-5} = K_a = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{x \left(\frac{2.5}{75.0} + x \right)}{\frac{2.5}{75.0} - x} \approx \frac{x \left(\frac{2.5}{75.0} \right)}{\frac{2.5}{75.0}}$$

$$x = 1.8 \times 10^{-5} = [\text{H}^+] \quad \text{and} \quad \text{pH} = 4.74$$

This is a special point in the titration because it is *halfway to the equivalence point*. The original solution, 50.0 mL of 0.10 M $\text{HC}_2\text{H}_3\text{O}_2$, contained 5.0 mmol $\text{HC}_2\text{H}_3\text{O}_2$. Thus 5.0 mmol OH^- is required to reach the equivalence point. That is, 50 mL NaOH is required, since

$$(50.0 \text{ mL})(0.10 \text{ M}) = 5.0 \text{ mmol}$$

After 25.0 mL NaOH has been added, half the original $\text{HC}_2\text{H}_3\text{O}_2$ has been converted to $\text{C}_2\text{H}_3\text{O}_2^-$. At this point in the titration $[\text{HC}_2\text{H}_3\text{O}_2]_0$ is equal to $[\text{C}_2\text{H}_3\text{O}_2^-]_0$. We can neglect the effect of dissociation; that is,

At this point, half the acid has been used up, so

$$[\text{HC}_2\text{H}_3\text{O}_2] = [\text{C}_2\text{H}_3\text{O}_2^-]$$

$$[\text{HC}_2\text{H}_3\text{O}_2] = [\text{HC}_2\text{H}_3\text{O}_2]_0 - x \approx [\text{HC}_2\text{H}_3\text{O}_2]_0$$

$$[\text{C}_2\text{H}_3\text{O}_2^-] = [\text{C}_2\text{H}_3\text{O}_2^-]_0 + x \approx [\text{C}_2\text{H}_3\text{O}_2^-]_0$$

The expression for K_a at the halfway point is

$$K_a = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]_0}{[\text{HC}_2\text{H}_3\text{O}_2]_0} = [\text{H}^+]$$

Equal at the
halfway point

Then, *at the halfway point* in the titration,

$$[\text{H}^+] = K_a \quad \text{and} \quad \text{pH} = \text{p}K_a$$

D. 40.0 mL (total) of 0.10 M NaOH has been added.

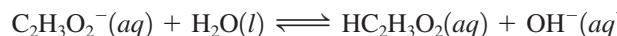
The procedures required here are the same as those used for points B and C. The pH is 5.35. (Check this yourself.)

E. 50.0 mL (total) of 0.10 M NaOH has been added.

This is the equivalence point of the titration; 5.0 mmol OH^- has been added, which will just react with the 5.0 mmol $\text{HC}_2\text{H}_3\text{O}_2$ originally present. At this point the solution contains the major species



Note that the solution contains $\text{C}_2\text{H}_3\text{O}_2^-$, which is a base. Remember that a base wants to combine with a proton, and the only source of protons in this solution is water. Thus the reaction will be



This is a *weak base* reaction characterized by K_b :

$$K_b = \frac{[\text{HC}_2\text{H}_3\text{O}_2][\text{OH}^-]}{[\text{C}_2\text{H}_3\text{O}_2^-]} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

The relevant concentrations are as follows:

Initial Concentration (before any $\text{C}_2\text{H}_3\text{O}_2^-$ reacts with H_2O)			Equilibrium Concentration
$[\text{C}_2\text{H}_3\text{O}_2^-]_0 = \frac{5.0 \text{ mmol}}{(50.0 + 50.0) \text{ mL}}$ $= 0.050 \text{ M}$	$x \text{ mmol/mL}$ $\xrightarrow{\text{C}_2\text{H}_3\text{O}_2^- \text{ reacts with H}_2\text{O}}$		$[\text{C}_2\text{H}_3\text{O}_2^-] = 0.050 - x$ $[\text{OH}^-] = x$ $[\text{HC}_2\text{H}_3\text{O}_2] = x$
$[\text{OH}^-]_0 \approx 0$			
$[\text{HC}_2\text{H}_3\text{O}_2]_0 = 0$			

The corresponding ICE table is

	$\text{C}_2\text{H}_3\text{O}_2^-(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{HC}_2\text{H}_3\text{O}_2(aq)$	+	$\text{OH}^-(aq)$
Initial:	0.050		—		0		≈ 0
Change:	$-x$		—		$+x$		$+x$
Equilibrium:	$0.050 - x$		—		x		x

Therefore,

$$5.6 \times 10^{-10} = K_b = \frac{[\text{HC}_2\text{H}_3\text{O}_2][\text{OH}^-]}{[\text{C}_2\text{H}_3\text{O}_2^-]} = \frac{(x)(x)}{0.050 - x} \approx \frac{x^2}{0.050}$$

$$x \approx 5.3 \times 10^{-6}$$

The approximation is valid (by the 5% rule), so

$$[\text{OH}^-] = 5.3 \times 10^{-6} \text{ M}$$

and

$$[\text{H}^+][\text{OH}^-] = K_w = 1.0 \times 10^{-14}$$

$$[\text{H}^+] = 1.9 \times 10^{-9} \text{ M}$$

$$\text{pH} = 8.72$$

The pH at the equivalence point of a titration of a weak acid with a strong base is always greater than 7.

This is another important result: *The pH at the equivalence point of a titration of a weak acid with a strong base is always greater than 7.* This is so because the anion of the acid, which remains in solution at the equivalence point, is a base. In contrast, for the titration of a strong acid with a strong base, the pH at the equivalence point is 7.0, because the anion remaining in this case is *not* an effective base.

F. 60.0 mL (total) of 0.10 M NaOH has been added.

At this point, excess OH^- has been added. The stoichiometric calculations are as follows:

	OH^-	+	$\text{HC}_2\text{H}_3\text{O}_2$	\longrightarrow	$\text{C}_2\text{H}_3\text{O}_2^-$	+	H_2O
Before reaction:	$60.0 \text{ mL} \times 0.10 \text{ M}$		$50.0 \text{ mL} \times 0.10 \text{ M}$				
	= 6.0 mmol		= 5.0 mmol				0 mmol
After reaction:	$6.0 - 5.0$						
	= 1.0 mmol in excess		$5.0 - 5.0 = 0$				5.0 mmol

After the reaction is complete, the solution contains the major species



There are two bases in this solution, OH^- and $\text{C}_2\text{H}_3\text{O}_2^-$. However, $\text{C}_2\text{H}_3\text{O}_2^-$ is a weak base compared with OH^- . Therefore, the amount of OH^- produced by reaction of $\text{C}_2\text{H}_3\text{O}_2^-$ with H_2O will be small compared with the excess OH^- already in solution. You can verify this conclusion by looking at point E, where only $5.3 \times 10^{-6} \text{ M}$ OH^- was produced by $\text{C}_2\text{H}_3\text{O}_2^-$. The amount in this case will be even smaller, since the excess OH^- will push the K_b equilibrium to the left.

Thus the pH is determined by the excess OH^- :

$$[\text{OH}^-] = \frac{\text{mmol of OH}^- \text{ in excess}}{\text{volume (in mL)}} = \frac{1.0 \text{ mmol}}{(50.0 + 60.0) \text{ mL}} \\ = 9.1 \times 10^{-3} \text{ M}$$

and

$$[\text{H}^+] = \frac{1.0 \times 10^{-14}}{9.1 \times 10^{-3}} = 1.1 \times 10^{-12} \text{ M}$$

$$\text{pH} = 11.96$$

G. 75.0 mL (total) of 0.10 M NaOH has been added.

The procedure needed here is very similar to that for point F. The pH is 12.30. (Check this yourself.)

The pH curve for this titration is shown in Fig. 15.3. It is important to note the differences between this curve and that in Fig. 15.1. For example, the shapes of the plots are

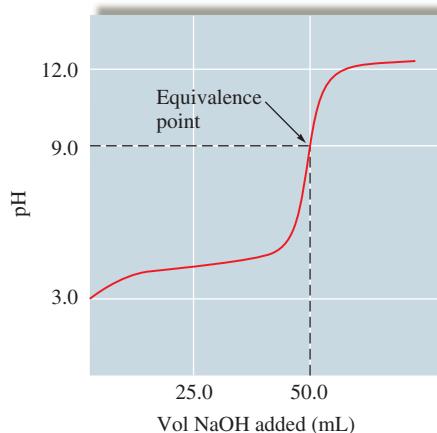
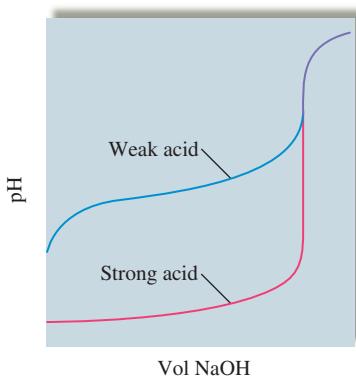


FIGURE 15.3

The pH curve for the titration of 50.0 mL of 0.100 M $\text{HC}_2\text{H}_3\text{O}_2$ with 0.100 M NaOH. Note that the equivalence point occurs at 50.0 mL of NaOH added, where the amount of added OH^- exactly equals the original amount of acid. The pH at the equivalence point is greater than 7.0 because the $\text{C}_2\text{H}_3\text{O}_2^-$ ion present at this point is a base and reacts with water to produce OH^- .



The equivalence point is defined by the stoichiometry, not by the pH.

Sample Exercise 15.9

Titration of a Weak Acid

Hydrogen cyanide gas (HCN), a powerful respiratory inhibitor, is highly toxic. It is a very weak acid ($K_a = 6.2 \times 10^{-10}$) when dissolved in water. If a 50.0-mL sample of 0.100 M HCN is titrated with 0.100 M NaOH, calculate the pH of the solution

- after 8.00 mL of 0.100 M NaOH has been added.
- at the halfway point of the titration.
- at the equivalence point of the titration.

Solution

- a. *The stoichiometry problem.* After 8.00 mL of 0.100 M NaOH has been added, the following calculations apply:

HCN	+	OH^-	\longrightarrow	CN^-	+ H_2O
Before reaction:	$50.0 \text{ mL} \times 0.100 \text{ M}$	$8.00 \text{ mL} \times 0.100 \text{ M}$		0 mmol	
	$= 5.00 \text{ mmol}$	$= 0.800 \text{ mmol}$			
After reaction:	$5.00 - 0.800$	$0.800 - 0.800 = 0$		0.800 mmol	
	$= 4.20 \text{ mmol}$				

The equilibrium problem. Since the solution contains the major species



the position of the acid dissociation equilibrium



will determine the pH.

Initial Concentration	Equilibrium Concentration		
$[\text{HCN}]_0 = \frac{4.2 \text{ mmol}}{(50.0 + 8.0) \text{ mL}}$	$x \text{ mmol/mL}$	$[\text{HCN}] = \frac{4.2}{58.0} - x$	
$[\text{CN}^-]_0 = \frac{0.800 \text{ mmol}}{(50.0 + 8.0) \text{ mL}}$	$\xrightarrow{\text{HCN dissociates}}$	$[\text{CN}^-] = \frac{0.80}{58.0} + x$	
$[\text{H}^+]_0 \approx 0$		$[\text{H}^+] = x$	

The corresponding ICE table is

	$\text{HCN}(aq)$	\rightleftharpoons	$\text{H}^+(aq)$	+	$\text{CN}^-(aq)$
Initial:	$\frac{4.2}{58.0}$		≈ 0		$\frac{0.80}{58.0}$
Change:	$-x$		$+x$		$+x$
Equilibrium:	$\frac{4.2}{58.0} - x$		x		$\frac{0.80}{58.0} + x$

Substituting the equilibrium concentrations into the expression for K_a gives

$$6.2 \times 10^{-10} = K_a = \frac{[\text{H}^+][\text{CN}^-]}{[\text{HCN}]} = \frac{x \left(\frac{0.80}{58.0} + x \right)}{\frac{4.2}{58.0} - x} \approx \frac{x \left(\frac{0.80}{58.0} \right)}{\left(\frac{4.2}{58.0} \right)} = x \left(\frac{0.80}{4.2} \right)$$

$$x = 3.3 \times 10^{-9} M = [\text{H}^+] \quad \text{and} \quad \text{pH} = 8.49$$

The approximations made here are well within the 5% rule.

- b.** At the halfway point of the titration. The amount of HCN originally present can be obtained from the original volume and molarity:

$$50.0 \text{ mL} \times 0.100 M = 5.00 \text{ mmol}$$

Thus the halfway point will occur when 2.50 mmol OH^- has been added:

$$\text{Volume of NaOH (in mL)} \times 0.100 M = 2.50 \text{ mmol OH}^-$$

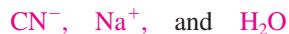
or

$$\text{Volume of NaOH} = 25.0 \text{ mL}$$

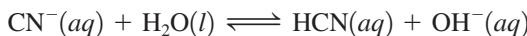
As was pointed out previously, at the halfway point $[\text{HCN}]$ is equal to $[\text{CN}^-]$ and pH is equal to $\text{p}K_a$. Thus, after 25.0 mL of 0.100 M NaOH has been added,

$$\text{pH} = \text{p}K_a = -\log(6.2 \times 10^{-10}) = 9.21$$

- c.** At the equivalence point. The equivalence point will occur when a total of 5.00 mmol OH^- has been added. Since the NaOH solution is 0.100 M, the equivalence point occurs when 50.0 mL NaOH has been added. This amount will form 5.00 mmol CN^- . The major species in solution at the equivalence point are



Thus the reaction that will control the pH involves the basic cyanide ion extracting a proton from water:



$$\text{and } K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.2 \times 10^{-10}} = 1.6 \times 10^{-5} = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]}$$

Initial Concentration	Equilibrium Concentration
$[\text{CN}^-]_0 = \frac{5.00 \text{ mmol}}{(50.0 + 50.0) \text{ mL}}$ $= 5.00 \times 10^{-2} M$	$[\text{CN}^-] = (5.00 \times 10^{-2}) - x$
$[\text{HCN}]_0 = 0$	$[\text{HCN}] = x$
$[\text{OH}^-]_0 \approx 0$	$[\text{OH}^-] = x$

The corresponding ICE table is

	$\text{CN}^-(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{HCN}(aq)$	+	$\text{OH}^-(aq)$
Initial:	0.050		—		0		0
Change:	$-x$		—		$+x$		$+x$
Equilibrium:	$0.050 - x$		—		x		x

Substituting the equilibrium concentrations into the expression for K_b and solving in the usual way gives

$$[\text{OH}^-] = x = 8.9 \times 10^{-4}$$

Then, from K_w , we have

$$[\text{H}^+] = 1.1 \times 10^{-11} \quad \text{and} \quad \text{pH} = 10.96$$

See Exercises 15.55, 15.57, and 15.58.

The amount of acid present, not its strength, determines the equivalence point.

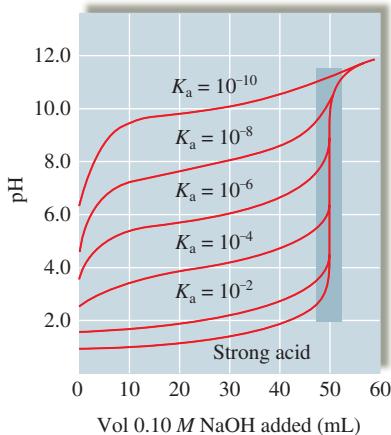


FIGURE 15.4

The pH curves for the titrations of 50.0-mL samples of 0.10 M acids with various K_a values with 0.10 M NaOH.

Two important conclusions can be drawn from a comparison of the titration of 50.0 mL of 0.1 M acetic acid covered earlier in this section and that of 50.0 mL of 0.1 M hydrocyanic acid analyzed in Sample Exercise 15.9. First, the same amount of 0.1 M NaOH is required to reach the equivalence point in both cases. The fact that HCN is a much weaker acid than $\text{HC}_2\text{H}_3\text{O}_2$ has no bearing on the amount of base required. It is the *amount* of acid, not its strength, that determines the equivalence point. Second, the pH value at the equivalence point *is* affected by the acid strength. For the titration of acetic acid, the pH at the equivalence point is 8.72; for the titration of hydrocyanic acid, the pH at the equivalence point is 10.96. This difference occurs because the CN^- ion is a much stronger base than the $\text{C}_2\text{H}_3\text{O}_2^-$ ion. Also, the pH at the halfway point of the titration is much higher for HCN than for $\text{HC}_2\text{H}_3\text{O}_2$, again because of the greater base strength of the CN^- ion (or equivalently, the smaller acid strength of HCN).

The strength of a weak acid has a significant effect on the shape of its pH curve. Figure 15.4 shows pH curves for 50-mL samples of 0.10 M solutions of various acids titrated with 0.10 M NaOH. Note that the equivalence point occurs in each case when the same volume of 0.10 M NaOH has been added but that the shapes of the curves are dramatically different. The weaker the acid, the greater the pH value at the equivalence point. In particular, note that the vertical region that surrounds the equivalence point becomes shorter as the acid being titrated becomes weaker. We will see in the next section that the choice of an indicator is more limited for such a titration.

Besides being used to analyze for the amount of acid or base in a solution, titrations can be used to determine the values of equilibrium constants, as shown in Sample Exercise 15.10.

Calculation of K_a

Sample Exercise 15.10

Calculating K_a

A chemist has synthesized a monoprotic weak acid and wants to determine its K_a value. To do so, the chemist dissolves 2.00 mmol of the solid acid in 100.0 mL water and titrates the resulting solution with 0.0500 M NaOH. After 20.0 mL NaOH has been added, the pH is 6.00. What is the K_a value for the acid?

Solution

The stoichiometry problem. We represent the monoprotic acid as HA. The stoichiometry for the titration reaction is shown below.

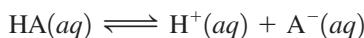
2.00 mmol HA
↓ add OH ⁻
1.00 mmol HA
1.00 mmol A ⁻

HA	+	OH ⁻	→	A ⁻	+	H ₂ O
Before reaction:	2.00 mmol	20.0 mL × 0.0500 M = 1.00 mmol		0 mmol		
After reaction:	2.00 – 1.00 = 1.00 mmol	1.00 – 1.00 = 0			1.00 mmol	

The equilibrium problem. After the reaction the solution contains the major species



The pH will be determined by the equilibrium



for which

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

Initial Concentration	Equilibrium Concentration	
$[\text{HA}]_0 = \frac{1.00 \text{ mmol}}{(100.0 + 20.0) \text{ mL}}$ $= 8.33 \times 10^{-3} \text{ M}$	$\xrightarrow{x \text{ mmol/mL HA dissociates}}$	$[\text{HA}] = 8.33 \times 10^{-3} - x$
$[\text{A}^-] = \frac{1.00 \text{ mmol}}{(100.0 + 20.0) \text{ mL}}$ $= 8.33 \times 10^{-3} \text{ M}$		$[\text{A}^-] = 8.33 \times 10^{-3} + x$
$[\text{H}^+]_0 \approx 0$		$[\text{H}^+] = x$

The corresponding ICE table is

	HA(aq)	↔	H ⁺ (aq)	+	A ⁻ (aq)
I nitial:	8.33×10^{-3}		≈ 0		8.33×10^{-3}
C hange:	$-x$		$+x$		$+x$
E quilibrium:	$8.33 \times 10^{-3} - x$		x		$8.33 \times 10^{-3} + x$

Note that x is known here because the pH at this point is known to be 6.00. Thus

$$x = [\text{H}^+] = \text{antilog}(-\text{pH}) = 1.0 \times 10^{-6} \text{ M}$$

Substituting the equilibrium concentrations into the expression for K_a allows calculation of the K_a value:

$$\begin{aligned} K_a &= \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{x(8.33 \times 10^{-3} + x)}{(8.33 \times 10^{-3}) - x} \\ &= \frac{(1.0 \times 10^{-6})(8.33 \times 10^{-3} + 1.0 \times 10^{-6})}{(8.33 \times 10^{-3}) - (1.0 \times 10^{-6})} \\ &\approx \frac{(1.0 \times 10^{-6})(8.33 \times 10^{-3})}{8.33 \times 10^{-3}} = 1.0 \times 10^{-6} \end{aligned}$$

There is an easier way to think about this problem. The original solution contained 2.00 mmol of HA, and since 20.0 mL of added 0.0500 M NaOH contains 1.0 mmol OH^- , this is the halfway point in the titration (where $[\text{HA}]$ is equal to $[\text{A}^-]$). Thus

$$[\text{H}^+] = K_a = 1.0 \times 10^{-6}$$

See Exercise 15.63.

Titrations of Weak Bases with Strong Acids

Titration of weak bases with strong acids can be treated using the procedures we introduced previously. As always, you should *think first about the major species in solution* and decide whether a reaction occurs that runs essentially to completion. If such a reaction does occur, let it run to completion and do the stoichiometric calculations. Finally, choose the dominant equilibrium and calculate the pH.

CASE STUDY: Weak Base–Strong Acid Titration

The calculations involved for the titration of a weak base with a strong acid will be illustrated by the titration of 100.0 mL of 0.050 M NH_3 with 0.10 M HCl.

Before the addition of any HCl.

- Major species:



NH_3 is a base and will seek a source of protons. In this case H_2O is the only available source.

- No reactions occur that go to completion, since NH_3 cannot readily take a proton from H_2O . This is evidenced by the small K_b value for NH_3 .
- The equilibrium that controls the pH involves the reaction of ammonia with water:



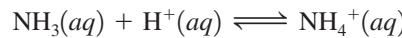
Use K_b to calculate $[\text{OH}^-]$. Although NH_3 is a weak base (compared with OH^-), it produces much more OH^- in this reaction than is produced from the autoionization of H_2O .

Before the equivalence point.

- Major species (before any reaction occurs):

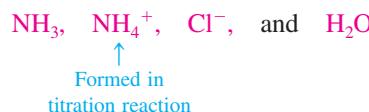


- The NH_3 will react with H^+ from the added HCl:



This reaction proceeds essentially to completion because the NH_3 readily reacts with a free proton. This case is much different from the previous case, where H_2O was the only source of protons. The stoichiometric calculations are then carried out using the known volume of 0.10 M HCl added.

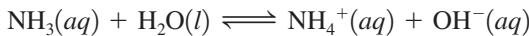
- After the reaction of NH_3 with H^+ is run to completion, the solution contains the following major species:



Note that the solution contains NH_3 and NH_4^+ , and the equilibria involving these species will determine $[\text{H}^+]$. You can use either the dissociation reaction of NH_4^+



or the reaction of NH_3 with H_2O



At the equivalence point.

1. By definition, the equivalence point occurs when all the original NH_3 is converted to NH_4^+ . Thus the major species in solution are



2. No reactions occur that go to completion.
3. The dominant equilibrium (the one that controls the $[\text{H}^+]$) will be the dissociation of the weak acid NH_4^+ , for which

$$K_a = \frac{K_w}{K_b(\text{for NH}_3)}$$

Beyond the equivalence point.

1. Excess HCl has been added, and the major species are



2. No reaction occurs that goes to completion.
3. Although NH_4^+ will dissociate, it is such a weak acid that $[\text{H}^+]$ will be determined simply by the excess H^+ :

$$[\text{H}^+] = \frac{\text{mmol H}^+ \text{ in excess}}{\text{mL solution}}$$

The results of these calculations are shown in Table 15.2. The pH curve is shown in Fig. 15.5.

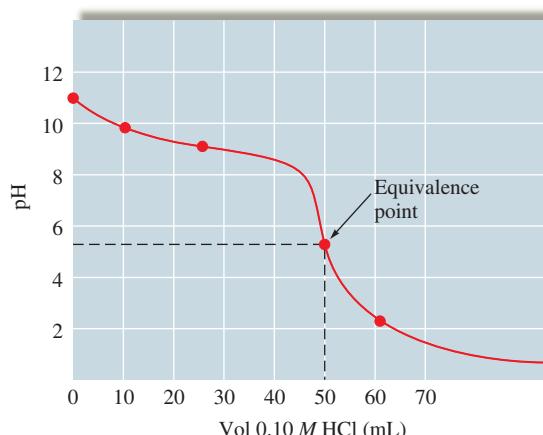
TABLE 15.2 Summary of Results for the Titration of 100.0 mL 0.050 M NH_3 with 0.10 M HCl

Volume of 0.10 M HCl Added (mL)	$[\text{NH}_3]_0$	$[\text{NH}_4^+]_0$	$[\text{H}^+]$	pH
0	0.05 M	0	$1.1 \times 10^{-11} M$	10.96
10.0	$\frac{4.0 \text{ mmol}}{(100 + 10) \text{ mL}}$	$\frac{1.0 \text{ mmol}}{(100 + 10) \text{ mL}}$	$1.4 \times 10^{-10} M$	9.85
25.0*	$\frac{2.5 \text{ mmol}}{(100 + 25) \text{ mL}}$	$\frac{2.5 \text{ mmol}}{(100 + 25) \text{ mL}}$	$5.6 \times 10^{-10} M$	9.25
50.0†	0	$\frac{5.0 \text{ mmol}}{(100 + 50) \text{ mL}}$	$4.3 \times 10^{-6} M$	5.36
60.0‡	0	$\frac{5.0 \text{ mmol}}{(100 + 60) \text{ mL}}$ $= 6.2 \times 10^{-3} M$	$\frac{1.0 \text{ mmol}}{160 \text{ mL}}$	2.21

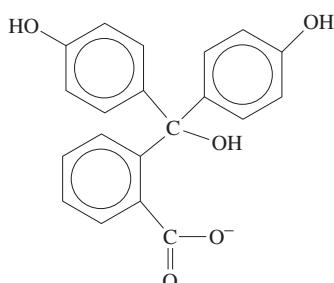
*Halfway point

†Equivalence point

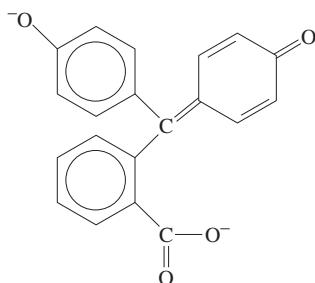
‡ $[\text{H}^+]$ determined by the 1.0 mmol of excess H^+

**FIGURE 15.5**

The pH curve for the titration of 100.0 mL of 0.050 M NH_3 with 0.10 M HCl. Note the pH at the equivalence point is less than 7, since the solution contains the weak acid NH_4^+ .



(Colorless acid form, HIn)

(Pink base form, In⁻)**FIGURE 15.6**

The acid and base forms of the indicator phenolphthalein. In the acid form (HIn), the molecule is colorless. When a proton (plus H_2O) is removed to give the base form (In^-), the color changes to pink.

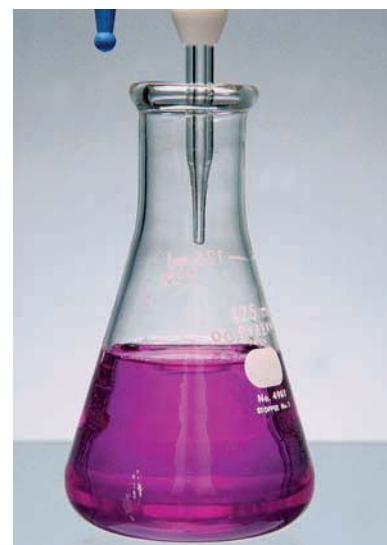
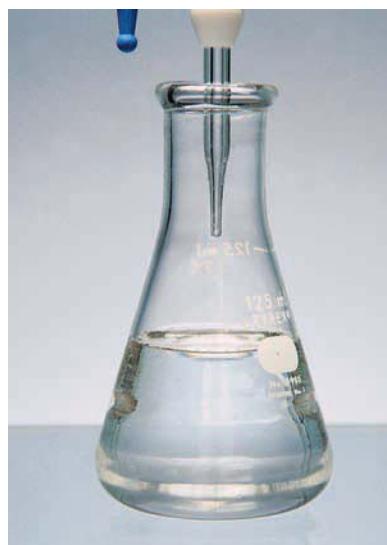
15.5 Acid–Base Indicators

There are two common methods for determining the equivalence point of an acid–base titration:

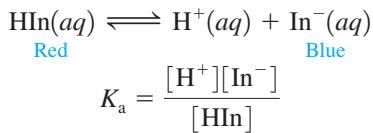
1. Use a pH meter (see Fig. 14.9) to monitor the pH and then plot the titration curve. The center of the vertical region of the pH curve indicates the equivalence point (for example, see Figs. 15.1 through 15.5).
2. Use an **acid–base indicator**, which marks the end point of a titration by changing color. Although the *equivalence point of a titration, defined by the stoichiometry, is not necessarily the same as the end point* (where the indicator changes color), careful selection of the indicator will ensure that the error is negligible.

The most common acid–base indicators are complex molecules that are themselves weak acids (represented by HIn). They exhibit one color when the proton is attached to the molecule and a different color when the proton is absent. For example, **phenolphthalein**, a commonly used indicator, is colorless in its HIn form and pink in its In^- , or basic, form. The actual structures of the two forms of phenolphthalein are shown in Fig. 15.6.

To see how molecules such as phenolphthalein function as indicators, consider the following equilibrium for some hypothetical indicator HIn, a weak acid with $K_a = 1.0 \times 10^{-8}$.



The indicator phenolphthalein is colorless in acidic solution and pink in basic solution.



By rearranging, we get

$$\frac{K_a}{[\text{H}^+]} = \frac{[\text{In}^-]}{[\text{HIn}]}$$

Suppose we add a few drops of this indicator to an acidic solution whose pH is 1.0 ($[\text{H}^+] = 1.0 \times 10^{-1}$). Then

$$\frac{K_a}{[\text{H}^+]} = \frac{1.0 \times 10^{-8}}{1.0 \times 10^{-1}} = 10^{-7} = \frac{1}{10,000,000} = \frac{[\text{In}^-]}{[\text{HIn}]}$$

The *end point* is defined by the change in color of the indicator. The *equivalence point* is defined by the reaction stoichiometry.

This ratio shows that the predominant form of the indicator is HIn, resulting in a red solution. As OH^- is added to this solution in a titration, $[\text{H}^+]$ decreases and the equilibrium shifts to the right, changing HIn to In^- . At some point in a titration, enough of the In^- form will be present in the solution so that a purple tint will be noticeable. That is, a color change from red to reddish purple will occur.

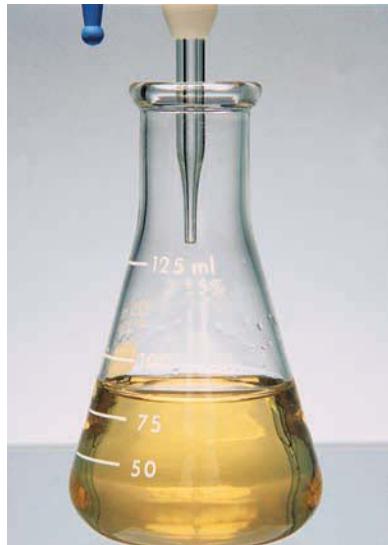
How much In^- must be present for the human eye to detect that the color is different from the original one? For most indicators, about a tenth of the initial form must be converted to the other form before a new color is apparent. We will assume, then, that in the titration of an acid with a base, the color change will occur at a pH where

$$\frac{[\text{In}^-]}{[\text{HIn}]} = \frac{1}{10}$$

Sample Exercise 15.11

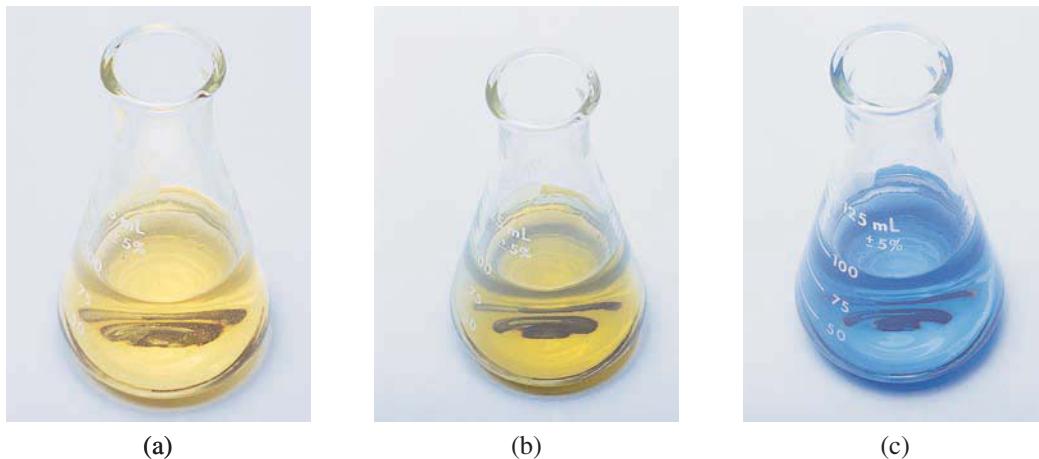
Indicator Color Change

Bromthymol blue, an indicator with a K_a value of 1.0×10^{-7} , is yellow in its HIn form and blue in its In^- form. Suppose we put a few drops of this indicator in a strongly acidic solution. If the solution is then titrated with NaOH, at what pH will the indicator color change first be visible?



Methyl orange indicator is yellow in basic solution and red in acidic solution.



**FIGURE 15.7**

(a) Yellow acid form of bromthymol blue; (b) a greenish tint is seen when the solution contains 1 part blue and 10 parts yellow; (c) blue basic form.

Solution

For bromthymol blue,

$$K_a = 1.0 \times 10^{-7} = \frac{[H^+][In^-]}{[HIn]}$$

We assume that the color change is visible when

$$\frac{[In^-]}{[HIn]} = \frac{1}{10}$$

That is, we assume that we can see the first hint of a greenish tint (yellow plus a little blue) when the solution contains 1 part blue and 10 parts yellow (see Fig. 15.7). Thus

$$K_a = 1.0 \times 10^{-7} = \frac{[H^+](1)}{10}$$

$$[H^+] = 1.0 \times 10^{-6} \quad \text{or} \quad pH = 6.00$$

The color change is first visible at pH 6.00.

See Exercises 15.65 through 15.68.

The Henderson–Hasselbalch equation is very useful in determining the pH at which an indicator changes color. For example, application of Equation (15.2) to the K_a expression for the general indicator HIn yields

$$pH = pK_a + \log\left(\frac{[In^-]}{[HIn]}\right)$$

where K_a is the dissociation constant for the acid form of the indicator (HIn). Since we assume that the color change is visible when

$$\frac{[In^-]}{[HIn]} = \frac{1}{10}$$

we have the following equation for determining the pH at which the color change occurs:

$$\text{pH} = \text{p}K_a + \log\left(\frac{1}{10}\right) = \text{p}K_a - 1$$

For bromthymol blue ($K_a = 1 \times 10^{-7}$, or $\text{p}K_a = 7$), the pH at the color change is

$$\text{pH} = 7 - 1 = 6$$

as we calculated in Sample Exercise 15.11.

When a basic solution is titrated, the indicator HIn will initially exist as In^- in solution, but as acid is added, more HIn will be formed. In this case the color change will be visible when there is a mixture of 10 parts In^- and 1 part HIn. That is, a color change from blue to blue-green will occur (see Fig. 15.7) due to the presence of some of the yellow HIn molecules. This color change will be first visible when

$$\frac{[\text{In}^-]}{[\text{HIn}]} = \frac{10}{1}$$

Note that this is the reciprocal of the ratio for the titration of an acid. Substituting this ratio into the Henderson–Hasselbalch equation gives

$$\text{pH} = \text{p}K_a + \log\left(\frac{10}{1}\right) = \text{p}K_a + 1$$

For bromthymol blue ($\text{p}K_a = 7$), we have a color change at

$$\text{pH} = 7 + 1 = 8$$

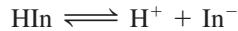
In summary, when bromthymol blue is used for the titration of an acid, the starting form will be HIn (yellow), and the color change occurs at a pH of about 6. When bromthymol blue is used for the titration of a base, the starting form is In^- (blue), and the color change occurs at a pH of about 8. Thus the useful pH range for bromthymol blue is

$$\text{p}K_a(\text{bromthymol blue}) \pm 1 = 7 \pm 1$$

or from 6 to 8. This is a general result. For a typical acid–base indicator with dissociation constant K_a , the color transition occurs over a range of pH values given by $\text{p}K_a \pm 1$. The useful pH ranges for several common indicators are shown in Fig. 15.8.

When we choose an indicator for a titration, we want the indicator end point (where the color changes) and the titration equivalence point to be as close as possible. Choosing an indicator is easier if there is a large change in pH near the equivalence point of the titration. The dramatic change in pH near the equivalence point in a strong acid–strong base titration (Figs. 15.1 and 15.2) produces a sharp end point; that is, the complete color change (from the acid-to-base or base-to-acid colors) usually occurs over one drop of added titrant.

What indicator should we use for the titration of 100.00 mL of 0.100 M HCl with 0.100 M NaOH? We know that the equivalence point occurs at pH 7.00. In the initially acidic solution, the indicator will be predominantly in the HIn form. As OH^- ions are added, the pH increases rather slowly at first (see Fig. 15.1) and then rises rapidly at the equivalence point. This sharp change causes the indicator dissociation equilibrium



to shift suddenly to the right, producing enough In^- ions to give a color change. Since we are titrating an acid, the indicator is predominantly in the acid form initially. Therefore, the first observable color change will occur at a pH where

$$\frac{[\text{In}^-]}{[\text{HIn}]} = \frac{1}{10}$$

Thus

$$\text{pH} = \text{p}K_a + \log\left(\frac{1}{10}\right) = \text{p}K_a - 1$$

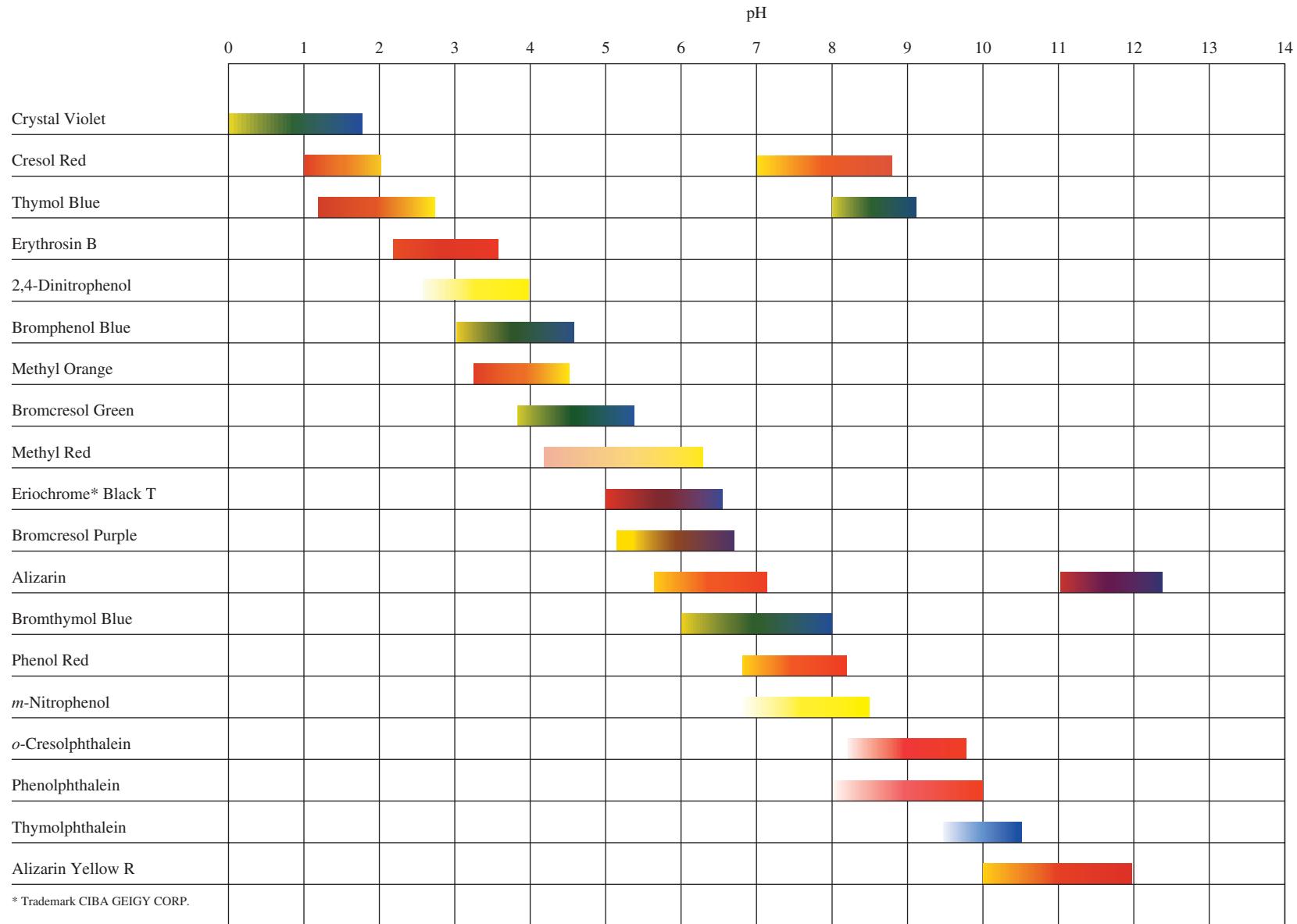


Universal indicator paper can be used to estimate the pH of a solution.

15.5 Acid–Base Indicators

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The pH ranges shown are approximate. Specific transition ranges depend on the indicator solvent chosen.

FIGURE 15.8

The useful pH ranges for several common indicators. Note that most indicators have a useful range of about two pH units, as predicted by the expression $pK_a \pm 1$.

* Trademark CIBA GEIGY CORP.

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TABLE 15.3 Selected pH Values Near the Equivalence Point in the Titration of 100.0 mL of 0.10 M HCl with 0.10 M NaOH

NaOH Added (mL)	pH
99.99	5.3
100.00	7.0
100.01	8.7

If we want an indicator that changes color at pH 7, we can use this relationship to find the pK_a value for a suitable indicator:

$$\text{pH} = 7 = pK_a - 1 \quad \text{or} \quad pK_a = 7 + 1 = 8$$

Thus an indicator with a pK_a value of 8 ($K_a = 1 \times 10^{-8}$) changes color at about pH 7 and is ideal for marking the end point for a strong acid-strong base titration.

How crucial is it for a strong acid-strong base titration that the indicator change color exactly at pH 7? We can answer this question by examining the pH change near the equivalence point of the titration of 100 mL of 0.10 M HCl and 0.10 M NaOH. The data for a few points at or near the equivalence point are shown in Table 15.3. Note that in going from 99.99 to 100.01 mL of added NaOH solution (about half of a drop), the pH changes from 5.3 to 8.7—a very dramatic change. This behavior leads to the following general conclusions about indicators for a strong acid-strong base titration:

Indicator color changes will be sharp, occurring with the addition of a single drop of titrant.

There is a wide choice of suitable indicators. The results will agree within one drop of titrant, using indicators with end points as far apart as pH 5 and pH 9 (see Fig. 15.9).

The titration of weak acids is somewhat different. Figure 15.4 shows that the weaker the acid being titrated, the smaller the vertical area around the equivalence point. This allows much less flexibility in choosing the indicator. We must choose an indicator whose useful pH range has a midpoint as close as possible to the pH at the equivalence point. For example, we saw earlier that in the titration of 0.1 M $\text{HC}_2\text{H}_3\text{O}_2$ with 0.1 M NaOH the pH at the equivalence point is 8.7 (see Fig. 15.3). A good indicator choice would be phenolphthalein, since its useful pH range is 8 to 10. Thymol blue (changes color, pH 8–9) also would be acceptable, but methyl red would not. The choice of an indicator is illustrated graphically in Fig. 15.10.

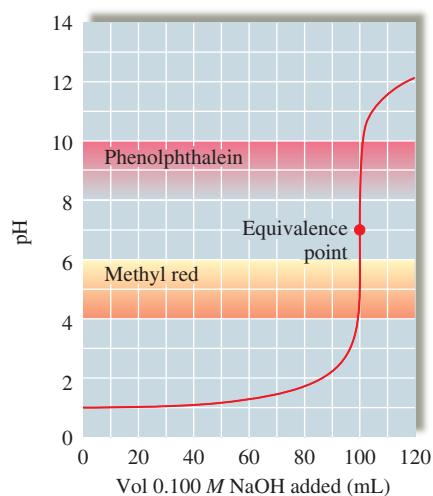


FIGURE 15.9

The pH curve for the titration of 100.0 mL of 0.10 M HCl with 0.10 M NaOH. Note that the end points of phenolphthalein and methyl red occur at virtually the same amounts of added NaOH.

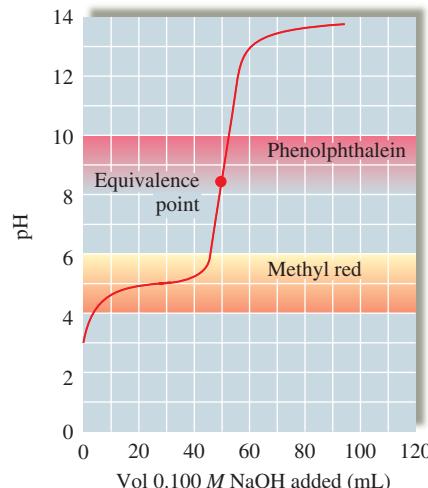


FIGURE 15.10

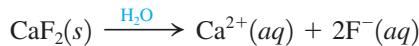
The pH curve for the titration of 50 mL of 0.1 M $\text{HC}_2\text{H}_3\text{O}_2$ with 0.1 M NaOH. Phenolphthalein will give an end point very close to the equivalence point of the titration. Methyl red would change color well before the equivalence point (so the end point would be very different from the equivalence point) and would not be a suitable indicator for this titration.

Solubility Equilibria

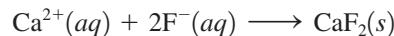
15.6 Solubility Equilibria and the Solubility Product

Solubility is a very important phenomenon. The fact that substances such as sugar and table salt dissolve in water allows us to flavor foods easily. The fact that calcium sulfate is less soluble in hot water than in cold water causes it to coat tubes in boilers, reducing thermal efficiency. Tooth decay involves solubility: When food lodges between the teeth, acids form that dissolve tooth enamel, which contains a mineral called *hydroxyapatite*, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$. Tooth decay can be reduced by treating teeth with fluoride (see Chemical Impact, p. 720). Fluoride replaces the hydroxide in hydroxyapatite to produce the corresponding fluorapatite, $\text{Ca}_5(\text{PO}_4)_3\text{F}$, and calcium fluoride, CaF_2 , both of which are less soluble in acids than the original enamel. Another important consequence of solubility involves the use of a suspension of barium sulfate to improve the clarity of X rays of the gastrointestinal tract. The very low solubility of barium sulfate, which contains the toxic ion Ba^{2+} , makes ingestion of the compound safe.

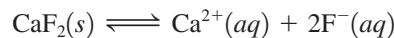
In this section we consider the equilibria associated with solids dissolving to form aqueous solutions. We will assume that when a typical ionic solid dissolves in water, it dissociates completely into separate hydrated cations and anions. For example, calcium fluoride dissolves in water as follows:



When the solid salt is first added to the water, no Ca^{2+} and F^- ions are present. However, as the dissolution proceeds, the concentrations of Ca^{2+} and F^- increase, making it more and more likely that these ions will collide and re-form the solid phase. Thus two competing processes are occurring—the dissolution reaction and its reverse:



Ultimately, dynamic equilibrium is reached:



At this point no more solid dissolves (the solution is said to be *saturated*).

We can write an equilibrium expression for this process according to the law of mass action:

$$K_{\text{sp}} = [\text{Ca}^{2+}][\text{F}^-]^2$$

where $[\text{Ca}^{2+}]$ and $[\text{F}^-]$ are expressed in mol/L. The constant K_{sp} is called the **solubility product constant** or simply the **solubility product** for the equilibrium expression.

Since CaF_2 is a pure solid, it is not included in the equilibrium expression. The fact that the amount of excess solid present does not affect the position of the solubility equilibrium might seem strange at first; more solid means more surface area exposed to the solvent, which would seem to result in greater solubility. This is not the case, however. When the ions in solution re-form the solid, they do so on the surface of the solid. Thus doubling the surface area of the solid not only doubles the rate of dissolving, but also doubles the rate of re-formation of the solid. The amount of excess solid present therefore has no effect on the equilibrium position. Similarly, although either increasing the surface area by grinding up the solid or stirring the solution speeds up the attainment of equilibrium, neither procedure changes the amount of solid dissolved at equilibrium. Neither the amount of excess solid nor the size of the particles present will shift the *position* of the solubility equilibrium.

It is very important to distinguish between the *solubility* of a given solid and its *solubility product*. The solubility product is an *equilibrium constant* and has only *one* value

Adding F^- to drinking water is controversial. See Geoff Rayner-Canham, "Fluoride: Trying to Separate Fact from Fallacy," *Chem 13 News*, Sept. 2001, pp. 16–19.

For simplicity, we will ignore the effects of ion associations in these solutions.



An X ray of the lower gastrointestinal tract using barium sulfate.

Pure liquids and pure solids are never included in an equilibrium expression (Section 13.4).

TABLE 15.4 K_{sp} Values at 25°C for Common Ionic Solids

Ionic Solid	K_{sp} (at 25°C)	Ionic Solid	K_{sp} (at 25°C)	Ionic Solid	K_{sp} (at 25°C)
Fluorides		$Hg_2CrO_4^*$	2×10^{-9}	$Co(OH)_2$	2.5×10^{-16}
BaF_2	2.4×10^{-5}	$BaCrO_4$	8.5×10^{-11}	$Ni(OH)_2$	1.6×10^{-16}
MgF_2	6.4×10^{-9}	Ag_2CrO_4	9.0×10^{-12}	$Zn(OH)_2$	4.5×10^{-17}
PbF_2	4×10^{-8}	$PbCrO_4$	2×10^{-16}	$Cu(OH)_2$	1.6×10^{-19}
SrF_2	7.9×10^{-10}			$Hg(OH)_2$	3×10^{-26}
CaF_2	4.0×10^{-11}			$Sn(OH)_2$	3×10^{-27}
		Carbonates			
		$NiCO_3$	1.4×10^{-7}	$Cr(OH)_3$	6.7×10^{-31}
Chlorides		$CaCO_3$	8.7×10^{-9}	$Al(OH)_3$	2×10^{-32}
$PbCl_2$	1.6×10^{-5}	$BaCO_3$	1.6×10^{-9}	$Fe(OH)_3$	4×10^{-38}
$AgCl$	1.6×10^{-10}	$SrCO_3$	7×10^{-10}	$Co(OH)_3$	2.5×10^{-43}
$Hg_2Cl_2^*$	1.1×10^{-18}	$CuCO_3$	2.5×10^{-10}		
		$ZnCO_3$	2×10^{-10}	Sulfides	
Bromides		$MnCO_3$	8.8×10^{-11}	MnS	2.3×10^{-13}
$PbBr_2$	4.6×10^{-6}	$FeCO_3$	2.1×10^{-11}	FeS	3.7×10^{-19}
$AgBr$	5.0×10^{-13}	Ag_2CO_3	8.1×10^{-12}	NiS	3×10^{-21}
$Hg_2Br_2^*$	1.3×10^{-22}	$CdCO_3$	5.2×10^{-12}	CoS	5×10^{-22}
		$PbCO_3$	1.5×10^{-15}	ZnS	2.5×10^{-22}
Iodides		$MgCO_3$	6.8×10^{-6}	SnS	1×10^{-26}
PbI_2	1.4×10^{-8}	$Hg_2CO_3^*$	9.0×10^{-15}	CdS	1.0×10^{-28}
AgI	1.5×10^{-16}			PbS	7×10^{-29}
$Hg_2I_2^*$	4.5×10^{-29}			CuS	8.5×10^{-45}
		Hydroxides		Ag_2S	1.6×10^{-49}
Sulfates		$Ba(OH)_2$	5.0×10^{-3}	HgS	1.6×10^{-54}
$CaSO_4$	6.1×10^{-5}	$Sr(OH)_2$	3.2×10^{-4}		
Ag_2SO_4	1.2×10^{-5}	$Ca(OH)_2$	1.3×10^{-6}	Phosphates	
$SrSO_4$	3.2×10^{-7}	$AgOH$	2.0×10^{-8}	Ag_3PO_4	1.8×10^{-18}
$PbSO_4$	1.3×10^{-8}	$Mg(OH)_2$	8.9×10^{-12}	$Sr_3(PO_4)_2$	1×10^{-31}
$BaSO_4$	1.5×10^{-9}	$Mn(OH)_2$	2×10^{-13}	$Ca_3(PO_4)_2$	1.3×10^{-32}
		$Cd(OH)_2$	5.9×10^{-15}	$Ba_3(PO_4)_2$	6×10^{-39}
Chromates		$Pb(OH)_2$	1.2×10^{-15}	$Pb_3(PO_4)_2$	1×10^{-54}
$SrCrO_4$	3.6×10^{-5}	$Fe(OH)_2$	1.8×10^{-15}		

*Contains Hg_2^{2+} ions. $K = [Hg_2^{2+}][X^-]^2$ for Hg_2X_2 salts, for example.



Visualization: Solution Equilibrium



Visualization: Supersaturated Sodium Acetate

K_{sp} is an equilibrium constant; solubility is an equilibrium position.

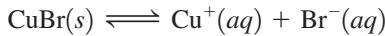
Sample Exercise 15.12

Calculating K_{sp} from Solubility I

Copper(I) bromide has a measured solubility of 2.0×10^{-4} mol/L at 25°C. Calculate its K_{sp} value.

Solution

In this experiment the solid was placed in contact with water. Thus, before any reaction occurred, the system contained solid CuBr and H₂O. The process that occurs is the dissolving of CuBr to form the separated Cu⁺ and Br⁻ ions:



where

$$K_{\text{sp}} = [\text{Cu}^+][\text{Br}^-]$$

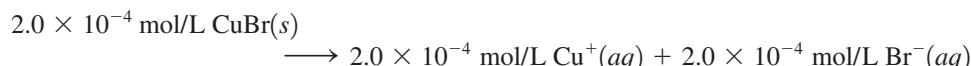
Initially, the solution contains no Cu^+ or Br^- , so the initial concentrations are

$$[\text{Cu}^+]_0 = [\text{Br}^-]_0 = 0$$

The equilibrium concentrations can be obtained from the measured solubility of CuBr , which is 2.0×10^{-4} mol/L. This means that 2.0×10^{-4} mol solid CuBr dissolves per 1.0 L of solution to come to equilibrium with the excess solid. The reaction is



Thus



We can now write the equilibrium concentrations:

$$\begin{aligned} [\text{Cu}^+] &= [\text{Cu}^+]_0 + \text{change to reach equilibrium} \\ &= 0 + 2.0 \times 10^{-4} \text{ mol/L} \end{aligned}$$

and

$$\begin{aligned} [\text{Br}^-] &= [\text{Br}^-]_0 + \text{change to reach equilibrium} \\ &= 0 + 2.0 \times 10^{-4} \text{ mol/L} \end{aligned}$$

These equilibrium concentrations allow us to calculate the value of K_{sp} for CuBr :

$$\begin{aligned} K_{\text{sp}} &= [\text{Cu}^+][\text{Br}^-] = (2.0 \times 10^{-4} \text{ mol/L})(2.0 \times 10^{-4} \text{ mol/L}) \\ &= 4.0 \times 10^{-8} \text{ mol}^2/\text{L}^2 = 4.0 \times 10^{-8} \end{aligned}$$

The units for K_{sp} values are usually omitted.

See Exercise 15.77.

Sample Exercise 15.13



Precipitation of bismuth sulfide.

Sulfide is a very basic anion and really exists in water as HS^- . We will not consider this complication.

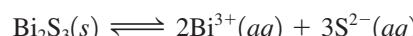
Solubilities must be expressed in mol/L in K_{sp} calculations.

Calculating K_{sp} from Solubility II

Calculate the K_{sp} value for bismuth sulfide (Bi_2S_3), which has a solubility of 1.0×10^{-15} mol/L at 25°C .

Solution

The system initially contains H_2O and solid Bi_2S_3 , which dissolves as follows:



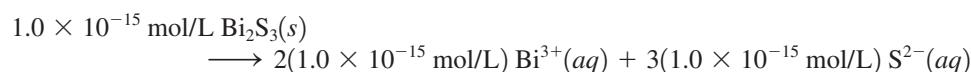
Therefore,

$$K_{\text{sp}} = [\text{Bi}^{3+}]^2[\text{S}^{2-}]^3$$

Since no Bi^{3+} and S^{2-} ions were present in solution before the Bi_2S_3 dissolved,

$$[\text{Bi}^{3+}]_0 = [\text{S}^{2-}]_0 = 0$$

Thus the equilibrium concentrations of these ions will be determined by the amount of salt that dissolves to reach equilibrium, which in this case is 1.0×10^{-15} mol/L. Since each Bi_2S_3 unit contains 2Bi^{3+} and 3S^{2-} ions:



The equilibrium concentrations are

$$\begin{aligned} [\text{Bi}^{3+}] &= [\text{Bi}^{3+}]_0 + \text{change} = 0 + 2.0 \times 10^{-15} \text{ mol/L} \\ [\text{S}^{2-}] &= [\text{S}^{2-}]_0 + \text{change} = 0 + 3.0 \times 10^{-15} \text{ mol/L} \end{aligned}$$

Then

$$K_{\text{sp}} = [\text{Bi}^{3+}]^2[\text{S}^{2-}]^3 = (2.0 \times 10^{-15})^2(3.0 \times 10^{-15})^3 = 1.1 \times 10^{-73}$$

See Exercises 15.78 through 15.80.



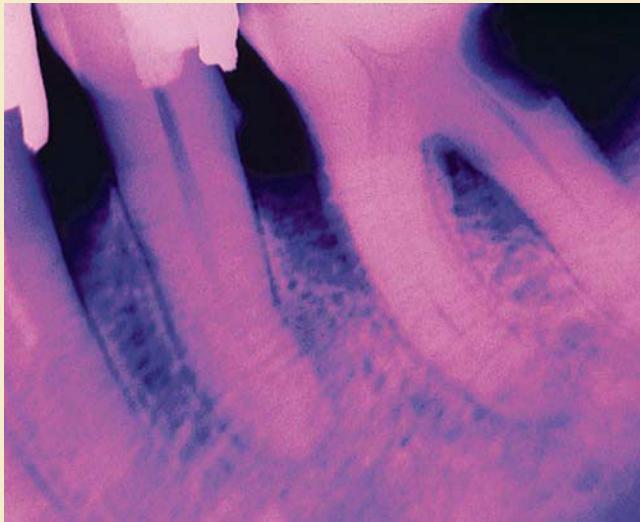
CHEMICAL IMPACT

The Chemistry of Teeth

If dental chemistry continues to progress at the present rate, tooth decay may soon be a thing of the past. Cavities are holes that develop in tooth enamel, which is composed of the mineral hydroxyapatite, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$. Recent research has shown that there is constant dissolving and re-forming of the tooth mineral in the saliva at the tooth's surface. Demineralization (dissolving of tooth enamel) is mainly caused by weak acids in the saliva created by bacteria as they metabolize carbohydrates in food. (The solubility of $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ in acidic saliva should come as no surprise to you if you understand how pH affects the solubility of a salt with basic anions.)

In the first stages of tooth decay, parts of the tooth surface become porous and spongy and develop swiss-cheese-like holes that, if untreated, eventually turn into cavities (see photo). However, recent results indicate that if the affected tooth is bathed in a solution containing appropriate amounts of Ca^{2+} , PO_4^{3-} , and F^- , it remineralizes. Because the F^- replaces OH^- in the tooth mineral ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$ is changed to $\text{Ca}_5(\text{PO}_4)_3\text{F}$), the remineralized area is more resistant to future decay, since fluoride is a weaker base than hydroxide ion. In addition, it has been shown that the presence of Sr^{2+} in the remineralizing fluid significantly increases resistance to decay.

If these results hold up under further study, the work of dentists will change dramatically. Dentists will be much



X-ray photo showing decay (dark area) on the molar (right).

more involved in preventing damage to teeth than in repairing damage that has already occurred. One can picture the routine use of a remineralization rinse that will repair problem areas before they become cavities. Dental drills could join leeches as a medical anachronism.

We have seen that the experimentally determined solubility of an ionic solid can be used to calculate its K_{sp} value.* The reverse is also possible: The solubility of an ionic solid can be calculated if its K_{sp} value is known.

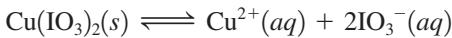
Sample Exercise 15.14

Calculating Solubility from K_{sp}

The K_{sp} value for copper(II) iodate, $\text{Cu}(\text{IO}_3)_2$, is 1.4×10^{-7} at 25°C . Calculate its solubility at 25°C .

Solution

The system initially contains H_2O and solid $\text{Cu}(\text{IO}_3)_2$, which dissolves according to the following equilibrium:



Therefore,

$$K_{\text{sp}} = [\text{Cu}^{2+}][\text{IO}_3^-]^2$$

*This calculation assumes that all the dissolved solid is present as separated ions. In some cases, such as CaSO_4 , large numbers of ion pairs exist in solution, so this method yields an incorrect value for K_{sp} .

To find the solubility of $\text{Cu}(\text{IO}_3)_2$, we must find the equilibrium concentrations of the Cu^{2+} and IO_3^- ions. We do this in the usual way by specifying the initial concentrations (before any solid has dissolved) and then defining the change required to reach equilibrium. Since in this case we do not know the solubility, we will assume that $x \text{ mol/L}$ of the solid dissolves to reach equilibrium. The 1:2 stoichiometry of the salt means that



The concentrations are as follows:

Initial Concentration (mol/L) (before any $\text{Cu}(\text{IO}_3)_2$ dissolves)		Equilibrium Concentration (mol/L)
$[\text{Cu}^{2+}]_0 = 0$ $[\text{IO}_3^-]_0 = 0$	$x \text{ mol/L}$ dissolves $\xrightarrow{\text{to reach equilibrium}}$	$[\text{Cu}^{2+}] = x$ $[\text{IO}_3^-] = 2x$

Substituting the equilibrium concentrations into the expression for K_{sp} gives

$$1.4 \times 10^{-7} = K_{\text{sp}} = [\text{Cu}^{2+}][\text{IO}_3^-]^2 = (x)(2x)^2 = 4x^3$$

Then

$$x = \sqrt[3]{3.5 \times 10^{-8}} = 3.3 \times 10^{-3} \text{ mol/L}$$

Thus the solubility of solid $\text{Cu}(\text{IO}_3)_2$ is $3.3 \times 10^{-3} \text{ mol/L}$.

See Exercises 15.81 and 15.82.

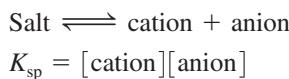
Relative Solubilities

A salt's K_{sp} value gives us information about its solubility. However, we must be careful in using K_{sp} values to predict the *relative* solubilities of a group of salts. There are two possible cases:

1. The salts being compared produce the same number of ions. For example, consider

$$\begin{array}{ll} \text{AgI}(s) & K_{\text{sp}} = 1.5 \times 10^{-16} \\ \text{CuI}(s) & K_{\text{sp}} = 5.0 \times 10^{-12} \\ \text{CaSO}_4(s) & K_{\text{sp}} = 6.1 \times 10^{-5} \end{array}$$

Each of these solids dissolves to produce two ions:



If x is the solubility in mol/L, then at equilibrium

$$\begin{aligned} [\text{Cation}] &= x \\ [\text{Anion}] &= x \\ K_{\text{sp}} &= [\text{cation}][\text{anion}] = x^2 \\ x &= \sqrt{K_{\text{sp}}} = \text{solubility} \end{aligned}$$

Therefore, in this case we can compare the solubilities for these solids by comparing the K_{sp} values:

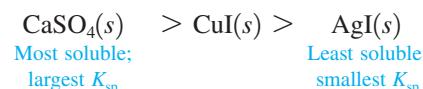


TABLE 15.5 Calculated Solubilities for CuS, Ag₂S, and Bi₂S₃ at 25°C

Salt	K _{sp}	Calculated Solubility (mol/L)
CuS	8.5 × 10 ⁻⁴⁵	9.2 × 10 ⁻²³
Ag ₂ S	1.6 × 10 ⁻⁴⁹	3.4 × 10 ⁻¹⁷
Bi ₂ S ₃	1.1 × 10 ⁻⁷³	1.0 × 10 ⁻¹⁵

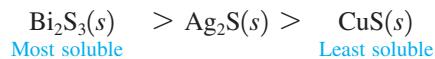
2. The salts being compared produce different numbers of ions. For example, consider

$$\text{CuS}(s) \quad K_{\text{sp}} = 8.5 \times 10^{-45}$$

$$\text{Ag}_2\text{S}(s) \quad K_{\text{sp}} = 1.6 \times 10^{-49}$$

$$\text{Bi}_2\text{S}_3(s) \quad K_{\text{sp}} = 1.1 \times 10^{-73}$$

Because these salts produce different numbers of ions when they dissolve, the K_{sp} values cannot be compared *directly* to determine relative solubilities. In fact, if we calculate the solubilities (using the procedure in Sample Exercise 15.14), we obtain the results summarized in Table 15.5. The order of solubilities is



which is opposite to the order of the K_{sp} values.

Remember that relative solubilities can be predicted by comparing K_{sp} values *only* for salts that produce the same total number of ions.

Common Ion Effect

So far we have considered ionic solids dissolved in pure water. We will now see what happens when the water contains an ion in common with the dissolving salt. For example, consider the solubility of solid silver chromate (Ag_2CrO_4 , $K_{\text{sp}} = 9.0 \times 10^{-12}$) in a 0.100 M solution of AgNO_3 . Before any Ag_2CrO_4 dissolves, the solution contains the major species Ag^+ , NO_3^- , and H_2O , with solid Ag_2CrO_4 on the bottom of the container. Since NO_3^- is not found in Ag_2CrO_4 , we can ignore it. The relevant initial concentrations (before any Ag_2CrO_4 dissolves) are

$$[\text{Ag}^+]_0 = 0.100 \text{ M} \text{ (from the dissolved } \text{AgNO}_3)$$

$$[\text{CrO}_4^{2-}]_0 = 0$$

The system comes to equilibrium as the solid Ag_2CrO_4 dissolves according to the reaction



for which $K_{\text{sp}} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}] = 9.0 \times 10^{-12}$

We assume that x mol/L of Ag_2CrO_4 dissolves to reach equilibrium, which means that



Now we can specify the equilibrium concentrations in terms of x :

$$[\text{Ag}^+] = [\text{Ag}^+]_0 + \text{change} = 0.100 + 2x$$

$$[\text{CrO}_4^{2-}] = [\text{CrO}_4^{2-}]_0 + \text{change} = 0 + x = x$$

Substituting these concentrations into the expression for K_{sp} gives

$$9.0 \times 10^{-12} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}] = (0.100 + 2x)^2(x)$$



A potassium chromate solution being added to aqueous silver nitrate, forming silver chromate.

The mathematics required here appear to be complicated, since the multiplication of terms on the right-hand side produces an expression that contains an x^3 term. However, as is usually the case, we can make simplifying assumptions. Since the K_{sp} value for Ag_2CrO_4 is small (the position of the equilibrium lies far to the left), x is expected to be small compared with 0.100 M. Therefore, $0.100 + 2x \approx 0.100$, which allows simplification of the expression:

$$9.0 \times 10^{-12} = (0.100 + 2x)^2(x) \approx (0.100)^2(x)$$

Then $x \approx \frac{9.0 \times 10^{-12}}{(0.100)^2} = 9.0 \times 10^{-10}$ mol/L

Since x is much less than 0.100 M, the approximation is valid (by the 5% rule). Thus

$$\text{Solubility of } \text{Ag}_2\text{CrO}_4 \text{ in } 0.100 \text{ M AgNO}_3 = x = 9.0 \times 10^{-10} \text{ mol/L}$$

and the equilibrium concentrations are

$$[\text{Ag}^+] = 0.100 + 2x = 0.100 + 2(9.0 \times 10^{-10}) = 0.100 \text{ M}$$

$$[\text{CrO}_4^{2-}] = x = 9.0 \times 10^{-10} \text{ M}$$

Now we compare the solubilities of Ag_2CrO_4 in pure water and in 0.100 M AgNO_3 :

$$\text{Solubility of } \text{Ag}_2\text{CrO}_4 \text{ in pure water} = 1.3 \times 10^{-4} \text{ mol/L}$$

$$\text{Solubility of } \text{Ag}_2\text{CrO}_4 \text{ in } 0.100 \text{ M AgNO}_3 = 9.0 \times 10^{-10} \text{ mol/L}$$

Note that the solubility of Ag_2CrO_4 is much less in the presence of Ag^+ ions from AgNO_3 . This is another example of the common ion effect. The solubility of a solid is lowered if the solution already contains ions common to the solid.

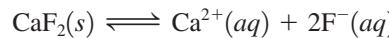
Sample Exercise 15.15

Solubility and Common Ions

Calculate the solubility of solid CaF_2 ($K_{\text{sp}} = 4.0 \times 10^{-11}$) in a 0.025 M NaF solution.

Solution

Before any CaF_2 dissolves, the solution contains the major species Na^+ , F^- , and H_2O . The solubility equilibrium for CaF_2 is



and

$$K_{\text{sp}} = 4.0 \times 10^{-11} = [\text{Ca}^{2+}][\text{F}^-]^2$$

Initial Concentration (mol/L) (before any CaF_2 dissolves)		Equilibrium Concentration (mol/L)
$[\text{Ca}^{2+}]_0 = 0$ $[\text{F}^-]_0 = 0.025 \text{ M}$ \uparrow From 0.025 M NaF	x mol/L CaF_2 dissolves $\xrightarrow{\text{to reach equilibrium}}$	$[\text{Ca}^{2+}] = x$ $[\text{F}^-] = 0.025 + 2x$ \uparrow \uparrow From NaF From CaF_2

Substituting the equilibrium concentrations into the expression for K_{sp} gives

$$K_{\text{sp}} = 4.0 \times 10^{-11} = [\text{Ca}^{2+}][\text{F}^-]^2 = (x)(0.025 + 2x)^2$$

Assuming that $2x$ is negligible compared with 0.025 (since K_{sp} is small) gives

$$4.0 \times 10^{-11} \approx (x)(0.025)^2$$

$$x \approx 6.4 \times 10^{-8}$$

The approximation is valid (by the 5% rule), and

$$\text{Solubility} = x = 6.4 \times 10^{-8} \text{ mol/L}$$

Thus 6.4×10^{-8} mol solid CaF_2 dissolves per liter of the 0.025 M NaF solution.

See Exercises 15.89 through 15.92.

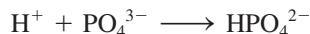
pH and Solubility

The pH of a solution can greatly affect a salt's solubility. For example, magnesium hydroxide dissolves according to the equilibrium



Addition of OH^- ions (an increase in pH) will, by the common ion effect, force the equilibrium to the left, decreasing the solubility of Mg(OH)_2 . On the other hand, an addition of H^+ ions (a decrease in pH) increases the solubility, because OH^- ions are removed from solution by reacting with the added H^+ ions. In response to the lower concentration of OH^- , the equilibrium position moves to the right. This is why a suspension of solid Mg(OH)_2 , known as *milk of magnesia*, dissolves as required in the stomach to combat excess acidity.

This idea also applies to salts with other types of anions. For example, the solubility of silver phosphate (Ag_3PO_4) is greater in acid than in pure water because the PO_4^{3-} ion is a strong base that reacts with H^+ to form the HPO_4^{2-} ion. The reaction



occurs in acidic solution, thus lowering the concentration of PO_4^{3-} and shifting the solubility equilibrium



to the right. This, in turn, increases the solubility of silver phosphate.

Silver chloride (AgCl), however, has the same solubility in acid as in pure water. Why? Since the Cl^- ion is a very weak base (that is, HCl is a very strong acid), no HCl molecules are formed. Thus the addition of H^+ to a solution containing Cl^- does not affect $[\text{Cl}^-]$ and has no effect on the solubility of a chloride salt.

The general rule is that if the anion X^- is an effective base—that is, if HX is a weak acid—the salt MX will show increased solubility in an acidic solution. Examples of common anions that are effective bases are OH^- , S^{2-} , CO_3^{2-} , $\text{C}_2\text{O}_4^{2-}$, and CrO_4^{2-} . Salts containing these anions are much more soluble in an acidic solution than in pure water.

As mentioned at the beginning of this chapter, one practical result of the increased solubility of carbonates in acid is the formation of huge limestone caves such as Mammoth Cave in Kentucky and Carlsbad Caverns in New Mexico. Carbon dioxide dissolved in groundwater makes it acidic, increasing the solubility of calcium carbonate and eventually producing huge caverns. As the carbon dioxide escapes to the air, the pH of the dripping water goes up and the calcium carbonate precipitates, forming stalactites and stalagmites.

15.7 Precipitation and Qualitative Analysis

So far we have considered solids dissolving in solutions. Now we will consider the reverse process—the formation of a solid from solution. When solutions are mixed, various reactions can occur. We have already considered acid–base reactions in some detail. In this section we show how to predict whether a precipitate will form when two solutions are

mixed. We will use the **ion product**, which is defined just like the expression for K_{sp} for a given solid except that *initial concentrations are used* instead of equilibrium concentrations. For solid CaF_2 , the expression for the ion product Q is written

$$Q = [\text{Ca}^{2+}]_0[\text{F}^-]_0^2$$

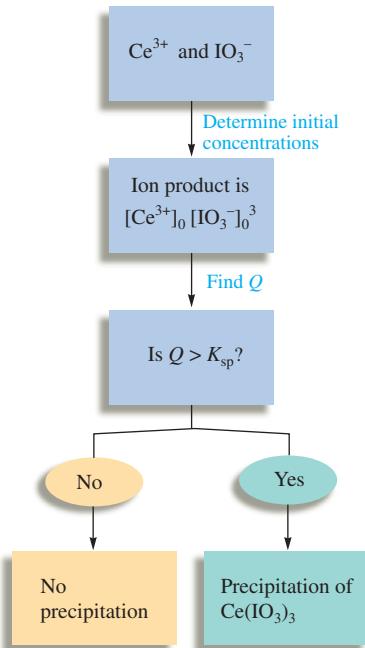
If we add a solution containing Ca^{2+} ions to a solution containing F^- ions, a precipitate may or may not form, depending on the concentrations of these ions in the resulting mixed solution. To predict whether precipitation will occur, we consider the relationship between Q and K_{sp} .

Q is used here in a very similar way to the use of the reaction quotient in Chapter 13.

If Q is greater than K_{sp} , precipitation occurs and will continue until the concentrations are reduced to the point that they satisfy K_{sp} .

If Q is less than K_{sp} , no precipitation occurs.

Sample Exercise 15.16



Determining Precipitation Conditions

A solution is prepared by adding 750.0 mL of $4.00 \times 10^{-3} M$ $\text{Ce}(\text{NO}_3)_3$ to 300.0 mL of $2.00 \times 10^{-2} M$ KIO_3 . Will $\text{Ce}(\text{IO}_3)_3$ ($K_{\text{sp}} = 1.9 \times 10^{-10}$) precipitate from this solution?

Solution

First, we calculate $[\text{Ce}^{3+}]_0$ and $[\text{IO}_3^-]_0$ in the mixed solution before any reaction occurs:

$$[\text{Ce}^{3+}]_0 = \frac{(750.0 \text{ mL})(4.00 \times 10^{-3} \text{ mmol/mL})}{(750.0 + 300.0) \text{ mL}} = 2.86 \times 10^{-3} M$$

$$[\text{IO}_3^-]_0 = \frac{(300.0 \text{ mL})(2.00 \times 10^{-2} \text{ mmol/mL})}{(750.0 + 300.0) \text{ mL}} = 5.71 \times 10^{-3} M$$

The ion product for $\text{Ce}(\text{IO}_3)_3$ is

$$Q = [\text{Ce}^{3+}]_0[\text{IO}_3^-]_0^3 = (2.86 \times 10^{-3})(5.71 \times 10^{-3})^3 = 5.32 \times 10^{-10}$$

Since Q is greater than K_{sp} , $\text{Ce}(\text{IO}_3)_3$ will precipitate from the mixed solution.

See Exercises 15.97 and 15.98.

For $\text{Ce}(\text{IO}_3)_3(s)$, $K_{\text{sp}} = [\text{Ce}^{3+}][\text{IO}_3^-]^3$.

Sometimes we want to do more than simply predict whether precipitation will occur; we may want to calculate the equilibrium concentrations in the solution after precipitation occurs. For example, let us calculate the equilibrium concentrations of Pb^{2+} and I^- ions in a solution formed by mixing 100.0 mL of $0.0500 M$ $\text{Pb}(\text{NO}_3)_2$ and 200.0 mL of $0.100 M$ NaI . First, we must determine whether solid PbI_2 ($K_{\text{sp}} = 1.4 \times 10^{-8}$) forms when the solutions are mixed. To do so, we need to calculate $[\text{Pb}^{2+}]_0$ and $[\text{I}^-]_0$ before any reaction occurs:

$$[\text{Pb}^{2+}]_0 = \frac{\text{mmol Pb}^{2+}}{\text{mL solution}} = \frac{(100.0 \text{ mL})(0.0500 \text{ mmol/mL})}{300.0 \text{ mL}} = 1.67 \times 10^{-2} M$$

$$[\text{I}^-]_0 = \frac{\text{mmol I}^-}{\text{mL solution}} = \frac{(200.0 \text{ mL})(0.100 \text{ mmol/mL})}{300.0 \text{ mL}} = 6.67 \times 10^{-2} M$$

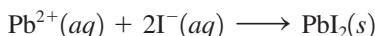
The ion product for PbI_2 is

$$Q = [\text{Pb}^{2+}]_0[\text{I}^-]_0^2 = (1.67 \times 10^{-2})(6.67 \times 10^{-2})^2 = 7.43 \times 10^{-5}$$

Since Q is greater than K_{sp} , a precipitate of PbI_2 will form.

The equilibrium constant for formation of solid PbI_2 is $1/K_{\text{sp}}$, or 7×10^7 , so this equilibrium lies far to the right.

Since the K_{sp} for PbI_2 is quite small (1.4×10^{-8}), only very small quantities of Pb^{2+} and I^- can coexist in aqueous solution. In other words, when Pb^{2+} and I^- are mixed, most of these ions will precipitate out as PbI_2 . That is, the reaction



(which is the reverse of the dissolution reaction) goes essentially to completion.

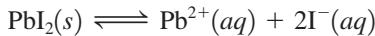
If, when two solutions are mixed, a reaction occurs that goes virtually to completion, it is essential to do the stoichiometry calculations before considering the equilibrium calculations. Therefore, in this case we let the system go completely in the direction toward which it tends. Then we will let it adjust back to equilibrium. If we let Pb^{2+} and I^- react to completion, we have the following concentrations:

	Pb^{2+}	+	2I^-	\longrightarrow	PbI_2
Before reaction:	(100.0 mL)(0.0500 M) = 5.00 mmol		(200.0 mL)(0.100 M) = 20.0 mmol		The amount of PbI_2 formed does not influence the equilibrium.
After reaction:	0 mmol		20.0 - 2(5.00) = 10.0 mmol		

In this reaction 10 mmol I^- is in excess.

Next we must allow the system to adjust to equilibrium. At equilibrium $[\text{Pb}^{2+}]$ is not actually zero because the reaction does not go quite to completion. The best way to think about this is that once the PbI_2 is formed, a very small amount redissolves to reach equilibrium. Since I^- is in excess, the PbI_2 is dissolving into a solution that contains 10.0 mmol I^- per 300.0 mL of solution, or $3.33 \times 10^{-2} \text{ M I}^-$.

We could state this problem as follows: What is the solubility of solid PbI_2 in a $3.33 \times 10^{-2} \text{ M NaI}$ solution? The lead iodide dissolves according to the equation



The concentrations are as follows:

Initial Concentration (mol/L)		Equilibrium Concentration (mol/L)
$[\text{Pb}^{2+}]_0 = 0$	$x \text{ mol/L}$	$[\text{Pb}^{2+}] = x$
$[\text{I}^-]_0 = 3.33 \times 10^{-2}$	$\xrightarrow{\text{PbI}_2(s) \text{ dissolves}}$	$[\text{I}^-] = 3.33 \times 10^{-2} + 2x$

Substituting into the expression for K_{sp} gives

$$K_{\text{sp}} = 1.4 \times 10^{-8} = [\text{Pb}^{2+}][\text{I}^-]^2 = (x)(3.33 \times 10^{-2} + 2x)^2 \approx (x)(3.33 \times 10^{-2})^2$$

Then

$$[\text{Pb}^{2+}] = x = 1.3 \times 10^{-5} \text{ M}$$

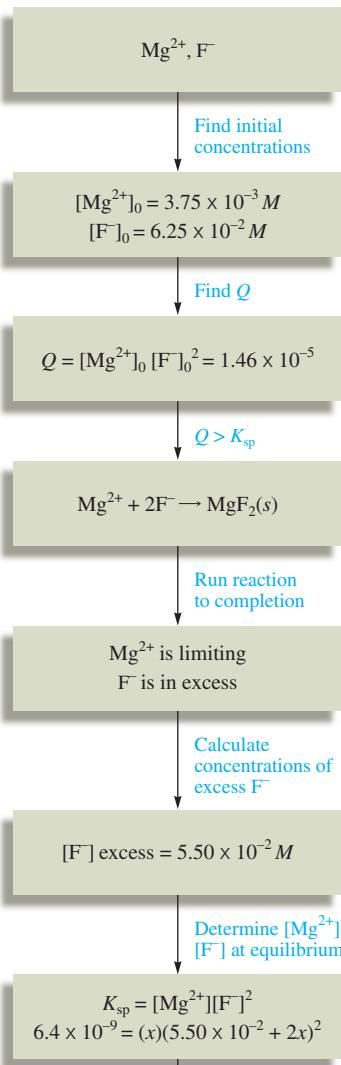
$$[\text{I}^-] = 3.33 \times 10^{-2} \text{ M}$$

Note that $3.33 \times 10^{-2} \gg 2x$, so the approximation is valid. These Pb^{2+} and I^- concentrations thus represent the equilibrium concentrations present in a solution formed by mixing 100.0 mL of 0.0500 M $\text{Pb}(\text{NO}_3)_2$ and 200.0 mL of 0.100 M NaI .

Sample Exercise 15.17

Precipitation

A solution is prepared by mixing 150.0 mL of $1.00 \times 10^{-2} \text{ M Mg}(\text{NO}_3)_2$ and 250.0 mL of $1.00 \times 10^{-1} \text{ M NaF}$. Calculate the concentrations of Mg^{2+} and F^- at equilibrium with solid MgF_2 ($K_{\text{sp}} = 6.4 \times 10^{-9}$).

**Solution**

The first step is to determine whether solid MgF_2 forms. To do this, we need to calculate the concentrations of Mg^{2+} and F^- in the mixed solution and find Q :

$$[\text{Mg}^{2+}]_0 = \frac{\text{mmol Mg}^{2+}}{\text{mL solution}} = \frac{(150.0 \text{ mL})(1.00 \times 10^{-2} \text{ M})}{400.0 \text{ mL}} = 3.75 \times 10^{-3} \text{ M}$$

$$[\text{F}^-]_0 = \frac{\text{mmol F}^-}{\text{mL solution}} = \frac{(250.0 \text{ mL})(1.00 \times 10^{-1} \text{ M})}{400.0 \text{ mL}} = 6.25 \times 10^{-2} \text{ M}$$

$$Q = [\text{Mg}^{2+}]_0[\text{F}^-]_0^2 = (3.75 \times 10^{-3})(6.25 \times 10^{-2})^2 = 1.46 \times 10^{-5}$$

Since Q is greater than K_{sp} , solid MgF_2 will form.

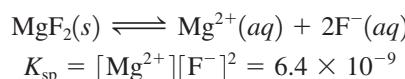
The next step is to run the precipitation reaction to completion:

	Mg^{2+}	+	2F^-	→	$\text{MgF}_2(s)$
Before reaction:	$(150.0)(1.00 \times 10^{-2})$ $= 1.50 \text{ mmol}$		$(250.0)(1.00 \times 10^{-1})$ $= 25.0 \text{ mmol}$		
After reaction:	$1.50 - 1.50 = 0$		$25.0 - 2(1.50)$ $= 22.0 \text{ mmol}$		

Note that excess F^- remains after the precipitation reaction goes to completion. The concentration is

$$[\text{F}^-]_{\text{excess}} = \frac{22.0 \text{ mmol}}{400.0 \text{ mL}} = 5.50 \times 10^{-2} \text{ M}$$

Although we have assumed that the Mg^{2+} is completely consumed, we know that $[\text{Mg}^{2+}]$ will not be zero at equilibrium. We can compute the equilibrium $[\text{Mg}^{2+}]$ by letting MgF_2 redissolve to satisfy the expression for K_{sp} . How much MgF_2 will dissolve in a $5.50 \times 10^{-2} \text{ M}$ NaF solution? We proceed as usual:



Initial Concentration (mol/L)	Equilibrium Concentration (mol/L)	
$[\text{Mg}^{2+}]_0 = 0$ $[\text{F}^-]_0 = 5.50 \times 10^{-2}$	$x \text{ mol/L}$ $\xrightarrow{\text{MgF}_2(s) \text{ dissolves}}$	$[\text{Mg}^{2+}] = x$ $[\text{F}^-] = 5.50 \times 10^{-2} + 2x$

$$\begin{aligned}
 K_{\text{sp}} &= 6.4 \times 10^{-9} = [\text{Mg}^{2+}][\text{F}^-]^2 \\
 &= (x)(5.50 \times 10^{-2} + 2x)^2 \approx (x)(5.50 \times 10^{-2})^2 \\
 [\text{Mg}^{2+}] &= x = 2.1 \times 10^{-6} \text{ M} \\
 [\text{F}^-] &= 5.50 \times 10^{-2} \text{ M}
 \end{aligned}$$

See Exercises 15.99 and 15.100.

Selective Precipitation

Mixtures of metal ions in aqueous solution are often separated by **selective precipitation**, that is, by using a reagent whose anion forms a precipitate with only one or a few of the

The approximations made here fall within the 5% rule.

metal ions in the mixture. For example, suppose we have a solution containing both Ba^{2+} and Ag^+ ions. If NaCl is added to the solution, AgCl precipitates as a white solid, but since BaCl_2 is soluble, the Ba^{2+} ions remain in solution.

Sample Exercise 15.18**Selective Precipitation**

A solution contains $1.0 \times 10^{-4} M \text{ Cu}^+$ and $2.0 \times 10^{-3} M \text{ Pb}^{2+}$. If a source of I^- is added gradually to this solution, will PbI_2 ($K_{\text{sp}} = 1.4 \times 10^{-8}$) or CuI ($K_{\text{sp}} = 5.3 \times 10^{-12}$) precipitate first? Specify the concentration of I^- necessary to begin precipitation of each salt.

Solution

For PbI_2 , the K_{sp} expression is

$$1.4 \times 10^{-8} = K_{\text{sp}} = [\text{Pb}^{2+}][\text{I}^-]^2$$

Since $[\text{Pb}^{2+}]$ in this solution is known to be $2.0 \times 10^{-3} M$, the greatest concentration of I^- that can be present without causing precipitation of PbI_2 can be calculated from the K_{sp} expression:

$$\begin{aligned} 1.4 \times 10^{-8} &= [\text{Pb}^{2+}][\text{I}^-]^2 = (2.0 \times 10^{-3})[\text{I}^-]^2 \\ [\text{I}^-] &= 2.6 \times 10^{-3} M \end{aligned}$$

Any I^- in excess of this concentration will cause solid PbI_2 to form.

Similarly, for CuI , the K_{sp} expression is

$$5.3 \times 10^{-12} = K_{\text{sp}} = [\text{Cu}^+][\text{I}^-] = (1.0 \times 10^{-4})[\text{I}^-]$$

and

$$[\text{I}^-] = 5.3 \times 10^{-8} M$$

A concentration of I^- in excess of $5.3 \times 10^{-8} M$ will cause formation of solid CuI .

As I^- is added to the mixed solution, CuI will precipitate first, since the $[\text{I}^-]$ required is less. Therefore, Cu^+ would be separated from Pb^{2+} using this reagent.

See Exercises 15.101 and 15.102.

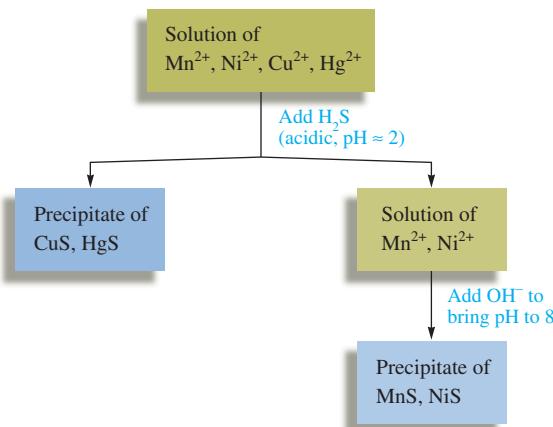
We can compare K_{sp} values to find relative solubilities because FeS and MnS produce the same number of ions in solution.

Since metal sulfide salts differ dramatically in their solubilities, the sulfide ion is often used to separate metal ions by selective precipitation. For example, consider a solution containing a mixture of $10^{-3} M \text{ Fe}^{2+}$ and $10^{-3} M \text{ Mn}^{2+}$. Since FeS ($K_{\text{sp}} = 3.7 \times 10^{-19}$) is much less soluble than MnS ($K_{\text{sp}} = 2.3 \times 10^{-13}$), careful addition of S^{2-} to the mixture will precipitate Fe^{2+} as FeS , leaving Mn^{2+} in solution.

One real advantage of the sulfide ion as a precipitating reagent is that because it is basic, its concentration can be controlled by regulating the pH of the solution. H_2S is a diprotic acid that dissociates in two steps:



Note from the small K_{a_2} value that S^{2-} ions have a high affinity for protons. In an acidic solution (large $[\text{H}^+]$), $[\text{S}^{2-}]$ will be relatively small, since under these conditions the dissociation equilibria will lie far to the left. On the other hand, in basic solutions $[\text{S}^{2-}]$ will be relatively large, since the very small value of $[\text{H}^+]$ will pull both equilibria to the right, producing S^{2-} .

**FIGURE 15.11**

The separation of Cu²⁺ and Hg²⁺ from Ni²⁺ and Mn²⁺ using H₂S. At a low pH, [S²⁻] is relatively low and only the very insoluble HgS and CuS precipitate. When OH⁻ is added to lower [H⁺], the value of [S²⁻] increases, and MnS and NiS precipitate.



Flame test for potassium.



Flame test for sodium.

This means that the most insoluble sulfide salts, such as CuS ($K_{sp} = 8.5 \times 10^{-45}$) and HgS ($K_{sp} = 1.6 \times 10^{-54}$), can be precipitated from an acidic solution, leaving the more soluble ones, such as MnS ($K_{sp} = 2.3 \times 10^{-13}$) and NiS ($K_{sp} = 3 \times 10^{-21}$), still dissolved. The manganese and nickel sulfides can then be precipitated by making the solution slightly basic. This procedure is diagrammed in Fig. 15.11.

Qualitative Analysis

The classic scheme for **qualitative analysis** of a mixture containing all the common cations (listed in Fig. 15.12) involves first separating them into five major groups based on solubilities. (These groups are not directly related to the groups of the periodic table.) Each group is then treated further to separate and identify the individual ions. We will be concerned here only with separation of the major groups.

Group I—Insoluble chlorides

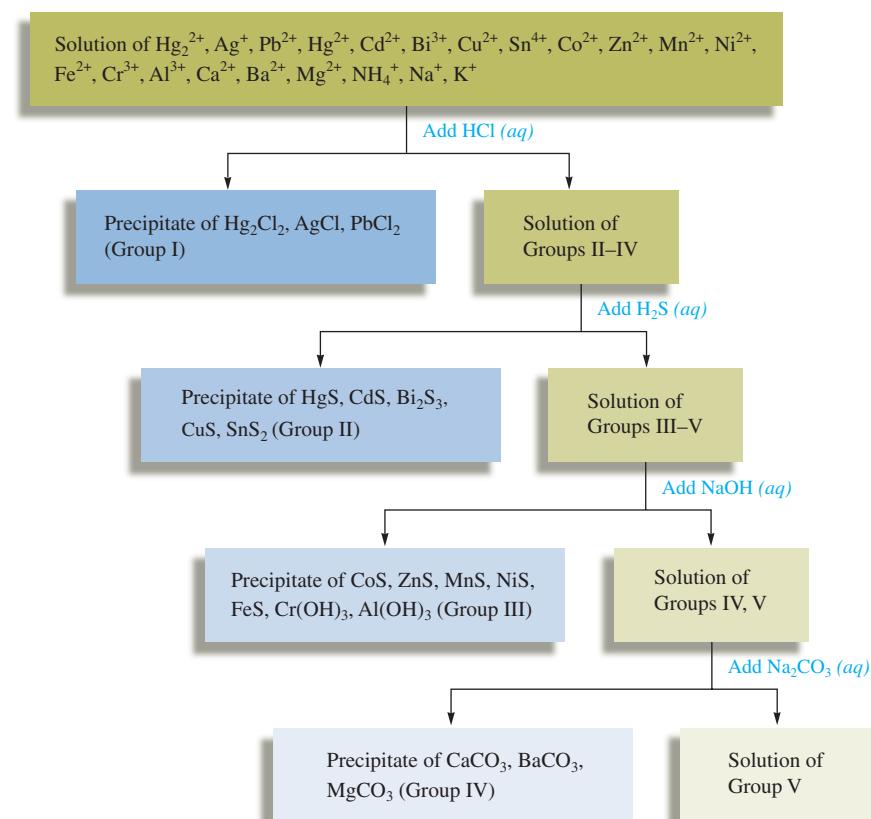
When dilute aqueous HCl is added to a solution containing a mixture of the common cations, only Ag⁺, Pb²⁺, and Hg₂²⁺ will precipitate out as insoluble chlorides. All other chlorides are soluble and remain in solution. The Group I precipitate is removed, leaving the other ions in solution for treatment with sulfide ion.

Group II—Sulfides insoluble in acid solution

After the insoluble chlorides are removed, the solution is still acidic, since HCl was added. If H₂S is added to this solution, only the most insoluble sulfides (those of Hg²⁺, Cd²⁺, Bi³⁺, Cu²⁺, and Sn⁴⁺) will precipitate, since [S²⁻] is relatively low because of the high concentration of H⁺. The more soluble sulfides will remain dissolved under these conditions, and the precipitate of the insoluble salt is removed.

Group III—Sulfides insoluble in basic solution

The solution is made basic at this stage, and more H₂S is added. As we saw earlier, a basic solution produces a higher [S²⁻], which leads to precipitation of the more soluble sulfides. The cations precipitated as sulfides at this stage are Co²⁺, Zn²⁺, Mn²⁺, Ni²⁺, and Fe²⁺. If any Cr³⁺ and Al³⁺ ions are present, they also will precipitate, but as insoluble hydroxides (remember the solution is now basic). The precipitate is separated from the solution containing the rest of the ions.

**FIGURE 15.12**

A schematic diagram of the classic method for separating the common cations by selective precipitation.

Group IV—Insoluble carbonates

At this point, all the cations have been precipitated except those from Groups 1A and 2A of the periodic table. The Group 2A cations form insoluble carbonates and can be precipitated by the addition of CO_3^{2-} . For example, Ba^{2+} , Ca^{2+} , and Mg^{2+} form solid carbonates and can be removed from the solution.



From left to right, cadmium sulfide, chromium(III) hydroxide, aluminum hydroxide, and nickel(II) hydroxide.

Group V—Alkali metal and ammonium ions

The only ions remaining in solution at this point are the Group 1A cations and the NH_4^+ ion, all of which form soluble salts with the common anions. The Group 1A cations are usually identified by the characteristic colors they produce when heated in a flame. These colors are due to the emission spectra of these ions.

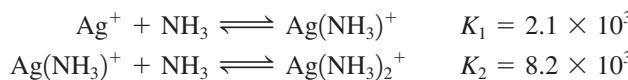
The qualitative analysis scheme for cations based on the selective precipitation procedure described above is summarized in Fig. 15.12.

Complex Ion Equilibria

15.8 Equilibria Involving Complex Ions

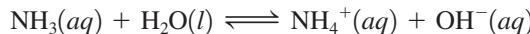
A **complex ion** is a charged species consisting of a metal ion surrounded by *ligands*. A ligand is simply a Lewis base—a molecule or ion having a lone electron pair that can be donated to an empty orbital on the metal ion to form a covalent bond. Some common ligands are H_2O , NH_3 , Cl^- , and CN^- . The number of ligands attached to a metal ion is called the *coordination number*. The most common coordination numbers are 6, for example, in $\text{Co}(\text{H}_2\text{O})_6^{2+}$ and $\text{Ni}(\text{NH}_3)_6^{2+}$; 4, for example, in CoCl_4^{2-} and $\text{Cu}(\text{NH}_3)_4^{2+}$; and 2, for example, in $\text{Ag}(\text{NH}_3)_2^+$; but others are known.

The properties of complex ions will be discussed in more detail in Chapter 21. For now, we will just look at the equilibria involving these species. Metal ions add ligands one at a time in steps characterized by equilibrium constants called **formation constants** or **stability constants**. For example, when solutions containing Ag^+ ions and NH_3 molecules are mixed, the following reactions take place:



where K_1 and K_2 are the formation constants for the two steps. In a solution containing Ag^+ and NH_3 , all the species NH_3 , Ag^+ , $\text{Ag}(\text{NH}_3)^+$, and $\text{Ag}(\text{NH}_3)_2^+$ exist at equilibrium. Calculating the concentrations of all these components can be complicated. However, usually the total concentration of the ligand is much larger than the total concentration of the metal ion, and approximations can greatly simplify the problems.

For example, consider a solution prepared by mixing 100.0 mL of 2.0 M NH_3 with 100.0 mL of 1.0×10^{-3} M AgNO_3 . *Before any reaction occurs*, the mixed solution contains the major species Ag^+ , NO_3^- , NH_3 , and H_2O . What reaction or reactions will occur in this solution? From our discussions of acid–base chemistry, we know that one reaction is

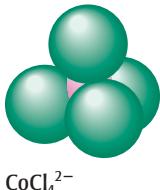


However, we are interested in the reaction between NH_3 and Ag^+ to form complex ions, and since the position of the preceding equilibrium lies far to the left (K_b for NH_3 is 1.8×10^{-5}), we can neglect the amount of NH_3 used up in the reaction with water. Therefore, before any complex ion formation, the concentrations in the mixed solution are

$$[\text{Ag}^+]_0 = \frac{(100.0 \text{ mL})(1.0 \times 10^{-3} \text{ M})}{(200.0 \text{ mL})} = 5.0 \times 10^{-4} \text{ M}$$

↑
Total volume

$$[\text{NH}_3]_0 = \frac{(100.0 \text{ mL})(2.0 \text{ M})}{(200.0 \text{ mL})} = 1.0 \text{ M}$$

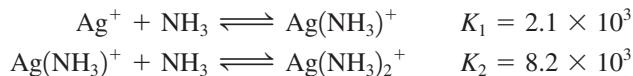


CoCl_4^{2-}



A solution containing the blue CoCl_4^{2-} complex ion.

As mentioned already, the Ag^+ ion reacts with NH_3 in a stepwise fashion to form AgNH_3^+ and then $\text{Ag}(\text{NH}_3)_2^+$:



Since both K_1 and K_2 are large, and since there is a large excess of NH_3 , *both reactions can be assumed to go essentially to completion*. This is equivalent to writing the net reaction in the solution as follows:



The relevant stoichiometric calculations are as follows:

	Ag^+	+	2NH_3	\longrightarrow	$\text{Ag}(\text{NH}_3)_2^+$
Before reaction:	$5.0 \times 10^{-4} M$		$1.0 M$		0
After reaction:	0		$1.0 - 2(5.0 \times 10^{-4}) \approx 1.0 M$		$5.0 \times 10^{-4} M$

Twice as much NH_3 as Ag^+ is required

Note that in this case we have used molarities when performing the stoichiometry calculations and we have assumed this reaction to be complete, using all the original Ag^+ to form $\text{Ag}(\text{NH}_3)_2^+$. In reality, a *very small amount* of the $\text{Ag}(\text{NH}_3)_2^+$ formed will dissociate to produce small amounts of $\text{Ag}(\text{NH}_3)^+$ and Ag^+ . However, since the amount of $\text{Ag}(\text{NH}_3)_2^+$ dissociating will be so small, we can safely assume that $[\text{Ag}(\text{NH}_3)_2^+]$ is $5.0 \times 10^{-4} M$ at equilibrium. Also, we know that since so little NH_3 has been consumed, $[\text{NH}_3]$ is $1.0 M$ at equilibrium. We can use these concentrations to calculate $[\text{Ag}^+]$ and $[\text{Ag}(\text{NH}_3)^+]$ using the K_1 and K_2 expressions.

To calculate the equilibrium concentration of $\text{Ag}(\text{NH}_3)^+$, we use

$$K_2 = 8.2 \times 10^3 = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}(\text{NH}_3)^+][\text{NH}_3]}$$

since $[\text{Ag}(\text{NH}_3)_2^+]$ and $[\text{NH}_3]$ are known. Rearranging and solving for $[\text{Ag}(\text{NH}_3)^+]$ give

$$[\text{Ag}(\text{NH}_3)^+] = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{K_2[\text{NH}_3]} = \frac{5.0 \times 10^{-4}}{(8.2 \times 10^3)(1.0)} = 6.1 \times 10^{-8} M$$

Now the equilibrium concentration of Ag^+ can be calculated using K_1 :

$$\begin{aligned}K_1 &= 2.1 \times 10^3 = \frac{[\text{Ag}(\text{NH}_3)^+]}{[\text{Ag}^+][\text{NH}_3]} = \frac{6.1 \times 10^{-8}}{[\text{Ag}^+](1.0)} \\ [\text{Ag}^+] &= \frac{6.1 \times 10^{-8}}{(2.1 \times 10^3)(1.0)} = 2.9 \times 10^{-11} M\end{aligned}$$

So far we have assumed that $\text{Ag}(\text{NH}_3)_2^+$ is the dominant silver-containing species in solution. Is this a valid assumption? The calculated concentrations are

$$\begin{aligned}[\text{Ag}(\text{NH}_3)_2^+] &= 5.0 \times 10^{-4} M \\ [\text{Ag}(\text{NH}_3)^+] &= 6.1 \times 10^{-8} M \\ [\text{Ag}^+] &= 2.9 \times 10^{-11} M\end{aligned}$$

These values clearly support the conclusion that

$$[\text{Ag}(\text{NH}_3)_2^+] \gg [\text{Ag}(\text{NH}_3)^+] \gg [\text{Ag}^+]$$

Essentially all the Ag^+ ions originally present end up in $\text{Ag}(\text{NH}_3)_2^+$.



Visualization: Nickel(II) Complexes

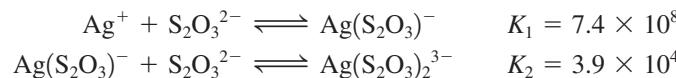
Thus the assumption that $\text{Ag}(\text{NH}_3)_2^+$ is the dominant Ag^+ -containing species is valid, and the calculated concentrations are correct.

This analysis shows that although complex ion equilibria have many species present and look complicated, the calculations are actually quite straightforward, especially if the ligand is present in large excess.

Sample Exercise 15.19

Complex Ions

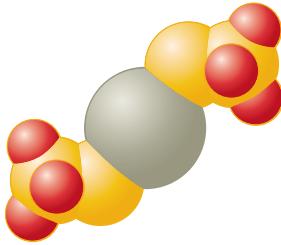
Calculate the concentrations of Ag^+ , $\text{Ag}(\text{S}_2\text{O}_3)^-$, and $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ in a solution prepared by mixing 150.0 mL of $1.00 \times 10^{-3} M$ AgNO_3 with 200.0 mL of $5.00 M$ $\text{Na}_2\text{S}_2\text{O}_3$. The stepwise formation equilibria are



Solution

The concentrations of the ligand and metal ion in the mixed solution *before any reaction occurs* are

$$\begin{aligned} [\text{Ag}^+]_0 &= \frac{(150.0 \text{ mL})(1.00 \times 10^{-3} M)}{(150.0 \text{ mL} + 200.0 \text{ mL})} = 4.29 \times 10^{-4} M \\ [\text{S}_2\text{O}_3^{2-}]_0 &= \frac{(200.0 \text{ mL})(5.00 M)}{(150.0 \text{ mL} + 200.0 \text{ mL})} = 2.86 M \end{aligned}$$



$\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$

Since $[\text{S}_2\text{O}_3^{2-}]_0 \gg [\text{Ag}^+]_0$, and since K_1 and K_2 are large, both formation reactions can be assumed to go to completion, and the net reaction in the solution is as follows:

	Ag^+	+	$2\text{S}_2\text{O}_3^{2-}$	→	$\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$
Before reaction:	$4.29 \times 10^{-4} M$		$2.86 M$		0
After reaction:	~ 0		$2.86 - 2(4.29 \times 10^{-4})$ $\approx 2.86 M$		$4.29 \times 10^{-4} M$

Note that Ag^+ is limiting and that the amount of $\text{S}_2\text{O}_3^{2-}$ consumed is negligible. Also note that since all these species are in the same solution, the molarities can be used to do the stoichiometry problem.

Of course, the concentration of Ag^+ is not zero at equilibrium, and there is some $\text{Ag}(\text{S}_2\text{O}_3)^-$ in the solution. To calculate the concentrations of these species, we must use the K_1 and K_2 expressions. We can calculate the concentration of $\text{Ag}(\text{S}_2\text{O}_3)^-$ from K_1 :

$$3.9 \times 10^4 = K_1 = \frac{[\text{Ag}(\text{S}_2\text{O}_3)^-]}{[\text{Ag}^+][\text{S}_2\text{O}_3^{2-}]} = \frac{4.29 \times 10^{-4}}{[\text{Ag}^+](2.86)}$$

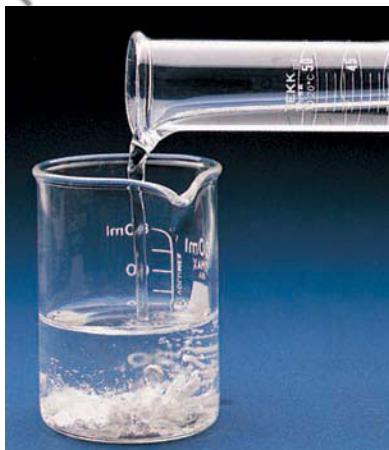
$$[\text{Ag}(\text{S}_2\text{O}_3)^-] = 3.8 \times 10^{-9} M$$

We can calculate $[\text{Ag}^+]$ from K_1 :

$$7.4 \times 10^8 = K_1 = \frac{[\text{Ag}(\text{S}_2\text{O}_3)^-]}{[\text{Ag}^+][\text{S}_2\text{O}_3^{2-}]} = \frac{3.8 \times 10^{-9}}{[\text{Ag}^+](2.86)}$$

$$[\text{Ag}^+] = 1.8 \times 10^{-18} M$$

These results show that $[\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}] \gg [\text{Ag}(\text{S}_2\text{O}_3)^-] \gg [\text{Ag}^+]$



(top) Aqueous ammonia is added to silver chloride (white). (bottom) Silver chloride, insoluble in water, dissolves to form $\text{Ag}(\text{NH}_3)_2^+(aq)$ and $\text{Cl}^-(aq)$.

Thus the assumption is valid that essentially all the original Ag^+ is converted to $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ at equilibrium.

See Exercises 15.109 and 15.110.

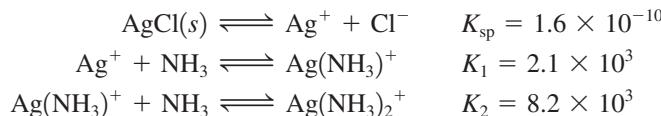
Complex Ions and Solubility

Often ionic solids that are very nearly water-insoluble must be dissolved somehow in aqueous solutions. For example, when the various qualitative analysis groups are precipitated out, the precipitates must be redissolved to separate the ions within each group. Consider a solution of cations that contains Ag^+ , Pb^{2+} , and Hg_2^{2+} , among others. When dilute aqueous HCl is added to this solution, the Group I ions will form the insoluble chlorides AgCl , PbCl_2 , and Hg_2Cl_2 . Once this mixed precipitate is separated from the solution, it must be redissolved to identify the cations individually. How can this be done? We know that some solids are more soluble in acidic than in neutral solutions. What about chloride salts? For example, can AgCl be dissolved by using a strong acid? The answer is no, because Cl^- ions have virtually no affinity for H^+ ions in aqueous solution. The position of the dissolution equilibrium



is not affected by the presence of H^+ .

How can we pull the dissolution equilibrium to the right, even though Cl^- is an extremely weak base? The key is to lower the concentration of Ag^+ in solution by forming complex ions. For example, Ag^+ reacts with excess NH_3 to form the stable complex ion $\text{Ag}(\text{NH}_3)_2^+$. As a result, AgCl is quite soluble in concentrated ammonia solutions. The relevant reactions are



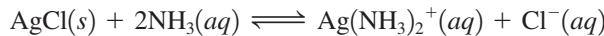
The Ag^+ ion produced by dissolving solid AgCl combines with NH_3 to form $\text{Ag}(\text{NH}_3)_2^+$, which causes more AgCl to dissolve, until the point at which

$$[\text{Ag}^+][\text{Cl}^-] = K_{\text{sp}} = 1.6 \times 10^{-10}$$

Here $[\text{Ag}^+]$ refers only to the Ag^+ ion that is present as a separate species in solution. It is *not* the total silver content of the solution, which is

$$[\text{Ag}]_{\text{total dissolved}} = [\text{Ag}^+] + [\text{Ag}(\text{NH}_3)^+] + [\text{Ag}(\text{NH}_3)_2^+]$$

For reasons discussed in the previous section, virtually all the Ag^+ from the dissolved AgCl ends up in the complex ion $\text{Ag}(\text{NH}_3)_2^+$. Thus we can represent the dissolving of solid AgCl in excess NH_3 by the equation

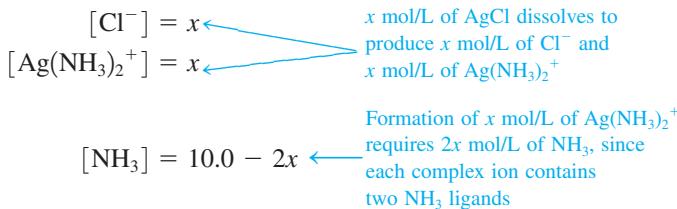


Since this equation is the *sum of the three stepwise reactions* given above, the equilibrium constant for the reaction is the product of the constants for the three reactions. (Demonstrate this to yourself by multiplying together the three expressions for K_{sp} , K_1 , and K_2 .) The equilibrium expression is

$$\begin{aligned}K &= \frac{[\text{Ag}(\text{NH}_3)_2^+][\text{Cl}^-]}{[\text{NH}_3]^2} \\ &= K_{\text{sp}} \times K_1 \times K_2 = (1.6 \times 10^{-10})(2.1 \times 10^3)(8.2 \times 10^3) = 2.8 \times 10^{-3}\end{aligned}$$

When reactions are added, the equilibrium constant for the overall process is the product of the constants for the individual reactions.

Using this expression, we will now calculate the solubility of solid AgCl in a 10.0 M NH₃ solution. If we let x be the solubility (in mol/L) of AgCl in the solution, we can then write the following expressions for the equilibrium concentrations of the pertinent species:



Substituting these concentrations into the equilibrium expression gives

$$K = 2.8 \times 10^{-3} = \frac{[\text{Ag}(\text{NH}_3)_2^+][\text{Cl}^-]}{[\text{NH}_3]^2} = \frac{(x)(x)}{(10.0 - 2x)^2} = \frac{x^2}{(10.0 - 2x)^2}$$

No approximations are necessary here. Taking the square root of both sides of the equation gives

$$\begin{aligned} \sqrt{2.8 \times 10^{-3}} &= \frac{x}{10.0 - 2x} \\ x &= 0.48 \text{ mol/L} = \text{solubility of AgCl}(s) \text{ in 10.0 } M \text{ NH}_3 \end{aligned}$$

Thus the solubility of AgCl in 10.0 M NH₃ is much greater than its solubility in pure water, which is

$$\sqrt{K_{\text{sp}}} = 1.3 \times 10^{-5} \text{ mol/L}$$

In this chapter we have considered two strategies for dissolving a water-insoluble ionic solid. If the *anion* of the solid is a good base, the solubility is greatly increased by acidifying the solution. In cases where the anion is not sufficiently basic, the ionic solid often can be dissolved in a solution containing a ligand that forms stable complex ions with its *cation*.

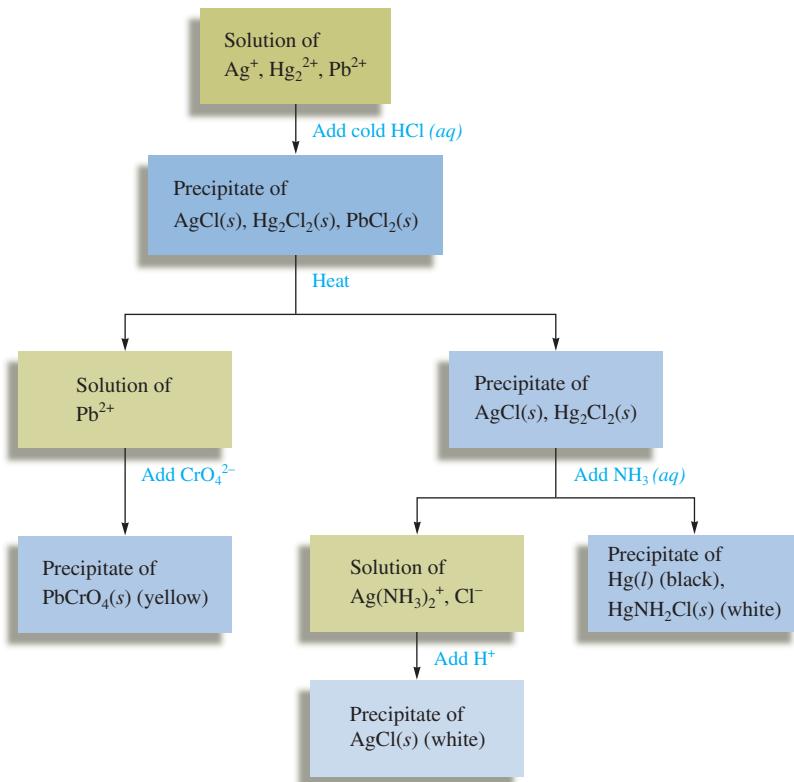
Sometimes solids are so insoluble that combinations of reactions are needed to dissolve them. For example, to dissolve the extremely insoluble HgS ($K_{\text{sp}} = 10^{-54}$), it is necessary to use a mixture of concentrated HCl and concentrated HNO₃, called *aqua regia*. The H⁺ ions in the aqua regia react with the S²⁻ ions to form H₂S, and Cl⁻ reacts with Hg²⁺ to form various complex ions, including HgCl₄²⁻. In addition, NO₃⁻ oxidizes S²⁻ to elemental sulfur. These processes lower the concentrations of Hg²⁺ and S²⁻ and thus promote the solubility of HgS.

Since the solubility of many salts increases with temperature, simple heating is sometimes enough to make a salt sufficiently soluble. For example, earlier in this section we considered the mixed chloride precipitates of the Group I ions—PbCl₂, AgCl, and Hg₂Cl₂. The effect of temperature on the solubility of PbCl₂ is such that we can precipitate PbCl₂ with cold aqueous HCl and then redissolve it by heating the solution to near boiling. The silver and mercury(I) chlorides remain precipitated, since they are not significantly soluble in hot water. However, solid AgCl can be dissolved using aqueous ammonia. The solid Hg₂Cl₂ reacts with NH₃ to form a mixture of elemental mercury and HgNH₂Cl:



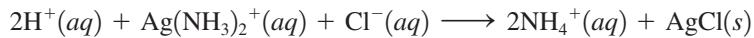
The mixed precipitate appears gray. This is an oxidation–reduction reaction in which one mercury(I) ion in Hg₂Cl₂ is oxidized to Hg²⁺ in HgNH₂Cl and the other mercury(I) ion is reduced to Hg, or elemental mercury.

The treatment of the Group I ions is summarized in Fig. 15.13. Note that the presence of Pb²⁺ is confirmed by adding CrO₄²⁻, which forms bright yellow lead(II) chromate

**FIGURE 15.13**

The separation of the Group I ions in the classic scheme of qualitative analysis.

(PbCrO₄). Also note that H⁺ added to a solution containing Ag(NH₃)₂⁺ reacts with the NH₃ to form NH₄⁺, destroying the Ag(NH₃)₂⁺ complex. Silver chloride then re-forms:



Note that the qualitative analysis of cations by selective precipitation involves all the types of reactions we have discussed and represents an excellent application of the principles of chemical equilibrium.

Key Terms

Section 15.1

common ion
common ion effect

Section 15.2

buffered solution
Henderson–Hasselbalch equation

Section 15.3

buffering capacity

Section 15.4

pH curve (titration curve)
millimole (mmol)
equivalence point (stoichiometric point)

For Review

Buffered solutions

- Contains a weak acid (HA) and its salt (NaA) or a weak base (B) and its salt (BHCl)
- Resists a change in its pH when H⁺ or OH⁻ is added
- For a buffered solution containing HA and A⁻
 - The Henderson–Hasselbalch equation is useful:

$$\text{pH} = \text{p}K_{\text{a}} + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$

- The capacity of the buffered solution depends on the amounts of HA and A⁻ present

Section 15.5

acid–base indicator
phenolphthalein

Section 15.6

solubility product constant (solubility product)

Section 15.7

ion product
selective precipitation
qualitative analysis

Section 15.8

complex ion
formation (stability) constants

- The most efficient buffering occurs when the $\frac{[A^-]}{[HA]}$ ratio is close to 1
- Buffering works because the amounts of HA (which reacts with added OH^-) and A^- (which reacts with added H^+) are large enough that the $\frac{[A^-]}{[HA]}$ ratio does not change significantly when strong acids or bases are added

Acid–base titrations

- The progress of a titration is represented by plotting the pH of the solution versus the volume of added titrant; the resulting graph is called a pH curve or titration curve
- Strong acid–strong base titrations show a sharp change in pH near the equivalence point
- The shape of the pH curve for a strong base–strong acid titration is quite different before the equivalence point from the shape of the pH curve for a strong base–weak acid titration
 - The strong base–weak acid pH curve shows the effects of buffering before the equivalence point
 - For a strong base–weak acid titration, the pH is greater than 7 at the equivalence point because of the basic properties of A^-
- Indicators are sometimes used to mark the equivalence point of an acid–base titration
 - The end point is where the indicator changes color
 - The goal is to have the end point and the equivalence point be as close as possible

Solids dissolving in water

- For a slightly soluble salt, an equilibrium is set up between the excess solid (MX) and the ions in solution



- The corresponding constant is called K_{sp} :

$$K_{\text{sp}} = [\text{M}^+][\text{X}^-]$$

- The solubility of $\text{MX}(s)$ is decreased by the presence from another source of either M^+ or X^- ; this is called the common ion effect
- Predicting whether precipitation will occur when two solutions are mixed involves calculating Q for the initial concentrations
 - If $Q > K_{\text{sp}}$, precipitation occurs
 - If $Q \leq K_{\text{sp}}$, no precipitation occurs

REVIEW QUESTIONS

- What is meant by the presence of a common ion? How does the presence of a common ion affect an equilibrium such as



What is an acid–base solution called that contains a common ion?

- Define a buffer solution. What makes up a buffer solution? How do buffers absorb added H^+ or OH^- with little pH change?

Is it necessary that the concentrations of the weak acid and the weak base in a buffered solution be equal? Explain. What is the pH of a buffer when the weak acid and conjugate base concentrations are equal?

A buffer generally contains a weak acid and its weak conjugate base, or a weak base and its weak conjugate acid, in water. You can solve for the pH by setting up the equilibrium problem using the K_a reaction of the weak acid or the

K_b reaction of the conjugate base. Both reactions give the same answer for the pH of the solution. Explain.

A third method that can be used to solve for the pH of a buffer solution is the Henderson–Hasselbalch equation. What is the Henderson–Hasselbalch equation? What assumptions are made when using this equation?

3. One of the most challenging parts of solving acid–base problems is writing out the correct reaction. When a strong acid or a strong base is added to solutions, they are great at what they do and we always react them first. If a strong acid is added to a buffer, what reacts with the H^+ from the strong acid and what are the products? If a strong base is added to a buffer, what reacts with the OH^- from the strong base and what are the products? Problems involving the reaction of a strong acid or strong base are assumed to be stoichiometry problems and not equilibrium problems. What is assumed when a strong acid or strong base reacts to make it a stoichiometry problem?

A good buffer generally contains relatively equal concentrations of weak acid and conjugate base. If you wanted to buffer a solution at pH = 4.00 or pH = 10.00, how would you decide which weak acid–conjugate base or weak base–conjugate acid pair to use? The second characteristic of a good buffer is good buffering capacity. What is the *capacity* of a buffer? How do the following buffers differ in capacity? How do they differ in pH?

0.01 M acetic acid/0.01 M sodium acetate

0.1 M acetic acid/0.1 M sodium acetate

1.0 M acetic acid/1.0 M sodium acetate

4. Draw the general titration curve for a strong acid titrated by a strong base. At the various points in the titration, list the major species present before any reaction takes place and the major species present after any reaction takes place. What reaction takes place in a strong acid–strong base titration? How do you calculate the pH at the various points along the curve? What is the pH at the equivalence point for a strong acid–strong base titration? Why? Answer the same questions for a strong base–strong acid titration. Compare and contrast a strong acid–strong base titration versus a strong base–strong acid titration.
5. Sketch the titration curve for a weak acid titrated by a strong base. When performing calculations concerning weak acid–strong base titrations, the general two-step procedure is to solve a stoichiometry problem first, then to solve an equilibrium problem to determine the pH. What reaction takes place in the stoichiometry part of the problem? What is assumed about this reaction?

At the various points in your titration curve, list the major species present after the strong base (NaOH, for example) reacts to completion with the weak acid, HA. What equilibrium problem would you solve at the various points in your titration curve to calculate the pH? Why is pH > 7.0 at the equivalence point of a weak acid–strong base titration? Does the pH at the halfway point to equivalence have to be less than 7.0? What does the pH at the halfway point equal? Compare and contrast the titration curves for a strong acid–strong base titration and a weak acid–strong base titration.

6. Sketch the titration curve for a weak base titrated by a strong acid. Weak base–strong acid titration problems also follow a two-step procedure. What reaction takes place in the stoichiometry part of the problem? What is assumed about this reaction? At the various points in your titration curve, list the major species present after the strong acid (HNO₃, for example) reacts to completion with the weak base, B. What equilibrium problem would you solve at the various points in your titration curve to calculate the pH? Why is pH < 7.0 at the equivalence point of a weak base–strong acid titration? If pH = 6.0 at the

halfway point to equivalence, what is the K_b value for the weak base titrated? Compare and contrast the titration curves for a strong base–strong acid titration and a weak base–strong acid titration.

7. What is an acid–base indicator? Define the equivalence (stoichiometric) point and the end point of a titration. Why should you choose an indicator so that the two points coincide? Do the pH values of the two points have to be within ± 0.01 pH unit of each other? Explain. Why does an indicator change from its acid color to its base color over a range of pH values? In general, when do color changes start to occur for indicators? Can the indicator thymol blue contain only a single $-\text{CO}_2\text{H}$ group and no other acidic or basic functional group? Explain.
 8. To what reaction does the solubility product constant, K_{sp} , refer? Table 15.4 lists K_{sp} values for several ionic solids. For any of these ionic compounds, you should be able to calculate the solubility. What is the solubility of a salt, and what procedures do you follow to calculate the solubility of a salt? How would you calculate the K_{sp} value for a salt given the solubility?
- Under what circumstances can you compare the relative solubilities of two salts directly by comparing the values of their solubility products? When can relative solubilities not be compared based on K_{sp} values? What is a common ion and how does its presence affect the solubility? List some salts whose solubility increases as the pH becomes more acidic. What is true about the anions in these salts? List some salts whose solubility remains unaffected by the solution pH. What is true about the anions in these salts?
9. What is the difference between the ion product, Q , and the solubility product, K_{sp} ? What happens when $Q > K_{sp}$? $Q < K_{sp}$? $Q = K_{sp}$? Mixtures of metal ions in aqueous solution can sometimes be separated by selective precipitation. What is selective precipitation? If a solution contained $0.10 \text{ M } \text{Mg}^{2+}$, $0.10 \text{ M } \text{Ca}^{2+}$, and $0.10 \text{ M } \text{Ba}^{2+}$, how could addition of NaF be used to separate the cations out of solution—that is, what would precipitate first, then second, then third? How could addition of K_3PO_4 be used to separate out the cations in a solution that $1.0 \text{ M } \text{Ag}^+$, $1.0 \text{ M } \text{Pb}^{2+}$, and $1.0 \text{ M } \text{Sr}^{2+}$?
 10. What is a complex ion? The stepwise formation constants for the complex ion $\text{Cu}(\text{NH}_3)_4^{2+}$ are $K_1 \approx 1 \times 10^3$, $K_2 \approx 1 \times 10^4$, $K_3 \approx 1 \times 10^3$, and $K_4 \approx 1 \times 10^3$. Write the reactions that refer to each of these formation constants. Given that the values of the formation constants are large, what can you deduce about the equilibrium concentration of $\text{Cu}(\text{NH}_3)_4^{2+}$ versus the equilibrium concentration of Cu^{2+} ? When 5 M ammonia is added to a solution containing $\text{Cu}(\text{OH})_2(s)$, the precipitate will eventually dissolve in solution. Why? If $5 \text{ M } \text{HNO}_3$ is then added, the $\text{Cu}(\text{OH})_2$ precipitate re-forms. Why? In general, what effect does the ability of a cation to form a complex ion have on the solubility of salts containing that cation?

Active Learning Questions

These questions are designed to be used by groups of students in class. The questions allow students to explore their understanding of concepts through discussion and peer teaching. The real value of these questions is the learning that occurs while students talk to each other about chemical concepts.

1. What are the major species in solution after NaHSO_4 is dissolved in water? What happens to the pH of the solution as more NaHSO_4 is added? Why? Would the results vary if baking soda (NaHCO_3) were used instead?

2. A friend asks the following: “Consider a buffered solution made up of the weak acid HA and its salt NaA. If a strong base like NaOH is added, the HA reacts with the OH^- to form A^- . Thus the amount of acid (HA) is decreased, and the amount of base (A^-) is increased. Analogously, adding HCl to the buffered solution forms more of the acid (HA) by reacting with the base (A^-). Thus how can we claim that a buffered solution resists changes in the pH of the solution?” How would you explain buffering to this friend?
3. Mixing together solutions of acetic acid and sodium hydroxide can make a buffered solution. Explain. How does the amount of

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- each solution added change the effectiveness of the buffer? Would a buffer solution made by mixing HCl and NaOH be effective? Explain.
4. Sketch two pH curves, one for the titration of a weak acid with a strong base and one for a strong acid with a strong base. How are they similar? How are they different? Account for the similarities and the differences.
 5. Sketch a pH curve for the titration of a weak acid (HA) with a strong base (NaOH). List the major species and explain how you would go about calculating the pH of the solution at various points, including the halfway point and the equivalence point.
 6. Devise as many ways as you can to experimentally determine the K_{sp} value of a solid. Explain why each of these would work.
 7. You are browsing through the *Handbook of Hypothetical Chemistry* when you come across a solid that is reported to have a K_{sp} value of zero in water at 25°C. What does this mean?
 8. A friend tells you: “The constant K_{sp} of a salt is called the solubility product constant and is calculated from the concentrations of ions in the solution. Thus, if salt A dissolves to a greater extent than salt B, salt A must have a higher K_{sp} than salt B.” Do you agree with your friend? Explain.
 9. Explain the following phenomenon: You have a test tube with about 20 mL of silver nitrate solution. Upon adding a few drops of sodium chromate solution, you notice a red solid forming in a relatively clear solution. Upon adding a few drops of a sodium chloride solution to the same test tube, you notice a white solid and a pale yellow solution. Use the K_{sp} values in the book to support your explanation, and include the balanced reactions.
 10. What happens to the K_{sp} value of a solid as the temperature of the solution changes? Consider both increasing and decreasing temperatures, and explain your answer.
 11. Which is more likely to dissolve in an acidic solution, silver sulfide or silver chloride? Why?
 12. You have two salts, AgX and AgY, with very similar K_{sp} values. You know that the K_a value for HX is much greater than the K_a value for HY. Which salt is more soluble in an acidic solution? Explain.

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide*.

Questions

13. The common ion effect for weak acids is to significantly decrease the dissociation of the acid in water. The common ion effect for ionic solids (salts) is to significantly decrease the solubility of the ionic compound in water. Explain both of these common ion effects.
14. Consider a buffer solution where [weak acid] > [conjugate base]. How is the pH of the solution related to the pK_a value of the weak acid? If [conjugate base] > [weak acid], how is pH related to pK_a ?
15. A best buffer has about equal quantities of weak acid and conjugate base present as well as having a large concentration of each species present. Explain.

16. Consider the following four titrations.

- i. 100.0 mL of 0.10 M HCl titrated by 0.10 M NaOH
- ii. 100.0 mL of 0.10 M NaOH titrated by 0.10 M HCl
- iii. 100.0 mL of 0.10 M CH_3NH_2 titrated by 0.10 M HCl
- iv. 100.0 mL of 0.10 M HF titrated by 0.10 M NaOH

Rank the titrations in order of:

- a. increasing volume of titrant added to reach the equivalence point.
- b. increasing pH initially before any titrant has been added.
- c. increasing pH at the halfway point in equivalence.
- d. increasing pH at the equivalence point.

How would the rankings change if $\text{C}_5\text{H}_5\text{N}$ replaced CH_3NH_2 and if HOC_6H_5 replaced HF?

17. Figure 15.4 shows the pH curves for the titrations of six different acids by NaOH. Make a similar plot for the titration of three different bases by 0.10 M HCl. Assume 50.0 mL of 0.20 M of the bases and assume the three bases are a strong base (KOH), a weak base with $K_b = 1 \times 10^{-5}$, and another weak base with $K_b = 1 \times 10^{-10}$.

18. Acid-base indicators mark the end point of titrations by “magically” turning a different color. Explain the “magic” behind acid-base indicators.

19. The salts in Table 15.4, with the possible exception of the hydroxide salts, have one of the following mathematical relationships between the K_{sp} value and the molar solubility, s .

- i. $K_{sp} = s^2$
- ii. $K_{sp} = 4s^3$
- iii. $K_{sp} = 27s^4$
- iv. $K_{sp} = 108s^5$

For each mathematical relationship, give an example of a salt in Table 15.4 that exhibits that relationship.

20. List some ways one can increase the solubility of a salt in water.

Exercises

In this section similar exercises are paired.

Buffers

21. A certain buffer is made by dissolving NaHCO_3 and Na_2CO_3 in some water. Write equations to show how this buffer neutralizes added H^+ and OH^- .

22. A buffer is prepared by dissolving HONH_2 and HONH_3NO_3 in some water. Write equations to show how this buffer neutralizes added H^+ and OH^- .

23. Calculate the pH of each of the following solutions.

- a. 0.100 M propanoic acid ($\text{HC}_3\text{H}_5\text{O}_2$, $K_a = 1.3 \times 10^{-5}$)
- b. 0.100 M sodium propanoate ($\text{NaC}_3\text{H}_5\text{O}_2$)
- c. pure H_2O
- d. a mixture containing 0.100 M $\text{HC}_3\text{H}_5\text{O}_2$ and 0.100 M $\text{NaC}_3\text{H}_5\text{O}_2$

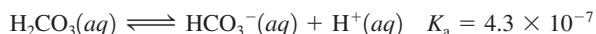
24. Calculate the pH of each of the following solutions.

- a. 0.100 M HONH_2 ($K_b = 1.1 \times 10^{-8}$)
- b. 0.100 M HONH_3Cl
- c. pure H_2O
- d. a mixture containing 0.100 M HONH_2 and 0.100 M HONH_3Cl

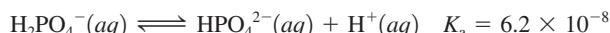
25. Compare the percent dissociation of the acid in Exercise 23a with the percent dissociation of the acid in Exercise 23d. Explain the large difference in percent dissociation of the acid.

- 26.** Compare the percent ionization of the base in Exercise 24a with the percent ionization of the base in Exercise 24d. Explain any differences.
- 27.** Calculate the pH after 0.020 mol HCl is added to 1.00 L of each of the four solutions in Exercise 23.
- 28.** Calculate the pH after 0.020 mol HCl is added to 1.00 L of each of the four solutions in Exercise 24.
- 29.** Calculate the pH after 0.020 mol NaOH is added to 1.00 L of each of the four solutions in Exercise 23.
- 30.** Calculate the pH after 0.020 mol NaOH is added to 1.00 L of each of the solutions in Exercise 24.
- 31.** Which of the solutions in Exercise 23 shows the least change in pH upon the addition of acid or base? Explain.
- 32.** Which of the solutions in Exercise 24 is a buffered solution?
- 33.** Calculate the pH of a solution that is 1.00 *M* HNO₂ and 1.00 *M* NaNO₂.
- 34.** Calculate the pH of a solution that is 0.60 *M* HF and 1.00 *M* KF.
- 35.** Calculate the pH after 0.10 mol of NaOH is added to 1.00 L of the solution in Exercise 33, and calculate the pH after 0.20 mol of HCl is added to 1.00 L of the solution in Exercise 33.
- 36.** Calculate the pH after 0.10 mol of NaOH is added to 1.00 L of the solution in Exercise 34, and calculate the pH after 0.20 mol of HCl is added to 1.00 L of the solution in Exercise 34.
- 37.** Calculate the pH of a buffer solution prepared by dissolving 21.46 g of benzoic acid (HC₇H₅O₂) and 37.68 g of sodium benzoate in 200.0 mL of solution.
- 38.** A buffered solution is made by adding 50.0 g NH₄Cl to 1.00 L of a 0.75 *M* solution of NH₃. Calculate the pH of the final solution. (Assume no volume change.)
- 39.** Calculate the pH after 0.010 mol gaseous HCl is added to 250.0 mL of each of the following buffered solutions.
- 0.050 *M* NH₃/0.15 *M* NH₄Cl
 - 0.50 *M* NH₃/1.50 *M* NH₄Cl
- Do the two original buffered solutions differ in their pH or their capacity? What advantage is there in having a buffer with a greater capacity?
- 40.** An aqueous solution contains dissolved C₆H₅NH₃Cl and C₆H₅NH₂. The concentration of C₆H₅NH₂ is 0.50 *M* and pH is 4.20.
- Calculate the concentration of C₆H₅NH₃⁺ in this buffer solution.
 - Calculate the pH after 4.0 g of NaOH(s) is added to 1.0 L of this solution. (Neglect any volume change.)
- 41.** Calculate the mass of sodium acetate that must be added to 500.0 mL of 0.200 *M* acetic acid to form a pH = 5.00 buffer solution.
- 42.** What volumes of 0.50 *M* HNO₂ and 0.50 *M* NaNO₂ must be mixed to prepare 1.00 L of a solution buffered at pH = 3.55?
- 43.** Consider a solution that contains both C₅H₅N and C₅H₅NHNO₃. Calculate the ratio [C₅H₅N]/[C₅H₅NH⁺] if the solution has the following pH values.
- pH = 4.50
 - pH = 5.00
 - pH = 5.23
 - pH = 5.50

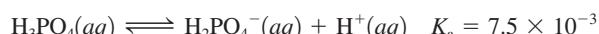
- 44. a.** Carbonate buffers are important in regulating the pH of blood at 7.40. What is the concentration ratio of CO₂ (usually written H₂CO₃) to HCO₃⁻ in blood at pH = 7.40?



- b.** Phosphate buffers are important in regulating the pH of intracellular fluids at pH values generally between 7.1 and 7.2. What is the concentration ratio of H₂PO₄⁻ to HPO₄²⁻ in intracellular fluid at pH = 7.15?



- c.** Why is a buffer composed of H₃PO₄ and H₂PO₄⁻ ineffective in buffering the pH of intracellular fluid?



- 45.** Consider the acids in Table 14.2. Which acid would be the best choice for preparing a pH = 7.00 buffer? Explain how to make 1.0 L of this buffer.

- 46.** Consider the bases in Table 14.3. Which base would be the best choice for preparing a pH = 5.00 buffer? Explain how to make 1.0 L of this buffer.

- 47.** Which of the following mixtures would result in buffered solutions when 1.0 L of each of the two solutions are mixed?

- 0.1 *M* KOH and 0.1 *M* CH₃NH₃Cl
- 0.1 *M* KOH and 0.2 *M* CH₃NH₂
- 0.2 *M* KOH and 0.1 *M* CH₃NH₃Cl
- 0.1 *M* KOH and 0.2 *M* CH₃NH₃Cl

- 48.** Which of the following mixtures would result in a buffered solution when 1.0 L of each of the two solutions are mixed?

- 0.2 *M* HNO₃ and 0.4 *M* NaNO₃
- 0.2 *M* HNO₃ and 0.4 *M* HF
- 0.2 *M* HNO₃ and 0.4 *M* NaF
- 0.2 *M* HNO₃ and 0.4 *M* NaOH

- 49.** How many moles of NaOH must be added to 1.0 L of 2.0 *M* HC₂H₃O₂ to produce a solution buffered at each pH?

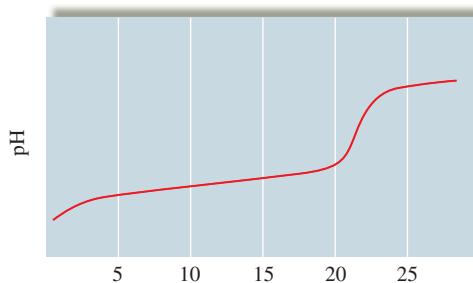
- pH = pK_a
- pH = 4.00
- pH = 5.00

- 50.** Calculate the number of moles of HCl(*g*) that must be added to 1.0 L of 1.0 *M* NaC₂H₃O₂ to produce a solution buffered at each pH.

- pH = pK_a
- pH = 4.20
- pH = 5.00

Acid–Base Titrations

- 51.** Consider the titration of a generic weak acid HA with a strong base that gives the following titration curve:



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- On the curve, indicate the points that correspond to the following:
- the stoichiometric (equivalence) point
 - the region with maximum buffering
 - $pH = pK_a$
 - pH depends only on $[HA]$
 - pH depends only on $[A^-]$
 - pH depends only on the amount of excess strong base added
52. Sketch the titration curve for the titration of a generic weak base B with a strong acid. The titration reaction is
- $$B + H^+ \rightleftharpoons BH^+$$
- On this curve, indicate the points that correspond to the following:
- the stoichiometric (equivalence) point
 - the region with maximum buffering
 - $pH = pK_a$
 - pH depends only on $[B]$
 - pH depends only on $[BH^+]$
 - pH depends only on the amount of excess strong acid added
53. Consider the titration of 40.0 mL of 0.200 M $HClO_4$ by 0.100 M KOH. Calculate the pH of the resulting solution after the following volumes of KOH have been added.
- 0.0 mL
 - 10.0 mL
 - 40.0 mL
 - 80.0 mL
 - 100.0 mL
 - 40.0 mL
54. Consider the titration of 80.0 mL of 0.100 M $Ba(OH)_2$ by 0.400 M HCl. Calculate the pH of the resulting solution after the following volumes of HCl have been added.
- 0.0 mL
 - 20.0 mL
 - 30.0 mL
 - 40.0 mL
 - 80.0 mL
 - 100.0 mL
55. Consider the titration of 100.0 mL of 0.200 M acetic acid ($K_a = 1.8 \times 10^{-5}$) by 0.100 M KOH. Calculate the pH of the resulting solution after the following volumes of KOH have been added.
- 0.0 mL
 - 50.0 mL
 - 100.0 mL
 - 150.0 mL
 - 200.0 mL
 - 250.0 mL
56. Consider the titration of 100.0 mL of 0.100 M H_2NNH_2 ($K_b = 3.0 \times 10^{-6}$) by 0.200 M HNO_3 . Calculate the pH of the resulting solution after the following volumes of HNO_3 have been added.
- 0.0 mL
 - 20.0 mL
 - 25.0 mL
 - 40.0 mL
 - 50.0 mL
 - 100.0 mL
57. A 25.0-mL sample of 0.100 M lactic acid ($HC_3H_5O_3$, $pK_a = 3.86$) is titrated with 0.100 M NaOH solution. Calculate the pH after the addition of 0.0 mL, 4.0 mL, 8.0 mL, 12.5 mL, 20.0 mL, 24.0 mL, 24.5 mL, 24.9 mL, 25.0 mL, 25.1 mL, 26.0 mL, 28.0 mL, and 30.0 mL of the NaOH. Plot the results of your calculations as pH versus milliliters of NaOH added.
58. Repeat the procedure in Exercise 57, but for the titration of 25.0 mL of 0.100 M propanoic acid ($HC_3H_5O_2$, $K_a = 1.3 \times 10^{-5}$) with 0.100 M NaOH.
59. Repeat the procedure in Exercise 57, but for the titration of 25.0 mL of 0.100 M NH_3 ($K_b = 1.8 \times 10^{-5}$) with 0.100 M HCl.

60. Repeat the procedure in Exercise 57, but for the titration of 25.0 mL of 0.100 M pyridine with 0.100 M hydrochloric acid (K_b for pyridine is 1.7×10^{-9}). Do not do the points at 24.9 and 25.1 mL.

61. Calculate the pH at the halfway point and at the equivalence point for each of the following titrations.

- 100.0 mL of 0.10 M $HC_7H_5O_2$ ($K_a = 6.4 \times 10^{-5}$) titrated by 0.10 M NaOH
- 100.0 mL of 0.10 M $C_2H_5NH_2$ ($K_b = 5.6 \times 10^{-4}$) titrated by 0.20 M HNO_3
- 100.0 mL of 0.50 M HCl titrated by 0.25 M NaOH

62. In the titration of 50.0 mL of 1.0 M methylamine, CH_3NH_2 ($K_b = 4.4 \times 10^{-4}$), with 0.50 M HCl, calculate the pH under the following conditions.

- after 50.0 mL of 0.50 M HCl has been added
- at the stoichiometric point

63. You have 75.0 mL of 0.10 M HA. After adding 30.0 mL of 0.10 M NaOH, the pH is 5.50. What is the K_a value of HA?

64. A sample of an ionic compound NaA, where A^- is the anion of a weak acid, was dissolved in enough water to make 100.0 mL of solution and was then titrated with 0.100 M HCl. After 500.0 mL of HCl was added, the pH was measured and found to be 5.00. The experimenter found that 1.00 L of 0.100 M HCl was required to reach the stoichiometric point of the titration.

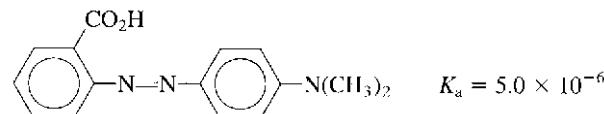
- What is the K_b value for A^- ?
- Calculate the pH of the solution at the stoichiometric point of the titration.

Indicators

65. Two drops of indicator HIn ($K_a = 1.0 \times 10^{-9}$), where HIn is yellow and In⁻ is blue, are placed in 100.0 mL of 0.10 M HCl.

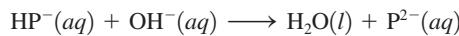
- What color is the solution initially?
- The solution is titrated with 0.10 M NaOH. At what pH will the color change (yellow to greenish yellow) occur?
- What color will the solution be after 200.0 mL of NaOH has been added?

66. Methyl red has the following structure:



It undergoes a color change from red to yellow as a solution gets more basic. Calculate an approximate pH range for which methyl red is useful. What is the color change and the pH at the color change when a weak acid is titrated with a strong base using methyl red as an indicator? What is the color change and the pH at the color change when a weak base is titrated with a strong acid using methyl red as an indicator? For which of these two types of titrations is methyl red a possible indicator?

67. Potassium hydrogen phthalate, known as KHP (molar mass = 204.22 g/mol), can be obtained in high purity and is used to determine the concentration of solutions of strong bases by the reaction



If a typical titration experiment begins with approximately 0.5 g of KHP and has a final volume of about 100 mL, what is an appropriate indicator to use? The pK_a for HP^- is 5.51.

68. A certain indicator HIn has a pK_a of 3.00 and a color change becomes visible when 7.00% of the indicator has been converted to In^- . At what pH is this color change visible?
69. Which of the indicators in Fig. 15.8 could be used for the titrations in Exercises 53 and 55?
70. Which of the indicators in Fig. 15.8 could be used for the titrations in Exercises 54 and 56?
71. Which of the indicators in Fig. 15.8 could be used for the titrations in Exercises 57 and 59?
72. Which of the indicators in Fig. 15.8 could be used for the titrations in Exercises 58 and 60?
73. Estimate the pH of a solution in which brom cresol green is blue and thymol blue is yellow. (See Fig. 15.8.)
74. A solution has a pH of 7.0. What would be the color of the solution if each of the following indicators were added? (See Fig. 15.8.)
 - a. thymol blue
 - b. bromthymol blue
 - c. methyl red
 - d. crystal violet

Solubility Equilibria

75. Write balanced equations for the dissolution reactions and the corresponding solubility product expressions for each of the following solids.
 - a. $\text{AgC}_2\text{H}_3\text{O}_2$
 - b. Al(OH)_3
 - c. $\text{Ca}_3(\text{PO}_4)_2$
76. Write balanced equations for the dissolution reactions and the corresponding solubility product expressions for each of the following solids.
 - a. Ag_2CO_3
 - b. $\text{Ce}(\text{IO}_3)_3$
 - c. BaF_2
77. Use the following data to calculate the K_{sp} value for each solid.
 - a. The solubility of CaC_2O_4 is 6.1×10^{-3} g/L.
 - b. The solubility of BiI_3 is 1.32×10^{-5} mol/L.
78. Use the following data to calculate the K_{sp} value for each solid.
 - a. The solubility of $\text{Pb}_3(\text{PO}_4)_2$ is 6.2×10^{-12} mol/L.
 - b. The solubility of Li_2CO_3 is 7.4×10^{-2} mol/L.
79. The concentration of Pb^{2+} in a solution saturated with $\text{PbBr}_2(s)$ is $2.14 \times 10^{-2} M$. Calculate K_{sp} for PbBr_2 .
80. The concentration of Ag^+ in a solution saturated with $\text{Ag}_2\text{C}_2\text{O}_4(s)$ is $2.2 \times 10^{-4} M$. Calculate K_{sp} for $\text{Ag}_2\text{C}_2\text{O}_4$.
81. Calculate the solubility of each of the following compounds in moles per liter. Ignore any acid–base properties.
 - a. Ag_3PO_4 , $K_{sp} = 1.8 \times 10^{-18}$
 - b. CaCO_3 , $K_{sp} = 8.7 \times 10^{-9}$
 - c. Hg_2Cl_2 , $K_{sp} = 1.1 \times 10^{-18}$ (Hg_2^{2+} is the cation in solution.)
82. Calculate the solubility of each of the following compounds in moles per liter. Ignore any acid–base properties.
 - a. PbI_2 , $K_{sp} = 1.4 \times 10^{-8}$
 - b. CdCO_3 , $K_{sp} = 5.2 \times 10^{-12}$
 - c. $\text{Sr}_3(\text{PO}_4)_2$, $K_{sp} = 1 \times 10^{-31}$
83. The solubility of the ionic compound M_2X_3 , having a molar mass of 288 g/mol, is 3.60×10^{-7} g/L. Calculate the K_{sp} of the compound.

84. A solution contains 0.018 mol each of I^- , Br^- , and Cl^- . When the solution is mixed with 200. mL of 0.24 M AgNO_3 , what mass of $\text{AgCl}(s)$ precipitates out, and what is the $[\text{Ag}^+]$? Assume no volume change.

$$\text{AgI}, K_{sp} = 1.5 \times 10^{-16}$$

$$\text{AgBr}, K_{sp} = 5.0 \times 10^{-13}$$

$$\text{AgCl}, K_{sp} = 1.6 \times 10^{-10}$$

85. Calculate the molar solubility of $\text{Co}(\text{OH})_3$, $K_{sp} = 2.5 \times 10^{-43}$.

86. Calculate the molar solubility of $\text{Cd}(\text{OH})_2$, $K_{sp} = 5.9 \times 10^{-11}$.

87. For each of the following pairs of solids, determine which solid has the smallest molar solubility.

- a. $\text{CaF}_2(s)$, $K_{sp} = 4.0 \times 10^{-11}$, or $\text{BaF}_2(s)$, $K_{sp} = 2.4 \times 10^{-5}$
- b. $\text{Ca}_3(\text{PO}_4)_2(s)$, $K_{sp} = 1.3 \times 10^{-32}$, or $\text{FePO}_4(s)$, $K_{sp} = 1.0 \times 10^{-22}$

88. For each of the following pairs of solids, determine which solid has the smallest molar solubility.

- a. FeC_2O_4 , $K_{sp} = 2.1 \times 10^{-7}$, or $\text{Cu}(\text{IO}_4)_2$, $K_{sp} = 1.4 \times 10^{-7}$
- b. Ag_2CO_3 , $K_{sp} = 8.1 \times 10^{-12}$, or $\text{Mn}(\text{OH})_2$, $K_{sp} = 2 \times 10^{-13}$

89. Calculate the solubility (in moles per liter) of $\text{Fe}(\text{OH})_3$ ($K_{sp} = 4 \times 10^{-38}$) in each of the following.

- a. water
- b. a solution buffered at pH = 5.0
- c. a solution buffered at pH = 11.0

90. The K_{sp} for silver sulfate (Ag_2SO_4) is 1.2×10^{-5} . Calculate the solubility of silver sulfate in each of the following.

- a. water
- b. 0.10 M AgNO_3
- c. 0.20 M K_2SO_4

91. Calculate the solubility of solid $\text{Ca}_3(\text{PO}_4)_2$ ($K_{sp} = 1.3 \times 10^{-32}$) in a 0.20 M Na_3PO_4 solution.

92. The solubility of $\text{Ce}(\text{IO}_3)_3$ in a 0.20 M KIO_3 solution is 4.4×10^{-8} mol/L. Calculate K_{sp} for $\text{Ce}(\text{IO}_3)_3$.

93. What mass of ZnS ($K_{sp} = 2.5 \times 10^{-22}$) will dissolve in 300.0 mL of 0.050 M $\text{Zn}(\text{NO}_3)_2$? Ignore the basic properties of S^{2-} .

94. The concentration of Mg^{2+} in seawater is 0.052 M. At what pH will 99% of the Mg^{2+} be precipitated as the hydroxide salt? [K_{sp} for $\text{Mg}(\text{OH})_2 = 8.9 \times 10^{-12}$.]

95. Which of the substances in Exercises 81 and 82 show increased solubility as the pH of the solution becomes more acidic? Write equations for the reactions that occur to increase the solubility.

96. For which salt in each of the following groups will the solubility depend on pH?

- a. AgF , AgCl , AgBr
- b. $\text{Pb}(\text{OH})_2$, PbCl_2
- c. $\text{Sr}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_2)_2$
- d. $\text{Ni}(\text{NO}_3)_2$, $\text{Ni}(\text{CN})_2$

97. Will a precipitate form when 75.0 mL of 0.020 M BaCl_2 and 125 mL of 0.040 M Na_2SO_4 are mixed together?

98. Will a precipitate form when 100.0 mL of 4.0×10^{-4} M $\text{Mg}(\text{NO}_3)_2$ is added to 100.0 mL of 2.0×10^{-4} M NaOH ?

99. Calculate the final concentrations of $\text{K}^+(aq)$, $\text{C}_2\text{O}_4^{2-}(aq)$, $\text{Ba}^{2+}(aq)$, and $\text{Br}^-(aq)$ in a solution prepared by adding 0.100 L of 0.200 M $\text{K}_2\text{C}_2\text{O}_4$ to 0.150 L of 0.250 M BaBr_2 . (For BaC_2O_4 , $K_{sp} = 2.3 \times 10^{-8}$.)

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100. A solution is prepared by mixing 50.0 mL of 0.10 M $\text{Pb}(\text{NO}_3)_2$ with 50.0 mL of 1.0 M KCl. Calculate the concentrations of Pb^{2+} and Cl^- at equilibrium. K_{sp} for $\text{PbCl}_2(s)$ is 1.6×10^{-5} .

101. A solution contains 1.0×10^{-5} M Na_3PO_4 . What is the minimum concentration of AgNO_3 that would cause precipitation of solid Ag_3PO_4 ($K_{\text{sp}} = 1.8 \times 10^{-18}$)?

102. A solution contains 0.25 M $\text{Ni}(\text{NO}_3)_2$ and 0.25 M $\text{Cu}(\text{NO}_3)_2$. Can the metal ions be separated by slowly adding Na_2CO_3 ? Assume that for successful separation 99% of the metal ion must be precipitated before the other metal ion begins to precipitate, and assume no volume change on addition of Na_2CO_3 .

Complex Ion Equilibria

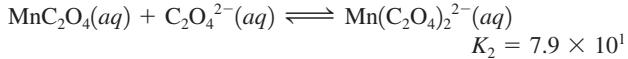
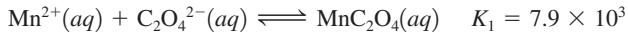
103. Write equations for the stepwise formation of each of the following complex ions.

- $\text{Ni}(\text{CN})_4^{2-}$
- $\text{V}(\text{C}_2\text{O}_4)_3^{3-}$

104. Write equations for the stepwise formation of each of the following complex ions.

- CoF_6^{3-}
- $\text{Zn}(\text{NH}_3)_4^{2+}$

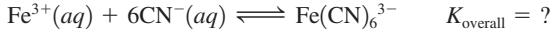
105. Given the following data,



calculate the value for the overall formation constant for $\text{Mn}(\text{C}_2\text{O}_4)_2^{2-}$:

$$K = \frac{[\text{Mn}(\text{C}_2\text{O}_4)_2^{2-}]}{[\text{Mn}^{2+}][\text{C}_2\text{O}_4^{2-}]^2}$$

106. In the presence of CN^- , Fe^{3+} forms the complex ion $\text{Fe}(\text{CN})_6^{3-}$. The equilibrium concentrations of Fe^{3+} and $\text{Fe}(\text{CN})_6^{3-}$ are 8.5×10^{-40} M and 1.5×10^{-3} M, respectively, in a 0.11 M KCN solution. Calculate the value for the overall formation constant of $\text{Fe}(\text{CN})_6^{3-}$.



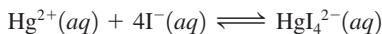
107. When aqueous KI is added gradually to mercury(II) nitrate, an orange precipitate forms. Continued addition of KI causes the precipitate to dissolve. Write balanced equations to explain these observations. (Hint: Hg^{2+} reacts with I^- to form HgI_4^{2-} .)

108. As sodium chloride solution is added to a solution of silver nitrate, a white precipitate forms. Ammonia is added to the mixture and the precipitate dissolves. When potassium bromide solution is then added, a pale yellow precipitate appears. When a solution of sodium thiosulfate is added, the yellow precipitate dissolves. Finally, potassium iodide is added to the solution and a yellow precipitate forms. Write reactions for all the changes mentioned above. What conclusions can you draw concerning the sizes of the K_{sp} values for AgCl , AgBr , and AgI ?

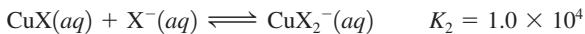
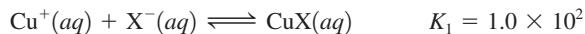
109. The overall formation constant for HgI_4^{2-} is 1.0×10^{30} . That is,

$$1.0 \times 10^{30} = \frac{[\text{HgI}_4^{2-}]}{[\text{Hg}^{2+}][\text{I}^-]^4}$$

What is the concentration of Hg^{2+} in 500.0 mL of a solution that was originally 0.010 M Hg^{2+} and 0.78 M I^- ? The reaction is



110. A solution is formed by mixing 50.0 mL of 10.0 M NaX with 50.0 mL of 2.0×10^{-3} M CuNO_3 . Assume that Cu(I) forms complex ions with X^- as follows:



with an overall reaction



Calculate the following concentrations at equilibrium.

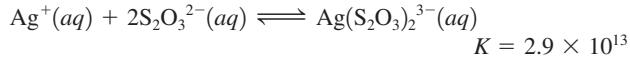
- CuX_3^{2-}
- CuX_2^-
- Cu^+

111. **a.** Calculate the molar solubility of AgI in pure water. K_{sp} for AgI is 1.5×10^{-16} .

b. Calculate the molar solubility of AgI in 3.0 M NH_3 . The overall formation constant for $\text{Ag}(\text{NH}_3)_2^+$ is 1.7×10^7 .

c. Compare the calculated solubilities from parts a and b. Explain any differences.

112. Solutions of sodium thiosulfate are used to dissolve unexposed AgBr ($K_{\text{sp}} = 5.0 \times 10^{-13}$) in the developing process for black-and-white film. What mass of AgBr can dissolve in 1.00 L of 0.500 M $\text{Na}_2\text{S}_2\text{O}_3$? Ag^+ reacts with $\text{S}_2\text{O}_3^{2-}$ to form a complex ion:



113. K_f for the complex ion $\text{Ag}(\text{NH}_3)_2^+$ is 1.7×10^7 . K_{sp} for AgCl is 1.6×10^{-10} . Calculate the molar solubility of AgCl in 1.0 M NH_3 .

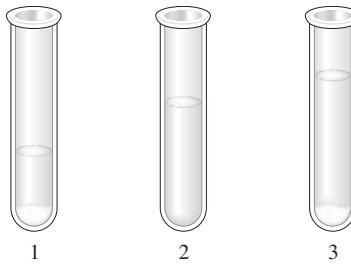
114. The copper(I) ion forms a chloride salt that has $K_{\text{sp}} = 1.2 \times 10^{-6}$. Copper(I) also forms a complex ion with Cl^- :



a. Calculate the solubility of copper(I) chloride in pure water. (Ignore CuCl_2^- formation for part a.)

b. Calculate the solubility of copper(I) chloride in 0.10 M NaCl .

115. A series of chemicals were added to some $\text{AgNO}_3(aq)$. $\text{NaCl}(aq)$ was added first to the silver nitrate solution with the end result shown below in test tube 1, $\text{NH}_3(aq)$ was then added with the end result shown in test tube 2, and $\text{HNO}_3(aq)$ was added last with the end result shown in test tube 3.



Explain the results shown in each test tube. Include a balanced equation for the reaction(s) taking place.

- 116.** The solubility of copper(II) hydroxide in water can be increased by adding either the base NH_3 or the acid HNO_3 . Explain. Would added NH_3 or HNO_3 have the same effect on the solubility of silver acetate or silver chloride? Explain.

Additional Exercises

- 117.** Derive an equation analogous to the Henderson–Hasselbalch equation but relating pOH and $\text{p}K_b$ of a buffered solution composed of a weak base and its conjugate acid, such as NH_3 and NH_4^+ .

- 118.** **a.** Calculate the pH of a buffered solution that is 0.100 M in $\text{C}_6\text{H}_5\text{CO}_2\text{H}$ (benzoic acid, $K_a = 6.4 \times 10^{-5}$) and 0.100 M in $\text{C}_6\text{H}_5\text{CO}_2\text{Na}$.
b. Calculate the pH after 20.0% (by moles) of the benzoic acid is converted to benzoate anion by addition of strong acid. Use the dissociation equilibrium



to calculate the pH.

- c.** Do the same as in part b, but use the following equilibrium to calculate the pH:



- d.** Do your answers in parts b and c agree? Explain.

- 119.** Consider a solution containing 0.10 M ethylamine ($\text{C}_2\text{H}_5\text{NH}_2$), 0.20 M $\text{C}_2\text{H}_5\text{NH}_3^+$, and 0.20 M Cl^- .

- a.** Calculate the pH of this solution.
b. Calculate the pH after 0.050 mol of $\text{KOH}(s)$ is added to 1.00 L of this solution. (Ignore any volume changes.)
120. You make 1.00 L of a buffered solution ($\text{pH} = 4.00$) by mixing acetic acid and sodium acetate. You have 1.00 M solutions of each component of the buffered solution. What volume of each solution do you mix to make such a buffered solution?

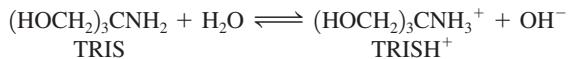
- 121.** You have the following reagents on hand:

Solids ($\text{p}K_a$ of Acid Form Is Given)	Solutions
Benzoic acid (4.19)	5.0 M HCl
Sodium acetate (4.74)	$1.0\text{ M acetic acid (4.74)}$
Potassium fluoride (3.14)	2.6 M NaOH
Ammonium chloride (9.26)	1.0 M HOCl (7.46)

What combinations of reagents would you use to prepare buffers at the following pH values?

- a.** 3.0 **b.** 4.0 **c.** 5.0 **d.** 7.0 **e.** 9.0

- 122.** Tris(hydroxymethyl)aminomethane, commonly called TRIS or Trizma, is often used as a buffer in biochemical studies. Its buffering range is pH 7 to 9, and K_b is 1.19×10^{-6} for the aqueous reaction



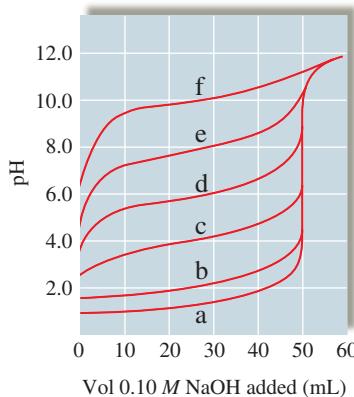
- a.** What is the optimal pH for TRIS buffers?
b. Calculate the ratio $[\text{TRIS}]/[\text{TRISH}^+]$ at pH = 7.00 and at pH = 9.00.
c. A buffer is prepared by diluting 50.0 g TRIS base and 65.0 g TRIS hydrochloride (written as TRISHCl) to a total volume of

2.0 L. What is the pH of this buffer? What is the pH after 0.50 mL of 12 M HCl is added to a 200.0-mL portion of the buffer?

- 123.** Calculate the value of the equilibrium constant for each of the following reactions in aqueous solution.

- a.** $\text{HC}_2\text{H}_3\text{O}_2 + \text{OH}^- \rightleftharpoons \text{C}_2\text{H}_3\text{O}_2^- + \text{H}_2\text{O}$
b. $\text{C}_2\text{H}_3\text{O}_2^- + \text{H}^+ \rightleftharpoons \text{HC}_2\text{H}_3\text{O}_2$
c. $\text{HCl} + \text{NaOH} \rightleftharpoons \text{NaCl} + \text{H}_2\text{O}$

- 124.** The following plot shows the pH curves for the titrations of various acids by 0.10 M NaOH (all of the acids were 50.0-mL samples of 0.10 M concentration).



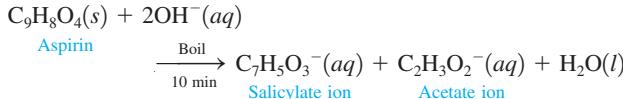
- a.** Which pH curve corresponds to the weakest acid?
b. Which pH curve corresponds to the strongest acid? Which point on the pH curve would you examine to see if this acid is a strong acid or a weak acid (assuming you did not know the initial concentration of the acid)?
c. Which pH curve corresponds to an acid with $K_a \approx 1 \times 10^{-6}$?

- 125.** Calculate the volume of $1.50 \times 10^{-2}\text{ M NaOH}$ that must be added to 500.0 mL of 0.200 M HCl to give a solution that has $\text{pH} = 2.15$.

- 126.** Repeat the procedure in Exercise 57, but for the titration of 25.0 mL of 0.100 M HNO_3 with 0.100 M NaOH .

- 127.** The active ingredient in aspirin is acetylsalicylic acid. A 2.51-g sample of acetylsalicylic acid required 27.36 mL of 0.5106 M NaOH for complete reaction. Addition of 13.68 mL of 0.5106 M HCl to the flask containing the aspirin and the sodium hydroxide produced a mixture with $\text{pH} = 3.48$. Find the molar mass of acetylsalicylic acid and its K_a value. State any assumptions you must make to reach your answer.

- 128.** One method for determining the purity of aspirin (empirical formula, $\text{C}_9\text{H}_8\text{O}_4$) is to hydrolyze it with NaOH solution and then to titrate the remaining NaOH . The reaction of aspirin with NaOH is as follows:



A sample of aspirin with a mass of 1.427 g was boiled in 50.00 mL of 0.500 M NaOH . After the solution was cooled, it took 31.92 mL of 0.289 M HCl to titrate the excess NaOH . Calculate the purity of the aspirin. What indicator should be used for this titration? Why?

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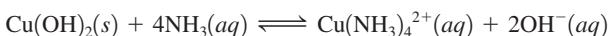
129. A certain acetic acid solution has pH = 2.68. Calculate the volume of 0.0975 M KOH required to reach the equivalence point in the titration of 25.0 mL of the acetic acid solution.

130. A 0.210-g sample of an acid (molar mass = 192 g/mol) is titrated with 30.5 mL of 0.108 M NaOH to a phenolphthalein end point. Is the acid monoprotic, diprotic, or tripasic?

131. A student intends to titrate a solution of a weak monoprotic acid with a sodium hydroxide solution but reverses the two solutions and places the weak acid solution in the buret. After 23.75 mL of the weak acid solution has been added to 50.0 mL of the 0.100 M NaOH solution, the pH of the resulting solution is 10.50. Calculate the original concentration of the solution of weak acid.

132. A student titrates an unknown weak acid, HA, to a pale pink phenolphthalein end point with 25.0 mL of 0.100 M NaOH. The student then adds 13.0 mL of 0.100 M HCl. The pH of the resulting solution is 4.7. How is the value of pK_a for the unknown acid related to 4.7?

133. a. Using the K_{sp} value for Cu(OH)₂ (1.6×10^{-19}) and the overall formation constant for Cu(NH₃)₄²⁺ (1.0×10^{13}), calculate the value for the equilibrium constant for the following reaction:



b. Use the value of the equilibrium constant you calculated in part a to calculate the solubility (in mol/L) of Cu(OH)₂ in 5.0 M NH₃. In 5.0 M NH₃ the concentration of OH⁻ is 0.0095 M.

134. The solubility rules outlined in Chapter 4 say that Ba(OH)₂, Sr(OH)₂, and Ca(OH)₂ are marginally soluble hydroxides. Calculate the pH of a saturated solution of each of these marginally soluble hydroxides.

135. The K_{sp} of hydroxyapatite, Ca₅(PO₄)₃OH, is 6.8×10^{-37} . Calculate the solubility of hydroxyapatite in pure water in moles per liter. How is the solubility of hydroxyapatite affected by adding acid? When hydroxyapatite is treated with fluoride, the mineral fluorapatite, Ca₅(PO₄)₃F, forms. The K_{sp} of this substance is 1×10^{-60} . Calculate the solubility of fluorapatite in water. How do these calculations provide a rationale for the fluoridation of drinking water?

136. In the chapter discussion of precipitate formation, we ran the precipitation reaction to completion and then let some of the precipitate redissolve to get back to equilibrium. To see why, redo Sample Exercise 15.17, where

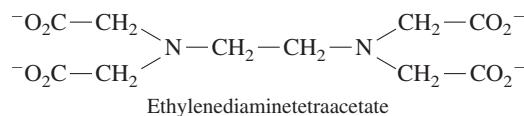
Initial Concentration (mol/L)	Equilibrium Concentration (mol/L)
$[\text{Mg}^{2+}]_0 = 3.75 \times 10^{-3}$	$[\text{Mg}^{2+}] = 3.75 \times 10^{-3} - y$
$[\text{F}^-]_0 = 6.25 \times 10^{-2}$	$[\text{F}^-] = 6.25 \times 10^{-2} - 2y$

$x \text{ mol/Mg}^{2+}$
 reacts to
 form MgF₂

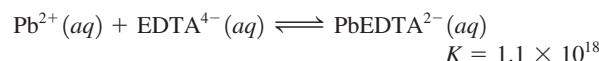
137. Calculate the concentration of Pb²⁺ in each of the following.

- a. a saturated solution of Pb(OH)₂, $K_{sp} = 1.2 \times 10^{-15}$
- b. a saturated solution of Pb(OH)₂ buffered at pH = 13.00

c. Ethylenediaminetetraacetate (EDTA⁴⁻) is used as a complexing agent in chemical analysis and has the following structure:



Solutions of EDTA⁴⁻ are used to treat heavy metal poisoning by removing the heavy metal in the form of a soluble complex ion. The complex ion virtually eliminates the heavy metal ions from reacting with biochemical systems. The reaction of EDTA⁴⁻ with Pb²⁺ is



Consider a solution with 0.010 mol Pb(NO₃)₂ added to 1.0 L of an aqueous solution buffered at pH = 13.00 and containing 0.050 M Na₄EDTA. Does Pb(OH)₂ precipitate from this solution?

Challenge Problems

138. Another way to treat data from a pH titration is to graph the absolute value of the change in pH per change in milliliters added versus milliliters added ($\Delta\text{pH}/\Delta\text{mL}$ versus mL added). Make this graph using your results from Exercise 57. What advantage might this method have over the traditional method for treating titration data?

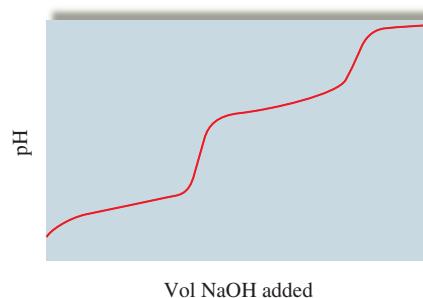
139. A buffer is made using 45.0 mL of 0.750 M HC₃H₅O₂ ($K_a = 1.3 \times 10^{-5}$) and 55.0 mL of 0.700 M NaC₃H₅O₂. What volume of 0.10 M NaOH must be added to change the pH of the original buffer solution by 2.5%?

140. A 0.400 M solution of ammonia was titrated with hydrochloric acid to the equivalence point, where the total volume was 1.50 times the original volume. At what pH does the equivalence point occur?

141. What volume of 0.0100 M NaOH must be added to 1.00 L of 0.0500 M HOCl to achieve a pH of 8.00?

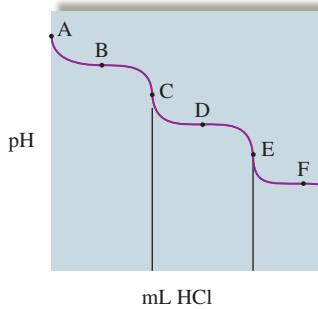
142. Consider a solution formed by mixing 50.0 mL of 0.100 M H₂SO₄, 30.0 mL of 0.100 M HOCl, 25.0 mL of 0.200 M NaOH, 25.0 mL of 0.100 M Ba(OH)₂, and 10.0 mL of 0.150 M KOH. Calculate the pH of this solution.

143. When a diprotic acid, H₂A, is titrated by NaOH, the protons on the diprotic acid are generally removed one at a time, resulting in a pH curve that has the following generic shape:



- a. Notice that the plot has essentially two titration curves. If the first equivalence point occurs at 100.0 mL of NaOH added, what volume of NaOH added corresponds to the second equivalence point?
- b. For the following volumes of NaOH added, list the major species present after the OH^- reacts completely.
- 0 mL NaOH added
 - between 0 and 100.0 mL NaOH added
 - 100.0 mL NaOH added
 - between 100.0 and 200.0 mL NaOH added
 - 200.0 mL NaOH added
 - after 200.0 mL NaOH added
- c. If the pH at 50.0 mL of NaOH added is 4.0 and the pH at 150.0 mL of NaOH added is 8.0, determine the values K_{a_1} and K_{a_2} for the diprotic acid.

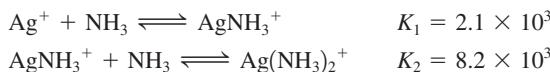
- 144.** The titration of Na_2CO_3 with HCl has the following qualitative profile:



- a. Identify the major species in solution as points A–F.
b. Calculate the pH at the halfway points to equivalence, B and D. Hint: Refer to Exercise 143.
- 145.** A few drops of each of the indicators shown in the accompanying table were placed in separate portions of a 1.0 M solution of a weak acid, HX . The results are shown in the last column of the table. What is the approximate pH of the solution containing HX ? Calculate the approximate value of K_{a} for HX .

Indicator	Color of HIn	Color of In^-	pK_{a} of HIn	HX
Bromphenol blue	Yellow	Blue	4.0	Blue
Bromcresol purple	Yellow	Purple	6.0	Yellow
Bromcresol green	Yellow	Blue	4.8	Green
Alizarin	Yellow	Red	6.5	Yellow

- 146.** Consider a solution made by mixing 500.0 mL of 4.0 M NH_3 and 500.0 mL of 0.40 M AgNO_3 . Ag^+ reacts with NH_3 to form AgNH_3^+ and $\text{Ag}(\text{NH}_3)_2^+$:



Determine the concentration of all species in solution.

- 147.** What is the maximum possible concentration of Ni^{2+} ion in water at 25°C that is saturated with 0.10 M H_2S and maintained at pH 3.0 with HCl?

- 148.** You add an excess of solid MX in 250 g of water. You measure the freezing point and find it to be -0.028°C . What is the K_{sp} of the solid? Assume the density of the solution is 1.0 g/cm³.

- 149.** a. Calculate the molar solubility of SrF_2 in water, ignoring the basic properties of F^- . (For SrF_2 , $K_{\text{sp}} = 7.9 \times 10^{-10}$.)
b. Would the measured molar solubility of SrF_2 be greater than or less than the value calculated in part a? Explain.
c. Calculate the molar solubility of SrF_2 in a solution buffered at pH = 2.00. (K_{a} for HF is 7.2×10^{-4} .)
150. A solution saturated with a salt of the type M_3X_2 has an osmotic pressure of 2.64×10^{-2} atm at 25°C. Calculate the K_{sp} value for the salt, assuming ideal behavior.

Integrative Problems

These problems require the integration of multiple concepts to find the solutions.

- 151.** A buffer solution is prepared by mixing 75.0 mL of 0.275 M fluorobenzoic acid ($\text{C}_7\text{H}_5\text{O}_2\text{F}$) with 55.0 mL of 0.472 M sodium fluorobenzoate. The pK_{a} of this weak acid is 2.90. What is the pH of the buffer solution?
152. The K_{sp} for Q, a slightly soluble ionic compound composed of M^{2+} and X^- ions, is 4.5×10^{-29} . The electron configuration of M^+ is $[\text{Xe}]6s^14f^145d^{10}$. The X^- anion has 54 electrons. What is the molar solubility of Q in a solution of NaX prepared by dissolving 1.98 g of NaX in 150. mL of water?
153. Calculate the pH of a solution prepared by mixing 250. mL of 0.174 M aqueous HF (density = 1.10 g/mL) with 38.7 g of an aqueous solution that is 1.50% NaOH by mass (density = 1.02 g/mL). (K_{a} for HF = 7.2×10^{-4} .)

Marathon Problem*

This problem is designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

- 154.** A 225-mg sample of a diprotic acid is dissolved in enough water to make 250. mL of solution. The pH of this solution is 2.06. A saturated solution of calcium hydroxide ($K_{\text{sp}} = 1.3 \times 10^{-6}$) is prepared by adding excess calcium hydroxide to pure water and then removing the undissolved solid by filtration. Enough of the calcium hydroxide solution is added to the solution of the acid to reach the second equivalence point. The pH at the second equivalence point (as determined by a pH meter) is 7.96. The first dissociation constant for the acid (K_{a_1}) is 5.90×10^{-2} . Assume that the volumes of the solutions are additive, all solutions are at 25°C, and that K_{a_1} is at least 1000 times greater than K_{a_2} .

- a. Calculate the molar mass of the acid.
b. Calculate the second dissociation constant for the acid (K_{a_2}).

 Get help understanding core concepts and visualizing molecular-level interactions, and practice problem solving, by visiting the Online Study Center at college.hmc.com/PIC/zumdash7e.

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16 Spontaneity, Entropy, and Free Energy

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Solid carbon dioxide (dry ice), when placed in water, causes violent bubbling as gaseous CO₂ is released. The “fog” is moisture condensed from the cold air.

T

The *first law of thermodynamics* is a statement of the law of conservation of energy: Energy can be neither created nor destroyed. In other words, *the energy of the universe is constant*. Although the total energy is constant, the various forms of energy can be interchanged in physical and chemical processes. For example, if you drop a book, some of the initial potential energy of the book is changed to kinetic energy, which is then transferred to the atoms in the air and the floor as random motion. The net effect of this process is to change a given quantity of potential energy to exactly the same quantity of thermal energy. Energy has been converted from one form to another, but the same quantity of energy exists before and after the process.

Now let's consider a chemical example. When methane is burned in excess oxygen, the major reaction is



This reaction produces a quantity of energy, which is released as heat. This energy flow results from the lowering of the potential energy stored in the bonds of CH_4 and O_2 as they react to form CO_2 and H_2O . This is illustrated in Fig. 16.1. Potential energy has been converted to thermal energy, but the energy content of the universe has remained constant in accordance with the first law of thermodynamics.

The first law of thermodynamics is used mainly for energy bookkeeping, that is, to answer such questions as

How much energy is involved in the change?

Does energy flow into or out of the system?

What form does the energy finally assume?

The first law of thermodynamics: The energy of the universe is constant.

Although the first law of thermodynamics provides the means for accounting for energy, it gives no hint as to why a particular process occurs in a given direction. This is the main question to be considered in this chapter.

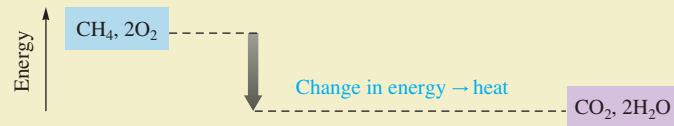
16.1 Spontaneous Processes and Entropy

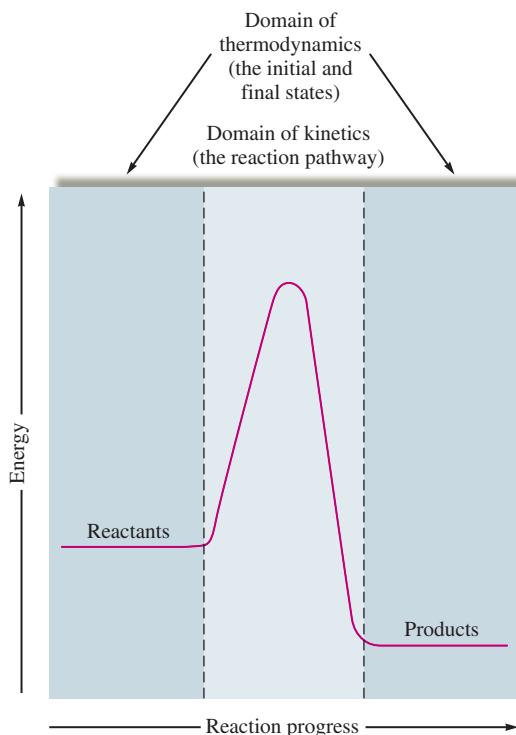
A process is said to be *spontaneous* if it occurs without outside intervention. **Spontaneous processes** may be fast or slow. As we will see in this chapter, thermodynamics can tell us the *direction* in which a process will occur but can say nothing about the *speed* of the process. As we saw in Chapter 12, the rate of a reaction depends on many factors, such as activation energy, temperature, concentration, and catalysts, and we were able to explain these effects using a simple collision model. In describing a chemical reaction, the discipline of chemical kinetics focuses on the pathway between reactants and products; thermodynamics considers only the initial and final states and does not require knowledge of the pathway between reactants and products (see Fig. 16.2).

Spontaneous does not mean fast.

FIGURE 16.1

When methane and oxygen react to form carbon dioxide and water, the products have lower potential energy than the reactants. This change in potential energy results in energy flow (heat) to the surroundings.



**FIGURE 16.2**

The rate of a reaction depends on the pathway from reactants to products; this is the domain of kinetics. Thermodynamics tells us whether a reaction is spontaneous based only on the properties of the reactants and products. The predictions of thermodynamics do not require knowledge of the pathway between reactants and products.

In summary, thermodynamics lets us predict whether a process will occur but gives no information about the amount of time required for the process. For example, according to the principles of thermodynamics, a diamond should change spontaneously to graphite. The fact that we do not observe this process does not mean the prediction is wrong; it simply means the process is very slow. Thus we need both thermodynamics and kinetics to describe reactions fully.

To explore the idea of spontaneity, consider the following physical and chemical processes:

A ball rolls down a hill but never spontaneously rolls back up the hill.

If exposed to air and moisture, steel rusts spontaneously. However, the iron oxide in rust does not spontaneously change back to iron metal and oxygen gas.

A gas fills its container uniformly. It never spontaneously collects at one end of the container.

Heat flow always occurs from a hot object to a cooler one. The reverse process never occurs spontaneously.

Wood burns spontaneously in an exothermic reaction to form carbon dioxide and water, but wood is not formed when carbon dioxide and water are heated together.

At temperatures below 0°C, water spontaneously freezes, and at temperatures above 0°C, ice spontaneously melts.

What thermodynamic principle will provide an explanation of why, under a given set of conditions, each of these diverse processes occurs in one direction and never in the reverse? In searching for an answer, we could explain the behavior of a ball on a hill in terms of gravity. But what does gravity have to do with the rusting of a nail or the freezing of water? Early developers of thermodynamics thought that exothermicity might be the key—that a process would be spontaneous if it were exothermic. Although this factor



Plant materials burn to form carbon dioxide and water.



A disordered pile of playing cards.

Probability refers to likelihood.



Visualization: Entropy

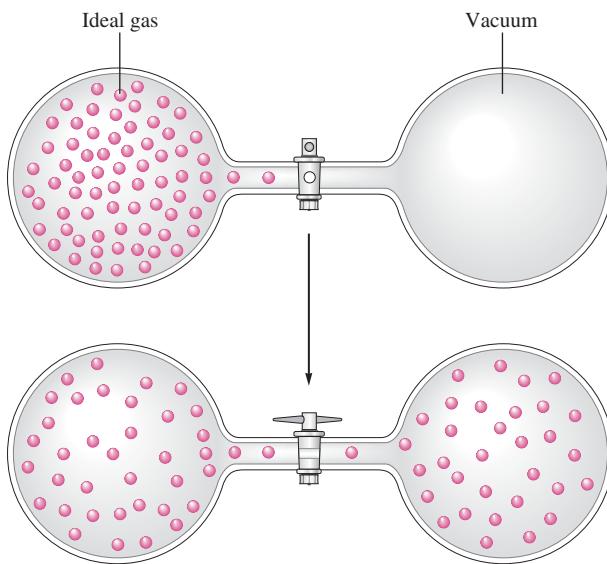
does appear to be important, since many spontaneous processes are exothermic, it is not the total answer. For example, the melting of ice, which occurs spontaneously at temperatures greater than 0°C , is an endothermic process.

What common characteristic causes the processes listed above to be spontaneous in one direction only? After many years of observation, scientists have concluded that the characteristic common to all spontaneous processes is an increase in a property called **entropy**, denoted by the symbol S . *The driving force for a spontaneous process is an increase in the entropy of the universe.*

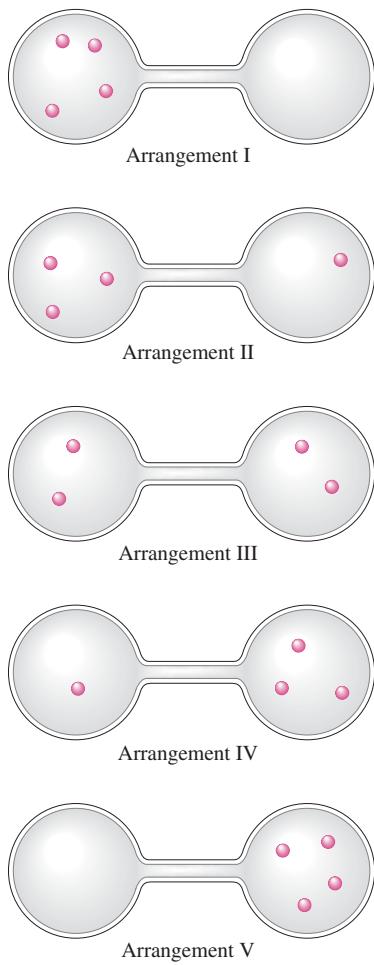
What is entropy? Although there is no simple definition that is completely accurate, *entropy can be viewed as a measure of molecular randomness or disorder*. The natural progression of things is from order to disorder, from lower entropy to higher entropy. To illustrate the natural tendency toward disorder, you only have to think about the condition of your room. Your room naturally tends to get messy (disordered), because an ordered room requires everything to be in its place. There are simply many more ways for things to be out of place than for them to be in their places.

As another example, suppose you have a deck of playing cards ordered in some particular way. You throw these cards into the air and pick them all up at random. Looking at the new sequence of the cards, you would be very surprised to find that it matched the original order. Such an event would be possible, but *very improbable*. There are billions of ways for the deck to be disordered, but only one way to be ordered according to your definition. Thus the chances of picking the cards up out of order are much greater than the chance of picking them up in order. It is natural for disorder to increase.

Entropy is a thermodynamic function that describes the *number of arrangements* (positions and/or energy levels) that are *available to a system* existing in a given state. Entropy is closely associated with probability. The key concept is that the more ways a particular state can be achieved, the greater is the likelihood (probability) of finding that state. In other words, *nature spontaneously proceeds toward the states that have the highest probabilities of existing*. This conclusion is not surprising at all. The difficulty comes in connecting this concept to real-life processes. For example, what does the spontaneous rusting of steel have to do with probability? Understanding the connection between entropy and spontaneity will allow us to answer such questions. We will begin to explore this connection by considering a very simple process, the expansion of an ideal gas into

**FIGURE 16.3**

The expansion of an ideal gas into an evacuated bulb.

**FIGURE 16.4**

Possible arrangements (states) of four molecules in a two-bulbed flask.

a vacuum, as represented in Fig. 16.3. Why is this process spontaneous? The driving force is probability. Because there are more ways of having the gas evenly spread throughout the container than there are ways for it to be in any other possible state, the gas spontaneously attains the uniform distribution.

To understand this conclusion, we will greatly simplify the system and consider the possible arrangements of only four gas molecules in the two-bulbed container (Fig. 16.4). How many ways can each arrangement (state) be achieved? Arrangements I and V can be achieved in only one way—all the molecules must be in one end. Arrangements II and V can be achieved in four ways, as shown in Table 16.1. Each configuration that gives a particular arrangement is called a *microstate*. Arrangement I has one microstate, and arrangement II has four microstates. Arrangement III can be achieved in six ways (six microstates), as shown in Table 16.1. *Which arrangement is most likely to occur?* The one that can be achieved in the greatest number of ways. Thus arrangement III is most probable. The relative probabilities of arrangements III, II, and I are 6 : 4 : 1. We have discovered an important principle: The probability of occurrence of a particular arrangement (state) depends on the number of ways (microstates) in which that arrangement can be achieved.

The consequences of this principle are dramatic for large numbers of molecules. One gas molecule in the flask in Fig. 16.4 has one chance in two of being in the left bulb. We say that the probability of finding the molecule in the left bulb is $\frac{1}{2}$. For two molecules in the flask, there is one chance in two of finding each molecule in the left bulb, so there is one chance in four ($\frac{1}{2} \times \frac{1}{2} = \frac{1}{4}$) that *both* molecules will be in the left bulb. As the number of molecules increases, the relative probability of finding all of them in the left bulb decreases, as shown in Table 16.2. For 1 mole of gas, the probability of finding all the molecules in the left bulb is so small that this arrangement would “never” occur.

Thus a gas placed in one end of a container will spontaneously expand to fill the entire vessel evenly because, for a large number of gas molecules, there is a huge number of microstates in which equal numbers of molecules are in both ends. On the other hand, the opposite process,

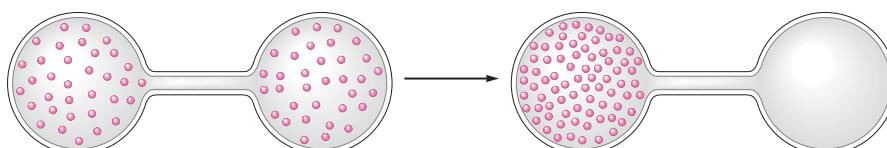
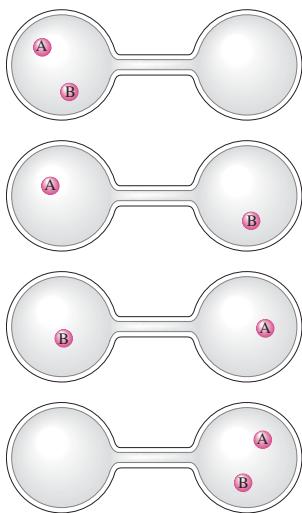


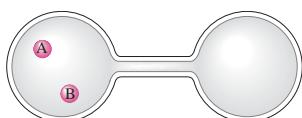
TABLE 16.1 The Microstates That Give a Particular Arrangement (State)

Arrangement	Microstates
I	
II	
III	
IV	
V	

For two molecules in the flask, there are four possible microstates:



Thus there is one chance in four of finding

**TABLE 16.2** Probability of Finding All the Molecules in the Left Bulb as a Function of the Total Number of Molecules

Number of Molecules	Relative Probability of Finding All Molecules in the Left Bulb
1	$\frac{1}{2}$
2	$\frac{1}{2} \times \frac{1}{2} = \frac{1}{2^2} = \frac{1}{4}$
3	$\frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} = \frac{1}{2^3} = \frac{1}{8}$
5	$\frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} = \frac{1}{2^5} = \frac{1}{32}$
10	$\frac{1}{2^{10}} = \frac{1}{1024}$
n	$\frac{1}{2^n} = \left(\frac{1}{2}\right)^n$
6×10^{23} (1 mole)	$\left(\frac{1}{2}\right)^{6 \times 10^{23}} \approx 10^{-(2 \times 10^{23})}$

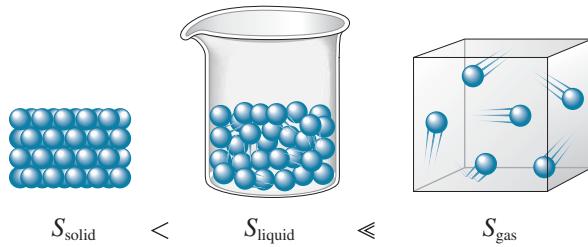
although not impossible, is *highly* improbable, since only one microstate leads to this arrangement. Therefore, this process does not occur spontaneously.

The type of probability we have been considering in this example is called **positional probability** because it depends on the number of configurations in space (positional microstates) that yield a particular state. A gas expands into a vacuum to give a uniform distribution because the expanded state has the highest positional probability, that is, the largest entropy, of the states available to the system.

Solid, liquid, and gaseous states were compared in Chapter 10.

Solids are more ordered than liquids or gases and thus have lower entropy.

Positional probability is also illustrated by changes of state. In general, positional entropy increases in going from solid to liquid to gas. A mole of a substance has a much smaller volume in the solid state than it does in the gaseous state. In the solid state, the molecules are close together, with relatively few positions available to them; in the gaseous state, the molecules are far apart, with many more positions available to them. The liquid state is closer to the solid state than it is to the gaseous state in these terms. We can summarize these comparisons as follows:



The tendency to mix is due to the increased volume available to the particles of each component of the mixture. For example, when two liquids are mixed, the molecules of each liquid have more available volume and thus more available positions.

Positional entropy is also very important in the formation of solutions. In Chapter 11 we saw that solution formation is favored by the natural tendency for substances to mix. We can now be more precise. The entropy change associated with the mixing of two pure substances is expected to be positive. An increase in entropy is expected because there are many more microstates for the mixed condition than for the separated condition. This effect is due principally to the increased volume available to a given “particle” after mixing occurs. For example, when two liquids are mixed to form a solution, the molecules of each liquid have more available volume and thus more available positions. Therefore, the increase in positional entropy associated with mixing favors the formation of solutions.

Sample Exercise 16.1

Positional Entropy

For each of the following pairs, choose the substance with the higher positional entropy (per mole) at a given temperature.

- a. Solid CO₂ and gaseous CO₂
- b. N₂ gas at 1 atm and N₂ gas at 1.0×10^{-2} atm

Solution

- a. Since a mole of gaseous CO₂ has the greater volume by far, the molecules have many more available positions than in a mole of solid CO₂. Thus gaseous CO₂ has the higher positional entropy.
- b. A mole of N₂ gas at 1×10^{-2} atm has a volume 100 times that (at a given temperature) of a mole of N₂ gas at 1 atm. Thus N₂ gas at 1×10^{-2} atm has the higher positional entropy.

See Exercise 16.23.

Sample Exercise 16.2**Predicting Entropy Changes**

Predict the sign of the entropy change for each of the following processes.

- Solid sugar is added to water to form a solution.
- Iodine vapor condenses on a cold surface to form crystals.

Solution

- The sugar molecules become randomly dispersed in the water when the solution forms and thus have access to a larger volume and a larger number of possible positions. The positional disorder is increased, and there will be an increase in entropy. ΔS is positive, since the final state has a larger entropy than the initial state, and $\Delta S = S_{\text{final}} - S_{\text{initial}}$.
- Gaseous iodine is forming a solid. This process involves a change from a relatively large volume to a much smaller volume, which results in lower positional disorder. For this process ΔS is negative (the entropy decreases).

See Exercise 16.24.

16.2 Entropy and the Second Law of Thermodynamics

The total energy of the universe is constant, but the entropy is increasing.

We have seen that processes are spontaneous when they result in an increase in disorder. Nature always moves toward the most probable state available to it. We can state this principle in terms of entropy: *In any spontaneous process there is always an increase in the entropy of the universe.* This is the **second law of thermodynamics**. Contrast this with the first law of thermodynamics, which tells us that the energy of the universe is constant. Energy is conserved in the universe, but entropy is not. In fact, the second law can be paraphrased as follows: *The entropy of the universe is increasing.*

As in Chapter 6, we find it convenient to divide the universe into a system and the surroundings. Thus we can represent the change in the entropy of the universe as

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

where ΔS_{sys} and ΔS_{surr} represent the changes in entropy that occur in the system and surroundings, respectively.

To predict whether a given process will be spontaneous, we must know the sign of ΔS_{univ} . If ΔS_{univ} is positive, the entropy of the universe increases, and the process is spontaneous in the direction written. If ΔS_{univ} is negative, the process is spontaneous in the *opposite* direction. If ΔS_{univ} is zero, the process has no tendency to occur, and the system is at equilibrium. To predict whether a process is spontaneous, we must consider the entropy changes that occur both in the system and in the surroundings and then take their sum.

Sample Exercise 16.3**The Second Law**

In a living cell, large molecules are assembled from simple ones. Is this process consistent with the second law of thermodynamics?

Solution

To reconcile the operation of an order-producing cell with the second law of thermodynamics, we must remember that ΔS_{univ} , not ΔS_{sys} , must be positive for a process to be spontaneous. A process for which ΔS_{sys} is negative can be spontaneous if the associated ΔS_{surr} is both larger and positive. The operation of a cell is such a process.

See Questions 16.7 and 16.8.



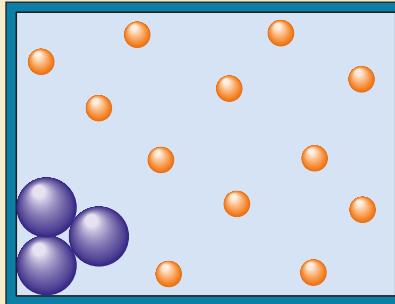
CHEMICAL IMPACT

Entropy: An Organizing Force?

In this text we have emphasized the meaning of the second law of thermodynamics—that the entropy of the universe is always increasing. Although the results of all our experiments support this conclusion, this does not mean that order cannot appear spontaneously in a given part of the universe. The best example of this phenomenon involves the assembly of cells in living organisms. Of course, when a process that creates an ordered system is examined in detail, it is found that other parts of the process involve an increase in disorder such that the sum of all the entropy changes is positive. In fact, scientists are now finding that the search for maximum entropy in one part of a system can be a powerful force for organization in another part of the system.

To understand how entropy can be an organizing force, look at the accompanying figure. In a system containing large and small “balls” as shown in the figure, the small balls can “herd” the large balls into clumps in the corners and near the walls. This clears out the maximum space for the small balls so that they can move more freely, thus maximizing the entropy of the system, as demanded by the second law of thermodynamics.

In essence, the ability to maximize entropy by sorting different-sized objects creates a kind of attractive force, called a *depletion*, or *excluded-volume*, *force*. These “entropic forces” operate for objects in the size range of approximately 10^{-8} to approximately 10^{-6} m. For entropy-induced ordering to occur, the particles must be constantly jostling each other and must be constantly agitated by solvent molecules, thus making gravity unimportant.



There is increasing evidence that entropic ordering is important in many biological systems. For example, this phenomenon seems to be responsible for the clumping of sickle-cell hemoglobin in the presence of much smaller proteins that act as the “smaller balls.” Entropic forces also have been linked to the clustering of DNA in cells without nuclei, and Allen Minton of the National Institutes of Health in Bethesda, Maryland, is studying the role of entropic forces in the binding of proteins to cell membranes.

Entropic ordering also appears in nonbiological settings, especially in the ways polymer molecules clump together. For example, polymers added to paint to improve the flow characteristics of the paint actually caused it to coagulate because of depletion forces.

Thus, as you probably have concluded already, entropy is a complex issue. As entropy drives the universe to its ultimate death of maximum chaos, it provides some order along the way.

16.3 The Effect of Temperature on Spontaneity

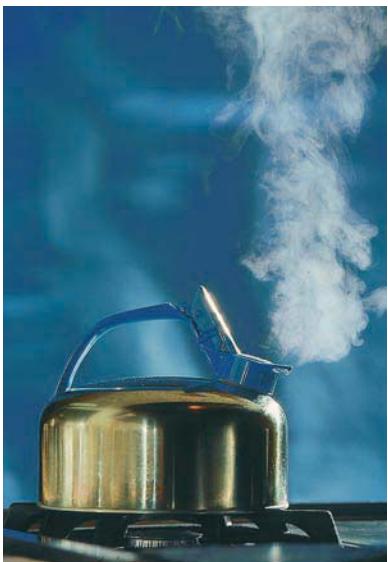
To explore the interplay of ΔS_{sys} and ΔS_{surr} in determining the sign of ΔS_{univ} , we will first discuss the change of state for one mole of water from liquid to gas,



considering the water to be the system and everything else the surroundings.

What happens to the entropy of water in this process? A mole of liquid water (18 grams) has a volume of approximately 18 mL. A mole of gaseous water at 1 atmosphere and 100°C occupies a volume of approximately 31 liters. Clearly, there are many more positions available to the water molecules in a volume of 31 L than in 18 mL, and the vaporization of water is favored by this increase in positional probability. That is, for this process the entropy of the system increases; ΔS_{sys} has a positive sign.

What about the entropy change in the surroundings? Although we will not prove it here, entropy changes in the surroundings are determined primarily by the flow of energy



Boiling water to form steam increases its volume and thus its entropy.

In an endothermic process, heat flows from the surroundings into the system. In an exothermic process, heat flows into the surroundings from the system.

In a process occurring at constant temperature, the tendency for the system to lower its energy results from the positive value of ΔS_{surr} .

into or out of the system as heat. To understand this, suppose an exothermic process transfers 50 J of energy as heat to the surroundings, where it becomes thermal energy, that is, kinetic energy associated with the random motions of atoms. Thus this flow of energy into the surroundings increases the random motions of atoms there and thereby increases the entropy of the surroundings. The sign of ΔS_{surr} is positive. When an endothermic process occurs in the system, it produces the opposite effect. Heat flows from the surroundings to the system, and the random motions of the atoms in the surroundings decrease, decreasing the entropy of the surroundings. The vaporization of water is an endothermic process. Thus, for this change of state, ΔS_{surr} is negative.

Remember it is the sign of ΔS_{univ} that tells us whether the vaporization of water is spontaneous. We have seen that ΔS_{sys} is positive and favors the process and that ΔS_{surr} is negative and unfavorable. Thus the components of ΔS_{univ} are in opposition. Which one controls the situation? The answer *depends on the temperature*. We know that at a pressure of 1 atmosphere, water changes spontaneously from liquid to gas at all temperatures above 100°C. Below 100°C, the opposite process (condensation) is spontaneous.

Since ΔS_{sys} and ΔS_{surr} are in opposition for the vaporization of water, the temperature must have an effect on the relative importance of these two terms. To understand why this is so, we must discuss in more detail the factors that control the entropy changes in the surroundings. The central idea is that *the entropy changes in the surroundings are primarily determined by heat flow*. An exothermic process in the system increases the entropy of the surroundings, because the resulting energy flow increases the random motions in the surroundings. This means that exothermicity is an important driving force for spontaneity. In earlier chapters we have seen that a system tends to undergo changes that lower its energy. We now understand the reason for this tendency. When a system at constant temperature moves to a lower energy, the energy it gives up is transferred to the surroundings, leading to an increase in entropy there.

The significance of exothermicity as a driving force *depends on the temperature at which the process occurs*. That is, the magnitude of ΔS_{surr} depends on the temperature at which the heat is transferred. We will not attempt to prove this fact here. Instead, we offer an analogy. Suppose that you have \$50 to give away. Giving it to a millionaire would not create much of an impression—a millionaire has money to spare. However, to a poor college student, \$50 would represent a significant sum and would be received with considerable joy. The same principle can be applied to energy transfer via the flow of heat. If 50 J of energy is transferred to the surroundings, the impact of that event depends greatly on the temperature. If the temperature of the surroundings is very high, the atoms there are in rapid motion. The 50 J of energy will not make a large percent change in these motions. On the other hand, if 50 J of energy is transferred to the surroundings at a very low temperature, where atomic motion is slow, the energy will cause a large percent change in these motions. *The impact of the transfer of a given quantity of energy as heat to or from the surroundings will be greater at lower temperatures.*

For our purposes, there are two important characteristics of the entropy changes that occur in the surroundings:

1. *The sign of ΔS_{surr} depends on the direction of the heat flow.* At constant temperature, an exothermic process in the system causes heat to flow into the surroundings, increasing the random motions and thus the entropy of the surroundings. For this case, ΔS_{surr} is positive. The opposite is true for an endothermic process in a system at constant temperature. Note that although the driving force described here really results from the change in entropy, it is often described in terms of energy: Nature tends to seek the lowest possible energy.
2. *The magnitude of ΔS_{surr} depends on the temperature.* The transfer of a given quantity of energy as heat produces a much greater percent change in the randomness of the surroundings at a low temperature than it does at a high temperature. Thus ΔS_{surr} depends directly on the quantity of heat transferred and inversely on temperature. In

other words, the tendency for the system to lower its energy becomes a more important driving force at lower temperatures.

$$\frac{\text{Driving force}}{\text{provided by the energy flow (heat)}} = \frac{\text{magnitude of the entropy change of the surroundings}}{\text{temperature (K)}}$$

$$= \frac{\text{quantity of heat (J)}}{\text{temperature (K)}}$$

These ideas are summarized as follows:

Exothermic process:
 $\Delta S_{\text{surr}} = \text{positive}$

Endothermic process:
 $\Delta S_{\text{surr}} = \text{negative}$

$$\text{Exothermic process: } \Delta S_{\text{surr}} = + \frac{\text{quantity of heat (J)}}{\text{temperature (K)}}$$

$$\text{Endothermic process: } \Delta S_{\text{surr}} = - \frac{\text{quantity of heat (J)}}{\text{temperature (K)}}$$

We can express ΔS_{surr} in terms of the change in enthalpy ΔH for a process occurring at constant pressure, since

$$\text{Heat flow (constant } P) = \text{change in enthalpy} = \Delta H$$

When no subscript is present, the quantity (for example, ΔH) refers to the system.

Recall that ΔH consists of two parts: a sign and a number. The *sign* indicates the direction of flow, where a plus sign means into the system (endothermic) and a minus sign means out of the system (exothermic). The *number* indicates the quantity of energy.

Combining all these concepts produces the following definition of ΔS_{surr} for a reaction that takes place under conditions of constant temperature (in kelvins) and pressure:

$$\Delta S_{\text{surr}} = - \frac{\Delta H}{T}$$

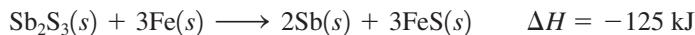
The minus sign changes the point of view from the system to the surroundings.

The minus sign is necessary because the sign of ΔH is determined with respect to the reaction system, and this equation expresses a property of the surroundings. This means that if the reaction is exothermic, ΔH has a negative sign, but since heat flows into the surroundings, ΔS_{surr} is positive.

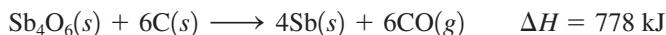
Sample Exercise 16.4

Determining ΔS_{surr}

In the metallurgy of antimony, the pure metal is recovered via different reactions, depending on the composition of the ore. For example, iron is used to reduce antimony in sulfide ores:



Carbon is used as the reducing agent for oxide ores:



Calculate ΔS_{surr} for each of these reactions at 25°C and 1 atm.

Solution

We use

$$\Delta S_{\text{surr}} = - \frac{\Delta H}{T}$$

where

$$T = 25 + 273 = 298 \text{ K}$$

For the sulfide ore reaction,

$$\Delta S_{\text{surr}} = - \frac{-125 \text{ kJ}}{298 \text{ K}} = 0.419 \text{ kJ/K} = 419 \text{ J/K}$$



The mineral stibnite contains Sb_2S_3 .

TABLE 16.3 Interplay of ΔS_{sys} and ΔS_{surr} in Determining the Sign of ΔS_{univ}

Signs of Entropy Changes			
ΔS_{sys}	ΔS_{surr}	ΔS_{univ}	<i>Process Spontaneous?</i>
+	+	+	Yes
-	-	-	No (reaction will occur in opposite direction)
+	-	?	Yes, if ΔS_{sys} has a larger magnitude than ΔS_{surr}
-	+	?	Yes, if ΔS_{surr} has a larger magnitude than ΔS_{sys}

Note that ΔS_{surr} is positive, as it should be, since this reaction is exothermic and heat flow occurs to the surroundings, increasing the randomness of the surroundings.

For the oxide ore reaction,

$$\Delta S_{\text{surr}} = -\frac{778 \text{ kJ}}{298} = -2.61 \text{ kJ/K} = -2.61 \times 10^3 \text{ J/K}$$

In this case ΔS_{surr} is negative because heat flow occurs from the surroundings to the system.

See Exercises 16.25 and 16.26.

We have seen that the spontaneity of a process is determined by the entropy change it produces in the universe. We also have seen that ΔS_{univ} has two components, ΔS_{sys} and ΔS_{surr} . If for some process both ΔS_{sys} and ΔS_{surr} are positive, then ΔS_{univ} is positive, and the process is spontaneous. If, on the other hand, both ΔS_{sys} and ΔS_{surr} are negative, the process does not occur in the direction indicated but is spontaneous in the opposite direction. Finally, if ΔS_{sys} and ΔS_{surr} have opposite signs, the spontaneity of the process depends on the sizes of the opposing terms. These cases are summarized in Table 16.3.

We can now understand why spontaneity is often dependent on temperature and thus why water spontaneously freezes below 0°C and melts above 0°C . The term ΔS_{surr} is temperature-dependent. Since

$$\Delta S_{\text{surr}} = -\frac{\Delta H}{T}$$

at constant pressure, the value of ΔS_{surr} changes markedly with temperature. The magnitude of ΔS_{surr} will be very small at high temperatures and will increase as the temperature decreases. That is, exothermicity is most important as a driving force at low temperatures.

16.4 Free Energy

So far we have used ΔS_{univ} to predict the spontaneity of a process. However, another thermodynamic function is also related to spontaneity and is especially useful in dealing with the temperature dependence of spontaneity. This function is called the **free energy**, which is symbolized by G and defined by the relationship

$$G = H - TS$$

where H is the enthalpy, T is the Kelvin temperature, and S is the entropy.

The symbol G for free energy honors Josiah Willard Gibbs (1839–1903), who was professor of mathematical physics at Yale University from 1871 to 1903. He laid the foundations of many areas of thermodynamics, particularly as they apply to chemistry.


Visualization: Spontaneous Reactions

For a process that occurs at constant temperature, the change in free energy (ΔG) is given by the equation

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

Note that all quantities here refer to the system. From this point on we will follow the usual convention that when no subscript is included, the quantity refers to the system.

To see how this equation relates to spontaneity, we divide both sides of the equation by $-T$ to produce

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

Remember that at constant temperature and pressure

$$\Delta S_{\text{surr}} = -\frac{\Delta H}{T}$$

So we can write

$$-\frac{\Delta G}{T} = -\frac{\Delta H}{T} + \Delta S = \Delta S_{\text{surr}} + \Delta S = \Delta S_{\text{univ}}$$

We have shown that

$$\Delta S_{\text{univ}} = -\frac{\Delta G}{T} \quad \text{at constant } T \text{ and } P$$

This result is very important. It means that a process carried out at constant temperature and pressure will be spontaneous only if ΔG is negative. That is, *a process (at constant T and P) is spontaneous in the direction in which the free energy decreases* ($-\Delta G$ means $+\Delta S_{\text{univ}}$).

Now we have two functions that can be used to predict spontaneity: the entropy of the universe, which applies to all processes, and free energy, which can be used for processes carried out at constant temperature and pressure. Since so many chemical reactions occur under the latter conditions, free energy is the more useful to chemists.

Let's use the free energy equation to predict the spontaneity of the melting of ice:



for which $\Delta H^\circ = 6.03 \times 10^3 \text{ J/mol}$ and $\Delta S^\circ = 22.1 \text{ J/K} \cdot \text{mol}$

Results of the calculations of ΔS_{univ} and ΔG° at -10°C , 0°C , and 10°C are shown in Table 16.4. These data predict that the process is spontaneous at 10°C ; that is, ice melts at this temperature because ΔS_{univ} is positive and ΔG° is negative. The opposite is true at -10°C , where water freezes spontaneously.

Why is this so? The answer lies in the fact that ΔS_{sys} (ΔS°) and ΔS_{surr} oppose each other. The term ΔS° favors the melting of ice because of the increase in positional entropy, and ΔS_{surr} favors the freezing of water because it is an exothermic process. At temperatures below

The superscript degree symbol ($^\circ$) indicates all substances are in their standard states.

To review the definitions of standard states, see page 246.

TABLE 16.4 Results of the Calculation of ΔS_{univ} and ΔG° for the Process $\text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(l)$ at -10°C , 0°C , and 10°C^*

T ($^\circ\text{C}$)	T (K)	ΔH° (J/mol)	ΔS° (J/K \cdot mol)	$\Delta S_{\text{surr}} = -\frac{\Delta H^\circ}{T}$ (J/K \cdot mol)	$\Delta S_{\text{univ}} = \Delta S^\circ + \Delta S_{\text{surr}}$ (J/K \cdot mol)	$T\Delta S^\circ$ (J/mol)	$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ (J/mol)
-10	263	6.03×10^3	22.1	-22.9	-0.8	5.81×10^3	$+2.2 \times 10^2$
0	273	6.03×10^3	22.1	-22.1	0	6.03×10^3	0
10	283	6.03×10^3	22.1	-21.3	+0.8	6.25×10^3	-2.2×10^2

*Note that at 10°C , ΔS° (ΔS_{sys}) controls, and the process occurs even though it is endothermic. At -10°C , the magnitude of ΔS_{surr} is larger than that of ΔS° , so the process is spontaneous in the opposite (exothermic) direction.

0°C, the change of state occurs in the exothermic direction because ΔS_{surr} is larger in magnitude than ΔS_{sys} . But above 0°C the change occurs in the direction in which ΔS_{sys} is favorable, since in this case ΔS_{sys} is larger in magnitude than ΔS_{surr} . At 0°C the *opposing tendencies just balance*, and the two states coexist; there is no driving force in either direction. An equilibrium exists between the two states of water. Note that ΔS_{univ} is equal to 0 at 0°C.

We can reach the same conclusions by examining ΔG° . At -10°, ΔG° is positive because the ΔH° term is larger than the $T\Delta S^\circ$ term. The opposite is true at 10°C. At 0°C, ΔH° is equal to $T\Delta S^\circ$ and ΔG° is equal to 0. This means that solid H₂O and liquid H₂O have the same free energy at 0°C ($\Delta G^\circ = G_{\text{liquid}} - G_{\text{solid}}$), and the system is at equilibrium.

We can understand the temperature dependence of spontaneity by examining the behavior of ΔG . For a process occurring at constant temperature and pressure,

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

If ΔH and ΔS favor opposite processes, spontaneity will depend on temperature in such a way that the exothermic direction will be favored at low temperatures. For example, for the process



ΔH is positive and ΔS is positive. The natural tendency for this system to lower its energy is in opposition to its natural tendency to increase its positional randomness. At low temperatures, ΔH dominates, and at high temperatures, ΔS dominates. The various possible cases are summarized in Table 16.5.

Sample Exercise 16.5

Free Energy and Spontaneity

At what temperatures is the following process spontaneous at 1 atm?



$$\Delta H^\circ = 31.0 \text{ kJ/mol} \quad \text{and} \quad \Delta S^\circ = 93.0 \text{ J/K} \cdot \text{mol}$$

What is the normal boiling point of liquid Br₂?

Solution

The vaporization process will be spontaneous at all temperatures where ΔG° is negative. Note that ΔS° favors the vaporization process because of the increase in positional entropy, and ΔH° favors the *opposite* process, which is exothermic. These opposite tendencies will exactly balance at the boiling point of liquid Br₂, since at this temperature liquid and gaseous Br₂ are in equilibrium ($\Delta G^\circ = 0$). We can find this temperature by setting $\Delta G^\circ = 0$ in the equation

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

$$0 = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta H^\circ = T\Delta S^\circ$$

TABLE 16.5 Various Possible Combinations of ΔH and ΔS for a Process and the Resulting Dependence of Spontaneity on Temperature

Case	Result
ΔS positive, ΔH negative	Spontaneous at all temperatures
ΔS positive, ΔH positive	Spontaneous at high temperatures (where exothermicity is relatively unimportant)
ΔS negative, ΔH negative	Spontaneous at low temperatures (where exothermicity is dominant)
ΔS negative, ΔH positive	Process not spontaneous at <i>any</i> temperature (reverse process is spontaneous at <i>all</i> temperatures)

Note that although ΔH and ΔS are somewhat temperature-dependent, it is a good approximation to assume they are constant over a relatively small temperature range.

Then

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{3.10 \times 10^4 \text{ J/mol}}{93.0 \text{ J/K} \cdot \text{mol}} = 333 \text{ K}$$

At temperatures above 333 K, $T\Delta S^\circ$ has a larger magnitude than ΔH° , and ΔG° (or $\Delta H^\circ - T\Delta S^\circ$) is negative. Above 333 K, the vaporization process is spontaneous; the opposite process occurs spontaneously below this temperature. At 333 K, liquid and gaseous Br_2 coexist in equilibrium. These observations can be summarized as follows (the pressure is 1 atm in each case):

1. $T > 333 \text{ K}$. The term ΔS° controls. The increase in entropy when liquid Br_2 is vaporized is dominant.
2. $T < 333 \text{ K}$. The process is spontaneous in the direction in which it is exothermic. The term ΔH° controls.
3. $T = 333 \text{ K}$. The opposing driving forces are just balanced ($\Delta G^\circ = 0$), and the liquid and gaseous phases of bromine coexist. This is the normal boiling point.

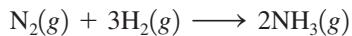
See Exercises 16.29 through 16.31.

16.5 Entropy Changes in Chemical Reactions

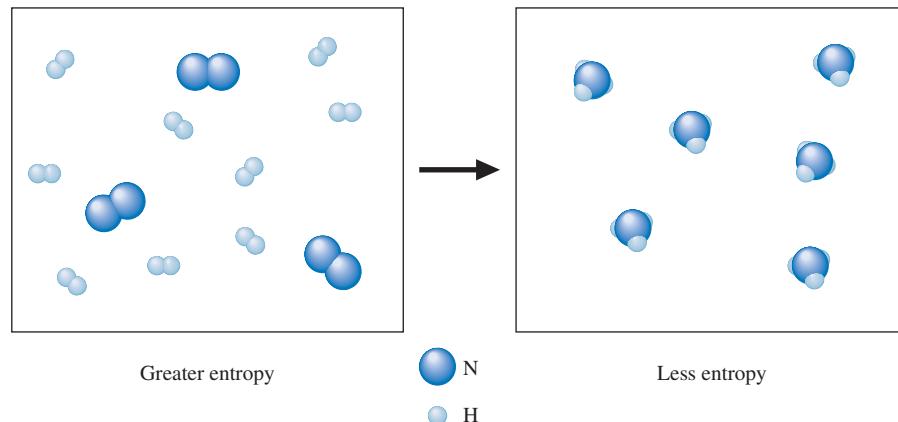
The second law of thermodynamics tells us that a process will be spontaneous if the entropy of the universe increases when the process occurs. We saw in Section 16.4 that for a process at constant temperature and pressure, we can use the change in free energy of the system to predict the sign of ΔS_{univ} and thus the direction in which it is spontaneous. So far we have applied these ideas only to physical processes, such as changes of state and the formation of solutions. However, the main business of chemistry is studying chemical reactions, and, therefore, we want to apply the second law to reactions.

First, we will consider the entropy changes accompanying chemical reactions that occur under conditions of constant temperature and pressure. As for the other types of processes we have considered, the entropy changes in the *surroundings* are determined by the heat flow that occurs as the reaction takes place. However, the entropy changes in the *system* (the reactants and products of the reaction) are determined by positional probability.

For example, in the ammonia synthesis reaction



four reactant molecules become two product molecules, lowering the number of independent units in the system, which leads to less positional disorder.



Fewer molecules mean fewer possible configurations. To help clarify this idea, consider a special container with a million compartments, each large enough to hold a hydrogen molecule. Thus there are a million ways one H₂ molecule can be placed in this container. But suppose we break the H—H bond and place the two independent H atoms in the same container. A little thought will convince you that there are *many* more than a million ways to place the two separate atoms. The number of arrangements possible for the two independent atoms is much greater than the number for the molecule. Thus for the process



positional entropy increases.

Does positional entropy increase or decrease when the following reaction takes place?



In this case 9 gaseous molecules are changed to 10 gaseous molecules, and the positional entropy increases. There are more independent units as products than as reactants. In general, when a reaction involves gaseous molecules, *the change in positional entropy is dominated by the relative numbers of molecules of gaseous reactants and products*. If the number of molecules of the gaseous products is greater than the number of molecules of the gaseous reactants, positional entropy typically increases, and ΔS will be positive for the reaction.

Sample Exercise 16.6

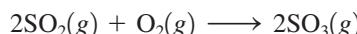
Predicting the Sign of ΔS°

Predict the sign of ΔS° for each of the following reactions.

- a. The thermal decomposition of solid calcium carbonate:



- b. The oxidation of SO₂ in air:



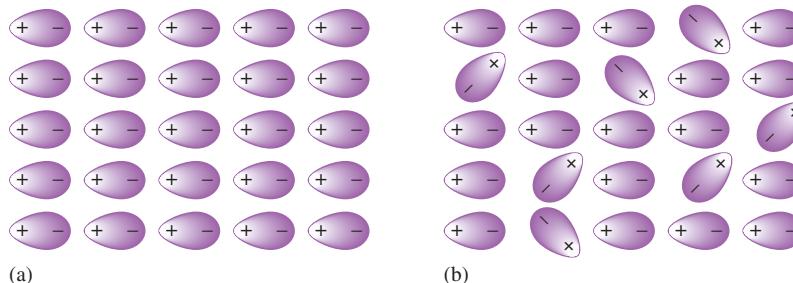
Solution

- a. Since in this reaction a gas is produced from a solid reactant, the positional entropy increases, and ΔS° is positive.
 b. Here three molecules of gaseous reactants become two molecules of gaseous products. Since the number of gas molecules decreases, positional entropy decreases, and ΔS° is negative.

See Exercises 16.33 and 16.34.

In thermodynamics it is the *change* in a certain function that is usually important. The change in enthalpy determines if a reaction is exothermic or endothermic at constant pressure. The change in free energy determines if a process is spontaneous at constant temperature and pressure. It is fortunate that changes in thermodynamic functions are sufficient for most purposes, since absolute values for many thermodynamic characteristics of a system, such as enthalpy or free energy, cannot be determined.

However, we can assign absolute entropy values. Consider a solid at 0 K, where molecular motion virtually ceases. If the substance is a perfect crystal, its internal arrangement is absolutely regular (see Fig. 16.5(a)). There is only *one way* to achieve this perfect order: Every particle must be in its place. For example, with N coins there is only one

**FIGURE 16.5**

- (a) A perfect crystal of hydrogen chloride at 0 K; the dipolar HCl molecules are represented by . The entropy is zero ($S = 0$) for this perfect crystal at 0 K.
 (b) As the temperature rises above 0 K, lattice vibrations allow some dipoles to change their orientations, producing some disorder and an increase in entropy ($S > 0$).

A perfect crystal at 0 K is an unattainable ideal, taken as a standard but never actually observed.

The standard entropy values represent the increase in entropy that occurs when a substance is heated from 0 K to 298 K at 1 atm pressure.

way to achieve the state of all heads. Thus a perfect crystal represents the lowest possible entropy; that is, *the entropy of a perfect crystal at 0 K is zero*. This is a statement of the **third law of thermodynamics**.

As the temperature of a perfect crystal is increased, the random vibrational motions increase, and disorder increases within the crystal [see Fig. 16.5(b)]. Thus the entropy of a substance increases with temperature. Since S is zero for a perfect crystal at 0 K, the entropy value for a substance at a particular temperature can be calculated by knowing the temperature dependence of entropy. (We will not show such calculations here.)

The *standard entropy values S°* of many common substances at 298 K and 1 atm are listed in Appendix 4. From these values you will see that the entropy of a substance does indeed increase in going from solid to liquid to gas. One especially interesting feature of this table is the very low S° value for diamond. The structure of diamond is highly ordered, with each carbon strongly bound to a tetrahedral arrangement of four other carbon atoms (see Section 10.5, Fig. 10.22). This type of structure allows very little disorder and has a very low entropy, even at 298 K. Graphite has a slightly higher entropy because its layered structure allows for a little more disorder.

Because *entropy is a state function of the system* (it is not pathway-dependent), the entropy change for a given chemical reaction can be calculated by taking the difference between the standard entropy values of products and those of the reactants:

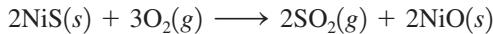
$$\Delta S_{\text{reaction}}^\circ = \sum n_p S_{\text{products}}^\circ - \sum n_r S_{\text{reactants}}^\circ$$

where, as usual, Σ represents the sum of the terms. It is important to note that entropy is an extensive property (it depends on the amount of substance present). This means that the number of moles of a given reactant (n_r) or product (n_p) must be taken into account.

Sample Exercise 16.7

Calculating ΔS°

Calculate ΔS° at 25°C for the reaction



given the following standard entropy values:

Substance	S° (J/K · mol)
$\text{SO}_2(g)$	248
$\text{NiO}(s)$	38
$\text{O}_2(g)$	205
$\text{NiS}(s)$	53

Solution

$$\begin{aligned}
 \text{Since } \Delta S^\circ &= \sum n_p S^\circ_{\text{products}} - \sum n_r S^\circ_{\text{reactants}} \\
 &= 2S^\circ_{\text{SO}_2(g)} + 2S^\circ_{\text{NiO}(s)} - 2S^\circ_{\text{NiS}(s)} - 3S^\circ_{\text{O}_2(s)} \\
 &= 2 \text{ mol} \left(248 \frac{\text{J}}{\text{K} \cdot \text{mol}} \right) + 2 \text{ mol} \left(38 \frac{\text{J}}{\text{K} \cdot \text{mol}} \right) \\
 &\quad - 2 \text{ mol} \left(53 \frac{\text{J}}{\text{K} \cdot \text{mol}} \right) - 3 \text{ mol} \left(205 \frac{\text{J}}{\text{K} \cdot \text{mol}} \right) \\
 &= 496 \text{ J/K} + 76 \text{ J/K} - 106 \text{ J/K} - 615 \text{ J/K} \\
 &= -149 \text{ J/K}
 \end{aligned}$$

We would expect ΔS° to be negative because the number of gaseous molecules decreases in this reaction.

See Exercise 16.37.

Sample Exercise 16.8**Calculating ΔS°**

Calculate ΔS° for the reduction of aluminum oxide by hydrogen gas:



Use the following standard entropy values:

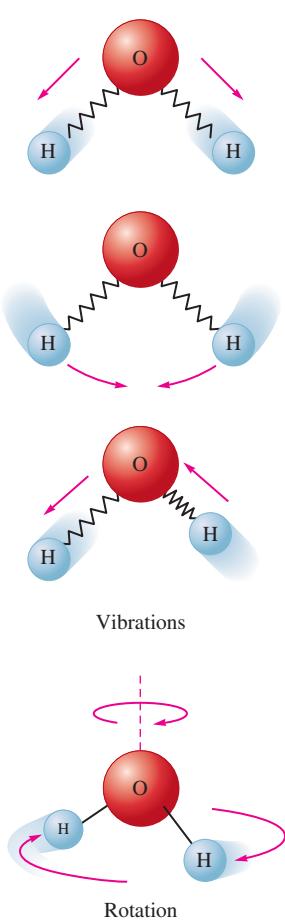
Substance	$S^\circ \text{ (J/K} \cdot \text{mol)}$
$\text{Al}_2\text{O}_3(s)$	51
$\text{H}_2(g)$	131
$\text{Al}(s)$	28
$\text{H}_2\text{O}(g)$	189

Solution

$$\begin{aligned}
 \Delta S^\circ &= \sum n_p S^\circ_{\text{products}} - \sum n_r S^\circ_{\text{reactants}} \\
 &= 2S^\circ_{\text{Al}(s)} + 3S^\circ_{\text{H}_2\text{O}(g)} - 3S^\circ_{\text{H}_2(g)} - S^\circ_{\text{Al}_2\text{O}_3(s)} \\
 &= 2 \text{ mol} \left(28 \frac{\text{J}}{\text{K} \cdot \text{mol}} \right) + 3 \text{ mol} \left(189 \frac{\text{J}}{\text{K} \cdot \text{mol}} \right) \\
 &\quad - 3 \text{ mol} \left(131 \frac{\text{J}}{\text{K} \cdot \text{mol}} \right) - 1 \text{ mol} \left(51 \frac{\text{J}}{\text{K} \cdot \text{mol}} \right) \\
 &= 56 \text{ J/K} + 567 \text{ J/K} - 393 \text{ J/K} - 51 \text{ J/K} \\
 &= 179 \text{ J/K}
 \end{aligned}$$

See Exercises 16.38 through 16.40.

The reaction considered in Sample Exercise 16.8 involves 3 moles of hydrogen gas on the reactant side and 3 moles of water vapor on the product side. Would you expect ΔS to be large or small for such a case? We have assumed that ΔS depends on the relative numbers of molecules of gaseous reactants and products. Based on this assumption, ΔS should be near zero for this reaction. However, ΔS is large and

**FIGURE 16.6**

The H_2O molecule can vibrate and rotate in several ways, some of which are shown here. This freedom of motion leads to a higher entropy for water than for a substance like hydrogen, a simple diatomic molecule with fewer possible motions.

The value of ΔG° tells us nothing about the rate of a reaction, only its eventual equilibrium position.

positive. Why is this so? The large value for ΔS results from the difference in the entropy values for hydrogen gas and water vapor. The reason for this difference can be traced to the difference in molecular structure. Because it is a nonlinear, triatomic molecule, H_2O has more rotational and vibrational motions (see Fig. 16.6) than does the diatomic H_2 molecule. Thus the standard entropy value for $\text{H}_2\text{O}(g)$ is greater than that for $\text{H}_2(g)$. Generally, *the more complex the molecule, the higher the standard entropy value*.

16.6 Free Energy and Chemical Reactions

For chemical reactions we are often interested in the **standard free energy change** (ΔG°), *the change in free energy that will occur if the reactants in their standard states are converted to the products in their standard states*. For example, for the ammonia synthesis reaction at 25°C ,



This ΔG° value represents the change in free energy when 1 mol nitrogen gas at 1 atm reacts with 3 mol hydrogen gas at 1 atm to produce 2 mol gaseous NH_3 at 1 atm.

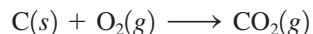
It is important to recognize that the standard free energy change for a reaction is not measured directly. For example, we can measure heat flow in a calorimeter to determine ΔH° , but we cannot measure ΔG° this way. The value of ΔG° for the ammonia synthesis in Equation (16.1) was *not* obtained by mixing 1 mol N_2 and 3 mol H_2 in a flask and measuring the change in free energy as 2 mol NH_3 formed. For one thing, if we mixed 1 mol N_2 and 3 mol H_2 in a flask, the system would go to equilibrium rather than to completion. Also, we have no instrument that measures free energy. However, while we cannot directly measure ΔG° for a reaction, we can calculate it from other measured quantities, as we will see later in this section.

Why is it useful to know ΔG° for a reaction? As we will see in more detail later in this chapter, knowing the ΔG° values for several reactions allows us to compare the relative tendency of these reactions to occur. The more negative the value of ΔG° , the further a reaction will go to the right to reach equilibrium. We must use standard-state free energies to make this comparison because free energy varies with pressure or concentration. Thus, to get an accurate comparison of reaction tendencies, we must compare all reactions under the same pressure or concentration conditions. We will have more to say about the significance of ΔG° later.

There are several ways to calculate ΔG° . One common method uses the equation

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

which applies to a reaction carried out at constant temperature. For example, for the reaction

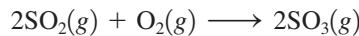


the values of ΔH° and ΔS° are known to be -393.5 kJ and 3.05 J/K , respectively, and ΔG° can be calculated at 298 K as follows:

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -3.935 \times 10^5 \text{ J} - (298 \text{ K})(3.05 \text{ J/K}) \\ &= -3.944 \times 10^5 \text{ J} \\ &= -394.4 \text{ kJ} \text{ (per mole of CO}_2\text{)}\end{aligned}$$

Sample Exercise 16.9**Calculating ΔH° , ΔS° , and ΔG°**

Consider the reaction



carried out at 25°C and 1 atm. Calculate ΔH° , ΔS° , and ΔG° using the following data:

Substance	ΔH_f° (kJ/mol)	S° (J/K · mol)
$\text{SO}_2(g)$	-297	248
$\text{SO}_3(g)$	-396	257
$\text{O}_2(g)$	0	205

Solution

The value of ΔH° can be calculated from the enthalpies of formation using the equation we discussed in Section 6.4:

$$\Delta H^\circ = \sum n_p \Delta H_f^\circ_{\text{(products)}} - \sum n_r \Delta H_f^\circ_{\text{(reactants)}}$$

$$\begin{aligned} \text{Then } \Delta H^\circ &= 2\Delta H_f^\circ_{(\text{SO}_3(g))} - 2\Delta H_f^\circ_{(\text{SO}_2(g))} - \Delta H_f^\circ_{(\text{O}_2(g))} \\ &= 2 \text{ mol}(-396 \text{ kJ/mol}) - 2 \text{ mol}(-297 \text{ kJ/mol}) - 0 \\ &= -792 \text{ kJ} + 594 \text{ kJ} \\ &= -198 \text{ kJ} \end{aligned}$$

The value of ΔS° can be calculated using the standard entropy values and the equation discussed in Section 16.5:

$$\Delta S^\circ = \sum n_p S^\circ_{\text{products}} - \sum n_r S^\circ_{\text{reactants}}$$

Thus

$$\begin{aligned} \Delta S^\circ &= 2S^\circ_{\text{SO}_3(g)} - 2S^\circ_{\text{SO}_2(g)} - S^\circ_{\text{O}_2(g)} \\ &= 2 \text{ mol}(257 \text{ J/K} \cdot \text{mol}) - 2 \text{ mol}(248 \text{ J/K} \cdot \text{mol}) - 1 \text{ mol}(205 \text{ J/K} \cdot \text{mol}) \\ &= 514 \text{ J/K} - 496 \text{ J/K} - 205 \text{ J/K} \\ &= -187 \text{ J/K} \end{aligned}$$

We would expect ΔS° to be negative because three molecules of gaseous reactants give two molecules of gaseous products.

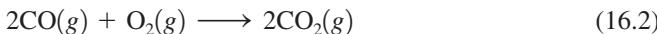
The value of ΔG° can now be calculated from the equation

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -198 \text{ kJ} - (298 \text{ K})\left(-187 \frac{\text{J}}{\text{K}}\right)\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right) \\ &= -198 \text{ kJ} + 55.7 \text{ kJ} = -142 \text{ kJ} \end{aligned}$$

See Exercises 16.45 through 16.47.

A second method for calculating ΔG for a reaction takes advantage of the fact that, like enthalpy, *free energy is a state function*. Therefore, we can use procedures for finding ΔG that are similar to those for finding ΔH using Hess's law.

To illustrate this method for calculating the free energy change, we will obtain ΔG° for the reaction

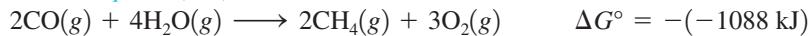


from the following data:

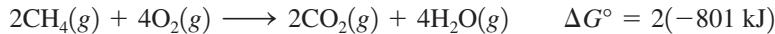


Note that $\text{CO}(g)$ is a reactant in Equation (16.2). This means that Equation (16.3) must be reversed, since $\text{CO}(g)$ is a product in that reaction as written. When a reaction is reversed, the sign of ΔG° is also reversed. In Equation (16.4), $\text{CO}_2(g)$ is a product, as it is in Equation (16.2), but only one molecule of CO_2 is formed. Thus Equation (16.4) must be multiplied by 2, which means the ΔG° value for Equation (16.4) also must be multiplied by 2. Free energy is an extensive property, since it is defined by two extensive properties, H and S .

Reversed Equation (16.3)



2 × Equation (16.4)



This example shows that the ΔG values for reactions are manipulated in exactly the same way as the ΔH values.

Sample Exercise 16.10

Calculating ΔG°

Using the following data (at 25°C)

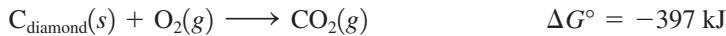


calculate ΔG° for the reaction

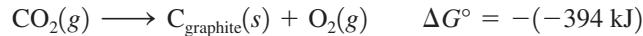


Solution

We reverse Equation (16.6) to make graphite a product, as required, and then add the new equation to Equation (16.5):

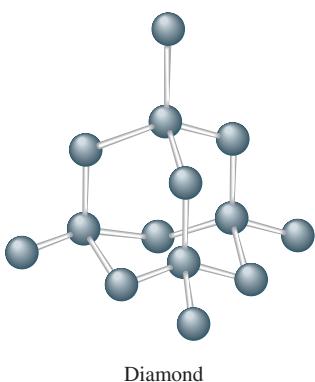
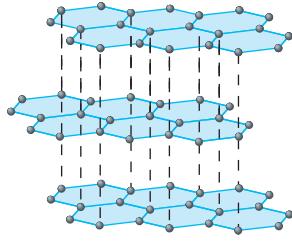


Reversed Equation (16.6)



Since ΔG° is negative for this process, diamond should spontaneously change to graphite at 25°C and 1 atm. However, the reaction is so slow under these conditions that we do not observe the process. This is another example of kinetic rather than thermodynamic control of a reaction. We can say that diamond is kinetically stable with respect to graphite even though it is thermodynamically unstable.

See Exercises 16.51 and 16.52.



In Sample Exercise 16.10 we saw that the process



is spontaneous but very slow at 25°C and 1 atm. The reverse process can be made to occur at high temperatures and pressures. Diamond has a more compact structure and thus a higher density than graphite, so exerting very high pressure causes it to become thermodynamically favored. If high temperatures are also used to make the process fast enough to be feasible, diamonds can be made from graphite. The conditions typically used involve temperatures greater than 1000°C and pressures of about 10⁵ atm. About half of all industrial diamonds are made this way.

A third method for calculating the free energy change for a reaction uses standard free energies of formation. The **standard free energy of formation** (ΔG_f°) of a substance is defined as the *change in free energy that accompanies the formation of 1 mole of that substance from its constituent elements with all reactants and products in their standard states*. For the formation of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$), the appropriate reaction is



The standard free energy associated with this process is called the *free energy of formation of glucose*. Values of the standard free energy of formation are useful in calculating ΔG° for specific chemical reactions using the equation

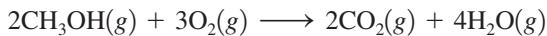
$$\Delta G^\circ = \sum n_p \Delta G_f^\circ_{\text{(products)}} - \sum n_r \Delta G_f^\circ_{\text{(reactants)}}$$

Values of ΔG_f° for many common substances are listed in Appendix 4. Note that, analogous to the enthalpy of formation, *the standard free energy of formation of an element in its standard state is zero*. Also note that the number of moles of each reactant (n_r) and product (n_p) must be used when calculating ΔG° for a reaction.

Sample Exercise 16.11

Calculating ΔG°

Methanol is a high-octane fuel used in high-performance racing engines. Calculate ΔG° for the reaction



given the following free energies of formation:

Substance	ΔG_f° (kJ/mol)
$\text{CH}_3\text{OH}(g)$	-163
$\text{O}_2(g)$	0
$\text{CO}_2(g)$	-394
$\text{H}_2\text{O}(g)$	-229

Solution

We use the equation

$$\begin{aligned} \Delta G^\circ &= \sum n_p \Delta G_f^\circ_{\text{(products)}} - \sum n_r \Delta G_f^\circ_{\text{(reactants)}} \\ &= 2\Delta G_f^\circ_{\text{(CO}_2\text{(g))}} + 4\Delta G_f^\circ_{\text{(H}_2\text{O(g))}} - 3\Delta G_f^\circ_{\text{(O}_2\text{(g))}} - 2\Delta G_f^\circ_{\text{(CH}_3\text{OH(g))}} \\ &= 2 \text{ mol}(-394 \text{ kJ/mol}) + 4 \text{ mol}(-229 \text{ kJ/mol}) - 3(0) \\ &\quad - 2 \text{ mol}(-163 \text{ kJ/mol}) \\ &= -1378 \text{ kJ} \end{aligned}$$

The standard state of an element is its most stable state of 25°C and 1 atm.

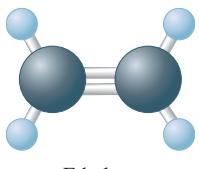
Calculating ΔG° is very similar to calculating ΔH° , as shown in Section 6.4.

The large magnitude and the negative sign of ΔG° indicate that this reaction is very favorable thermodynamically.

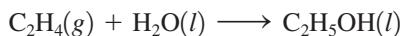
See Exercises 16.53 through 16.55.

Sample Exercise 16.12

Free Energy and Spontaneity



A chemical engineer wants to determine the feasibility of making ethanol (C_2H_5OH) by reacting water with ethylene (C_2H_4) according to the equation



Is this reaction spontaneous under standard conditions?

Solution

To determine the spontaneity of this reaction under standard conditions, we must determine ΔG° for the reaction. We can do this using standard free energies of formation at 25°C from Appendix 4:

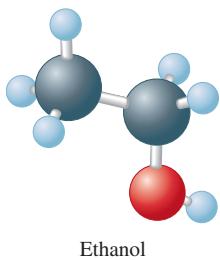
$$\Delta G_f^\circ(C_2H_5OH(l)) = -175 \text{ kJ/mol}$$

$$\Delta G_f^\circ(H_2O(l)) = -237 \text{ kJ/mol}$$

$$\Delta G_f^\circ(C_2H_4(g)) = 68 \text{ kJ/mol}$$

Then

$$\begin{aligned} \Delta G^\circ &= \Delta G_f^\circ(C_2H_5OH(l)) - \Delta G_f^\circ(H_2O(l)) - \Delta G_f^\circ(C_2H_4(g)) \\ &= -175 \text{ kJ} - (-237 \text{ kJ}) - 68 \text{ kJ} \\ &= -6 \text{ kJ} \end{aligned}$$



Thus the process is spontaneous under standard conditions at 25°C.

See Exercise 16.56.

Although the reaction considered in Sample Exercise 16.12 is spontaneous, other features of the reaction must be studied to see if the process is feasible. For example, the chemical engineer will need to study the kinetics of the reaction to determine whether it is fast enough to be useful and, if it is not, whether a catalyst can be found to enhance the rate. In doing these studies, the engineer must remember that ΔG° depends on temperature:

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

Thus, if the process must be carried out at high temperatures to be fast enough to be feasible, ΔG° must be recalculated at that temperature from the ΔH° and ΔS° values for the reaction.

16.7 The Dependence of Free Energy on Pressure

In this chapter we have seen that a system at constant temperature and pressure will proceed spontaneously in the direction that lowers its free energy. This is why reactions proceed until they reach equilibrium. As we will see later in this section, *the equilibrium position represents the lowest free energy value available to a particular reaction system*. The free energy of a reaction system changes as the reaction proceeds, because free energy is dependent on the pressure of a gas or on the concentration of species in solution. We will deal only with the pressure dependence of the free energy of an ideal gas. The dependence of free energy on concentration can be developed using similar reasoning.

To understand the pressure dependence of free energy, we need to know how pressure affects the thermodynamic functions that comprise free energy, that is, enthalpy and entropy (recall that $G = H - TS$). For an ideal gas, enthalpy is not pressure-dependent. However, entropy *does* depend on pressure because of its dependence on volume. Consider 1 mole of an ideal gas at a given temperature. At a volume of 10.0 L, the gas has many more positions available for its molecules than if its volume is 1.0 L. The positional entropy is greater in the larger volume. In summary, at a given temperature for 1 mole of ideal gas

$$S_{\text{large volume}} > S_{\text{small volume}}$$

or, since pressure and volume are inversely related,

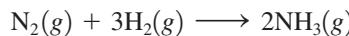
$$S_{\text{low pressure}} > S_{\text{high pressure}}$$

We have shown qualitatively that the entropy and therefore the free energy of an ideal gas depend on its pressure. Using a more detailed argument, which we will not consider here, it can be shown that

$$G = G^\circ + RT \ln(P)$$

where G° is the free energy of the gas at a pressure of 1 atm, G is the free energy of the gas at a pressure of P atm, R is the universal gas constant, and T is the Kelvin temperature.

To see how the change in free energy for a reaction depends on pressure, we will consider the ammonia synthesis reaction



In general,

$$\Delta G = \sum n_p G_{\text{products}} - \sum n_r G_{\text{reactants}}$$

For this reaction

$$\Delta G = 2G_{\text{NH}_3} - G_{\text{N}_2} - 3G_{\text{H}_2}$$

where

$$G_{\text{NH}_3} = G_{\text{NH}_3}^\circ + RT \ln(P_{\text{NH}_3})$$

$$G_{\text{N}_2} = G_{\text{N}_2}^\circ + RT \ln(P_{\text{N}_2})$$

$$G_{\text{H}_2} = G_{\text{H}_2}^\circ + RT \ln(P_{\text{H}_2})$$

Substituting these values into the equation gives

$$\begin{aligned}\Delta G &= 2[G_{\text{NH}_3}^\circ + RT \ln(P_{\text{NH}_3})] - [G_{\text{N}_2}^\circ + RT \ln(P_{\text{N}_2})] - 3[G_{\text{H}_2}^\circ + RT \ln(P_{\text{H}_2})] \\ &= 2G_{\text{NH}_3}^\circ - G_{\text{N}_2}^\circ - 3G_{\text{H}_2}^\circ + 2RT \ln(P_{\text{NH}_3}) - RT \ln(P_{\text{N}_2}) - 3RT \ln(P_{\text{H}_2}) \\ &= \underbrace{(2G_{\text{NH}_3}^\circ - G_{\text{N}_2}^\circ - 3G_{\text{H}_2}^\circ)}_{\Delta G^\circ \text{ reaction}} + RT[2 \ln(P_{\text{NH}_3}) - \ln(P_{\text{N}_2}) - 3 \ln(P_{\text{H}_2})]\end{aligned}$$

The first term (in parentheses) is ΔG° for the reaction. Thus we have

$$\Delta G = \Delta G_{\text{reaction}}^\circ + RT[2 \ln(P_{\text{NH}_3}) - \ln(P_{\text{N}_2}) - 3 \ln(P_{\text{H}_2})]$$

and since

$$2 \ln(P_{\text{NH}_3}) = \ln(P_{\text{NH}_3}^2)$$

$$-\ln(P_{\text{N}_2}) = \ln\left(\frac{1}{P_{\text{N}_2}}\right)$$

$$-3 \ln(P_{\text{H}_2}) = \ln\left(\frac{1}{P_{\text{H}_2}^3}\right)$$

the equation becomes

$$\Delta G = \Delta G^\circ + RT \ln\left(\frac{P_{\text{NH}_3}^2}{(P_{\text{N}_2})(P_{\text{H}_2}^3)}\right)$$

But the term

$$\frac{P_{\text{NH}_3}^2}{(P_{\text{N}_2})(P_{\text{H}_2}^3)}$$

is the reaction quotient Q discussed in Section 13.5. Therefore, we have

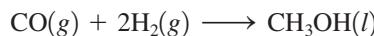
$$\Delta G = \Delta G^\circ + RT \ln(Q)$$

where Q is the reaction quotient (from the law of mass action), T is the temperature (K), R is the gas law constant and is equal to $8.3145 \text{ J/K} \cdot \text{mol}$, ΔG° is the free energy change for the reaction with all reactants and products at a pressure of 1 atm, and ΔG is the free energy change for the reaction for the specified pressures of reactants and products.

Sample Exercise 16.13

Calculating ΔG°

One method for synthesizing methanol (CH_3OH) involves reacting carbon monoxide and hydrogen gases:



Calculate ΔG at 25°C for this reaction where carbon monoxide gas at 5.0 atm and hydrogen gas at 3.0 atm are converted to liquid methanol.

Solution

To calculate ΔG for this process, we use the equation

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

We must first compute ΔG° from standard free energies of formation (see Appendix 4). Since

$$\Delta G_f^\circ(\text{CH}_3\text{OH}(l)) = -166 \text{ kJ}$$

$$\Delta G_f^\circ(\text{H}_2(g)) = 0$$

$$\Delta G_f^\circ(\text{CO}(g)) = -137 \text{ kJ}$$

$$\Delta G^\circ = -166 \text{ kJ} - (-137 \text{ kJ}) - 0 = -29 \text{ kJ} = -2.9 \times 10^4 \text{ J}$$

Note that this is the value of ΔG° for the reaction of 1 mol CO with 2 mol H_2 to produce 1 mol CH_3OH . We might call this the value of ΔG° for one “round” of the reaction or for one mole of the reaction. Thus the ΔG° value might better be written as $-2.9 \times 10^4 \text{ J/mol}$ of reaction, or $-2.9 \times 10^4 \text{ J/mol rxn}$.

We can now calculate ΔG using

$$\Delta G^\circ = -2.9 \times 10^4 \text{ J/mol rxn}$$

$$R = 8.3145 \text{ J/K} \cdot \text{mol}$$

$$T = 273 + 25 = 298 \text{ K}$$

$$Q = \frac{1}{(P_{\text{CO}})(P_{\text{H}_2}^2)} = \frac{1}{(5.0)(3.0)^2} = 2.2 \times 10^{-2}$$

Note that the pure liquid methanol is not included in the calculation of Q . Then

$$\begin{aligned} \Delta G &= \Delta G^\circ + RT \ln(Q) \\ &= (-2.9 \times 10^4 \text{ J/mol rxn}) + (8.3145 \text{ J/K} \cdot \text{mol rxn})(298 \text{ K}) \ln(2.2 \times 10^{-2}) \\ &= (-2.9 \times 10^4 \text{ J/mol rxn}) - (9.4 \times 10^3 \text{ J/mol rxn}) = -3.8 \times 10^4 \text{ J/mol rxn} \\ &= -38 \text{ kJ/mol rxn} \end{aligned}$$

Note that ΔG is significantly more negative than ΔG° , implying that the reaction is more spontaneous at reactant pressures greater than 1 atm. We might expect this result from Le Châtelier's principle.

See Exercises 16.57 and 16.58.

The Meaning of ΔG for a Chemical Reaction

In this section we have learned to calculate ΔG for chemical reactions under various conditions. For example, in Sample Exercise 16.13 the calculations show that the formation of $\text{CH}_3\text{OH}(l)$ from $\text{CO}(g)$ at 5.0 atm reacting with $\text{H}_2(g)$ at 3.0 atm is spontaneous. What does this result mean? Does it mean that if we mixed 1.0 mol $\text{CO}(g)$ and 2.0 mol $\text{H}_2(g)$ together at pressures of 5.0 and 3.0 atm, respectively, that 1.0 mol $\text{CH}_3\text{OH}(l)$ would form in the reaction flask? The answer is no. This answer may surprise you in view of what has been said in this section. It is true that 1.0 mol $\text{CH}_3\text{OH}(l)$ has a lower free energy than 1.0 mol $\text{CO}(g)$ at 5.0 atm plus 2.0 mol $\text{H}_2(g)$ at 3.0 atm. However, when $\text{CO}(g)$ and $\text{H}_2(g)$ are mixed under these conditions, there is *an even lower free energy available to this system than 1.0 mol pure $\text{CH}_3\text{OH}(l)$.* For reasons we will discuss shortly, *the system can achieve the lowest possible free energy by going to equilibrium, not by going to completion.* At the equilibrium position, some of the $\text{CO}(g)$ and $\text{H}_2(g)$ will remain in the reaction flask. So even though 1.0 mol pure $\text{CH}_3\text{OH}(l)$ is at a lower free energy than 1.0 mol $\text{CO}(g)$ and 2.0 mol $\text{H}_2(g)$ at 5.0 and 3.0 atm, respectively, the reaction system will stop short of forming 1.0 mol $\text{CH}_3\text{OH}(l)$. The reaction stops short of completion because the equilibrium mixture of $\text{CH}_3\text{OH}(l)$, $\text{CO}(g)$, and $\text{H}_2(g)$ exists at the lowest possible free energy available to the system.

To illustrate this point, we will explore a mechanical example. Consider balls rolling down the two hills shown in Fig. 16.7. Note that in both cases point *B* has a lower potential energy than point *A*.

In Fig. 16.7(a) the ball will roll to point *B*. This diagram is analogous to a phase change. For example, at 25°C ice will spontaneously change completely to liquid water, because the latter has the lowest free energy. In this case liquid water is the only choice. There is no intermediate mixture of ice and water with lower free energy.

The situation is different for a chemical reaction system, as illustrated in Fig. 16.7(b). In Fig. 16.7(b) the ball will not get to point *B* because there is a lower potential energy at point *C*. Like the ball, a chemical system will seek the *lowest possible* free energy, which, for reasons we will discuss below, is the equilibrium position.

Therefore, although the value of ΔG for a given reaction system tells us whether the products or reactants are favored under a given set of conditions, it does not mean that the system will proceed to pure products (if ΔG is negative) or remain at pure reactants (if ΔG is positive). Instead, the system will spontaneously go to the equilibrium position,

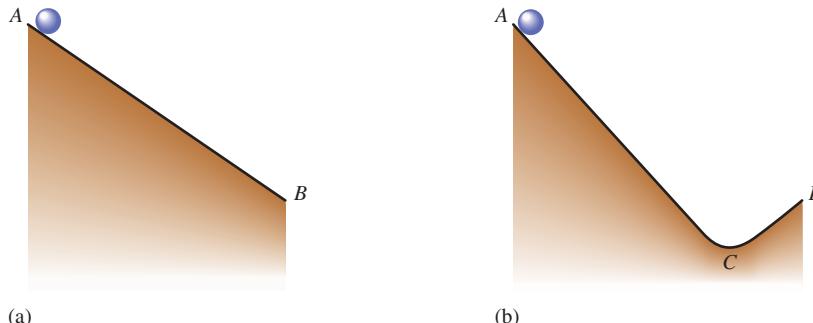


FIGURE 16.7

Schematic representations of balls rolling down two types of hills.

the lowest possible free energy available to it. In the next section we will see that the value of ΔG° for a particular reaction tells us exactly where this position will be.

16.8 Free Energy and Equilibrium

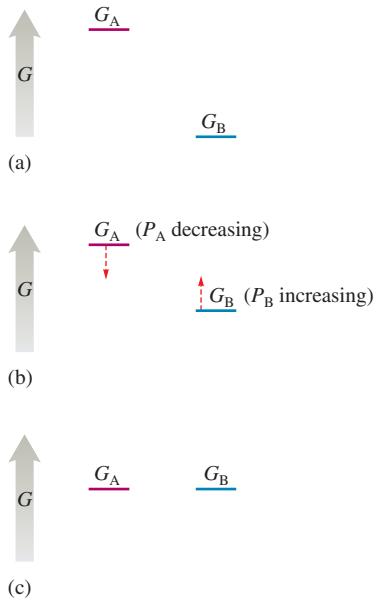


FIGURE 16.8

- (a) The initial free energies of A and B.
- (b) As $A(g)$ changes to $B(g)$, the free energy of A decreases and that of B increases.
- (c) Eventually, pressures of A and B are achieved such that $G_A = G_B$, the equilibrium position.

When the components of a given chemical reaction are mixed, they will proceed, rapidly or slowly depending on the kinetics of the process, to the equilibrium position. In Chapter 13 we defined the equilibrium position as the point at which the forward and reverse reaction rates are equal. In this chapter we look at equilibrium from a thermodynamic point of view, and we find that the **equilibrium point** occurs at the lowest value of free energy available to the reaction system. As it turns out, the two definitions give the same equilibrium state, which must be the case for both the kinetic and thermodynamic models to be valid.

To understand the relationship of free energy to equilibrium, let's consider the following simple hypothetical reaction:



where 1.0 mole of gaseous A is initially placed in a reaction vessel at a pressure of 2.0 atm. The free energies for A and B are diagramed as shown in Fig. 16.8(a). As A reacts to form B, the total free energy of the system changes, yielding the following results:

$$\text{Free energy of } A = G_A = G_A^\circ + RT \ln(P_A)$$

$$\text{Free energy of } B = G_B = G_B^\circ + RT \ln(P_B)$$

$$\text{Total free energy of system} = G = G_A + G_B$$

As A changes to B, G_A will decrease because P_A is decreasing [Fig. 16.8(b)]. In contrast, G_B will increase because P_B is increasing. The reaction will proceed to the right as long as the total free energy of the system decreases (as long as G_B is less than G_A). At some point the pressures of A and B reach the values P_A^e and P_B^e that make G_A equal to G_B . *The system has reached equilibrium* [Fig. 16.8(c)]. Since A at pressure P_A^e and B at pressure P_B^e have the same free energy (G_A equals G_B), ΔG is zero for A at pressure P_A^e changing to B at pressure P_B^e . *The system has reached minimum free energy*. There is no longer any driving force to change A to B or B to A, so the system remains at this position (the pressures of A and B remain constant).

Suppose that for the experiment described above the plot of free energy versus the mole fraction of A reacted is defined as shown in Fig. 16.9(a). In this experiment, minimum free energy is reached when 75% of A has been changed to B. At this point, the pressure of A is 0.25 times the original pressure, or

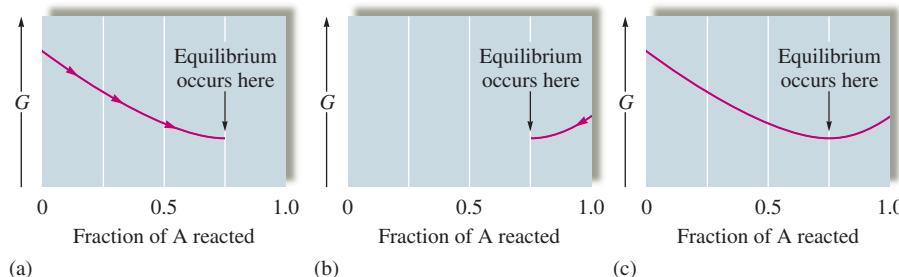
$$(0.25)(2.0 \text{ atm}) = 0.50 \text{ atm}$$

The pressure of B is

$$(0.75)(2.0 \text{ atm}) = 1.5 \text{ atm}$$

FIGURE 16.9

- (a) The change in free energy to reach equilibrium, beginning with 1.0 mol $A(g)$ at $P_A = 2.0 \text{ atm}$.
- (b) The change in free energy to reach equilibrium, beginning with 1.0 mol $B(g)$ at $P_B = 2.0 \text{ atm}$.
- (c) The free energy profile for $A(g) \rightleftharpoons B(g)$ in a system containing 1.0 mol (A plus B) at $P_{\text{TOTAL}} = 2.0 \text{ atm}$. Each point on the curve corresponds to the total free energy of the system for a given combination of A and B.



Since this is the equilibrium position, we can use the equilibrium pressures to calculate a value for K for the reaction in which A is converted to B at this temperature:

$$K = \frac{P_B^e}{P_A^e} = \frac{1.5 \text{ atm}}{0.50 \text{ atm}} = 3.0$$

For the reaction $A(g) \rightleftharpoons B(g)$, the pressure is constant during the reaction, since the same number of gas molecules is always present.

Exactly the same equilibrium point would be achieved if we placed 1.0 mol pure B(g) in the flask at a pressure of 2.0 atm. In this case B would change to A until equilibrium ($G_B = G_A$) is reached. This is shown in Fig. 16.9(b).

The overall free energy curve for this system is shown in Fig. 16.9(c). Note that any mixture of A(g) and B(g) containing 1.0 mol (A plus B) at a total pressure of 2.0 atm will react until it reaches the minimum in the curve.

In summary, when substances undergo a chemical reaction, the reaction proceeds to the minimum free energy (equilibrium), which corresponds to the point where

$$G_{\text{products}} = G_{\text{reactants}} \quad \text{or} \quad \Delta G = G_{\text{products}} - G_{\text{reactants}} = 0$$

We can now establish a quantitative relationship between free energy and the value of the equilibrium constant. We have seen that

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

and at equilibrium ΔG equals 0 and Q equals K .

$$\text{So} \quad \Delta G = 0 = \Delta G^\circ + RT \ln(K)$$

$$\text{or} \quad \Delta G^\circ = -RT \ln(K)$$

We must note the following characteristics of this very important equation.

Case 1: $\Delta G^\circ = 0$. When ΔG° equals zero for a particular reaction, the free energies of the reactants and products are equal when all components are in the standard states (1 atm for gases). The system is at equilibrium when the pressures of all reactants and products are 1 atm, which means that K equals 1.

Case 2: $\Delta G^\circ < 0$. In this case ΔG° ($G_{\text{products}}^\circ - G_{\text{reactants}}^\circ$) is negative, which means that

$$G_{\text{products}}^\circ < G_{\text{reactants}}^\circ$$

If a flask contains the reactants and products, all at 1 atm, the system will *not* be at equilibrium. Since $G_{\text{products}}^\circ$ is less than $G_{\text{reactants}}^\circ$, the system will adjust to the right to reach equilibrium. In this case K will be *greater than 1*, since the pressures of the products at equilibrium will be greater than 1 atm and the pressures of the reactants at equilibrium will be less than 1 atm.

Case 3: $\Delta G^\circ > 0$. Since ΔG° ($G_{\text{products}}^\circ - G_{\text{reactants}}^\circ$) is positive,

$$G_{\text{reactants}}^\circ < G_{\text{products}}^\circ$$

If a flask contains the reactants and products, all at 1 atm, the system will *not* be at equilibrium. In this case the system will adjust to the left (toward the reactants, which have a lower free energy) to reach equilibrium. The value of K will be *less than 1*, since at equilibrium the pressures of the reactants will be greater than 1 atm and the pressures of the products will be less than 1 atm.

These results are summarized in Table 16.6. The value of K for a specific reaction can be calculated from the equation

$$\Delta G^\circ = -RT \ln(K)$$

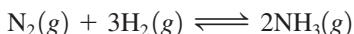
as is shown in Sample Exercises 16.14 and 16.15.

TABLE 16.6 Qualitative Relationship Between the Change in Standard Free Energy and the Equilibrium Constant for a Given Reaction

ΔG°	K
$\Delta G^\circ = 0$	$K = 1$
$\Delta G^\circ < 0$	$K > 1$
$\Delta G^\circ > 0$	$K < 1$

Sample Exercise 16.14**Free Energy and Equilibrium I**

Consider the ammonia synthesis reaction



where $\Delta G^\circ = -33.3 \text{ kJ}$ per mole of N_2 consumed at 25°C . For each of the following mixtures of reactants and products at 25°C , predict the direction in which the system will shift to reach equilibrium.

- a. $P_{\text{NH}_3} = 1.00 \text{ atm}$, $P_{\text{N}_2} = 1.47 \text{ atm}$, $P_{\text{H}_2} = 1.00 \times 10^{-2} \text{ atm}$
- b. $P_{\text{NH}_3} = 1.00 \text{ atm}$, $P_{\text{N}_2} = 1.00 \text{ atm}$, $P_{\text{H}_2} = 1.00 \text{ atm}$

Solution

- a. We can predict the direction of reaction to equilibrium by calculating the value of ΔG using the equation

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

where $Q = \frac{P_{\text{NH}_3}^2}{(P_{\text{N}_2})(P_{\text{H}_2}^3)} = \frac{(1.00)^2}{(1.47)(1.00 \times 10^{-2})^3} = 6.80 \times 10^5$
 $T = 25 + 273 = 298 \text{ K}$
 $R = 8.3145 \text{ J/K} \cdot \text{mol}$

and

$$\Delta G^\circ = -33.3 \text{ kJ/mol} = -3.33 \times 10^4 \text{ J/mol}$$

Then

$$\begin{aligned}\Delta G &= (-3.33 \times 10^4 \text{ J/mol}) + (8.3145 \text{ J/K} \cdot \text{mol})(298 \text{ K}) \ln(6.8 \times 10^5) \\ &= (-3.33 \times 10^4 \text{ J/mol}) + (3.33 \times 10^4 \text{ J/mol}) = 0\end{aligned}$$

Since $\Delta G = 0$, the reactants and products have the same free energies at these partial pressures. The system is already at equilibrium, and no shift will occur.

- b. The partial pressures given here are all 1.00 atm , which means that the system is in the standard state. That is,

$$\begin{aligned}\Delta G &= \Delta G^\circ + RT \ln(Q) = \Delta G^\circ + RT \ln \frac{(1.00)^2}{(1.00)(1.00)^3} \\ &= \Delta G^\circ + RT \ln(1.00) = \Delta G^\circ + 0 = \Delta G^\circ\end{aligned}$$

For this reaction at 25°C ,

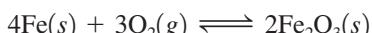
$$\Delta G^\circ = -33.3 \text{ kJ/mol}$$

The negative value for ΔG° means that in their standard states the products have a lower free energy than the reactants. Thus the system will move to the right to reach equilibrium. That is, K is greater than 1.

See Exercise 16.59.

Sample Exercise 16.15**Free Energy and Equilibrium II**

The overall reaction for the corrosion (rusting) of iron by oxygen is



Using the following data, calculate the equilibrium constant for this reaction at 25°C.

Substance	ΔH_f° (kJ/mol)	S° (J/K · mol)
$\text{Fe}_2\text{O}_3(s)$	-826	90
$\text{Fe}(s)$	0	27
$\text{O}_2(g)$	0	205

Solution

To calculate K for this reaction, we will use the equation

$$\Delta G^\circ = -RT \ln(K)$$

We must first calculate ΔG° from

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

where

$$\begin{aligned}\Delta H^\circ &= 2\Delta H_f^\circ(\text{Fe}_2\text{O}_3(s)) - 3\Delta H_f^\circ(\text{O}_2(g)) - 4\Delta H_f^\circ(\text{Fe}(s)) \\ &= 2 \text{ mol}(-826 \text{ kJ/mol}) - 0 - 0 \\ &= -1652 \text{ kJ} = -1.652 \times 10^6 \text{ J} \\ \Delta S^\circ &= 2S_{\text{Fe}_2\text{O}_3}^\circ - 3S_{\text{O}_2}^\circ - 4S_{\text{Fe}}^\circ \\ &= 2 \text{ mol}(90 \text{ J/K} \cdot \text{mol}) - 3 \text{ mol}(205 \text{ J/K} \cdot \text{mol}) - 4 \text{ mol}(27 \text{ J/K} \cdot \text{mol}) \\ &= -543 \text{ J/K}\end{aligned}$$

and

$$T = 273 + 25 = 298 \text{ K}$$

$$\begin{aligned}\text{Then } \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ = (-1.652 \times 10^6 \text{ J}) - (298 \text{ K})(-543 \text{ J/K}) \\ &= -1.490 \times 10^6 \text{ J}\end{aligned}$$

and

$$\Delta G^\circ = -RT \ln(K) = -1.490 \times 10^6 \text{ J} = -(8.3145 \text{ J/K} \cdot \text{mol})(298 \text{ K}) \ln(K)$$

$$\text{Thus } \ln(K) = \frac{1.490 \times 10^6}{2.48 \times 10^3} = 601$$

and

$$K = e^{601}$$

This is a very large equilibrium constant. The rusting of iron is clearly very favorable from a thermodynamic point of view.

See Exercise 16.62.



Formation of rust on bare steel is a spontaneous process.

The Temperature Dependence of K

In Chapter 13 we used Le Châtelier's principle to predict qualitatively how the value of K for a given reaction would change with a change in temperature. Now we can specify the quantitative dependence of the equilibrium constant on temperature from the relationship

$$\Delta G^\circ = -RT \ln(K) = \Delta H^\circ - T\Delta S^\circ$$

We can rearrange this equation to give

$$\ln(K) = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^\circ}{R}$$

Note that this is a linear equation of the form $y = mx + b$, where $y = \ln(K)$, $m = -\Delta H^\circ/R$ = slope, $x = 1/T$, and $b = \Delta S^\circ/R$ = intercept. This means that if values of K for a given reaction are determined at various temperatures, a plot of $\ln(K)$ versus $1/T$ will be linear, with slope $-\Delta H^\circ/R$ and intercept $\Delta S^\circ/R$. This result assumes that both ΔH° and ΔS° are independent of temperature over the temperature range considered. This assumption is a good approximation over a relatively small temperature range.

16.9 Free Energy and Work

One of the main reasons we are interested in physical and chemical processes is that we want to use them to do work for us, and we want this work done as efficiently and economically as possible. We have already seen that at constant temperature and pressure, the sign of the change in free energy tells us whether a given process is spontaneous. This is very useful information because it prevents us from wasting effort on a process that has no inherent tendency to occur. Although a thermodynamically favorable chemical reaction may not occur to any appreciable extent because it is too slow, it makes sense in this case to try to find a catalyst to speed up the reaction. On the other hand, if the reaction is prevented from occurring by its thermodynamic characteristics, we would be wasting our time looking for a catalyst.

In addition to its qualitative usefulness (telling us whether a process is spontaneous), the change in free energy is important quantitatively because it can tell us how much work can be done with a given process. In fact, the *maximum possible useful work obtainable from a process at constant temperature and pressure is equal to the change in free energy*:

$$w_{\max} = \Delta G$$

Note that “PV work” is not counted as useful work here.

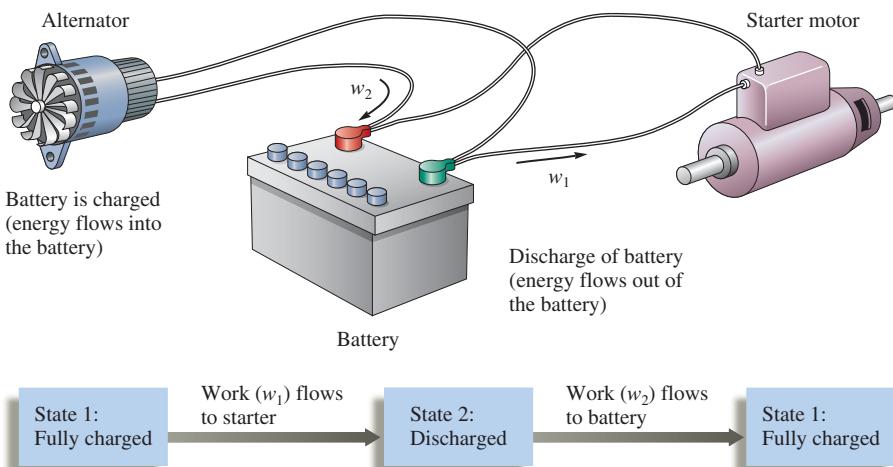
This relationship explains why this function is called the *free* energy. Under certain conditions, ΔG for a spontaneous process represents the energy that is *free to do useful work*. On the other hand, for a process that is not spontaneous, the value of ΔG tells us the minimum amount of work that must be *expended* to make the process occur.

Knowing the value of ΔG for a process thus gives us valuable information about how close the process is to 100% efficiency. For example, when gasoline is burned in a car’s engine, the work produced is about 20% of the maximum work available.

For reasons we will only briefly introduce in this book, the amount of work we actually obtain from a spontaneous process is *always* less than the maximum possible amount.

To explore this idea more fully, let’s consider an electric current flowing through the starter motor of a car. The current is generated from a chemical change in a battery, and we can calculate ΔG for the battery reaction and so determine the energy available to do work. Can we use all this energy to do work? No, because a current flowing through a wire causes frictional heating, and the greater the current, the greater the heat. This heat represents wasted energy—it is not useful for running the starter motor. We can minimize this energy waste by running very low currents through the motor circuit. However, zero current flow would be necessary to eliminate frictional heating entirely, and we cannot derive any work from the motor if no current flows. This represents the difficulty in which nature places us. Using a process to do work requires that some of the energy be wasted, and usually the faster we run the process, the more energy we waste.

Achieving the maximum work available from a spontaneous process can occur only via a hypothetical pathway. Any real pathway wastes energy. If we could discharge the battery infinitely slowly by an infinitesimal current flow, we would achieve the maximum useful work. Also, if we could then recharge the battery using an infinitesimally small

**FIGURE 16.10**

A battery can do work by sending current to a starter motor. The battery can then be recharged by forcing current through it in the opposite direction. If the current flow in both processes is infinitesimally small, $w_1 = w_2$. This is a *reversible process*. But if the current flow is finite, as it would be in any real case, $w_2 > w_1$. This is an *irreversible process* (the universe is different after the cyclic process occurs). All real processes are irreversible.

current, exactly the same amount of energy would be used to return the battery to its original state. After we cycle the battery in this way, the universe (the system and surroundings) is exactly the same as it was before the cyclic process. This is a **reversible process** (see Fig. 16.10).

However, if the battery is discharged to run the starter motor and then recharged using a *finite* current flow, as is the case in reality, *more* work will always be required to recharge the battery than the battery produces as it discharges. This means that even though the battery (the system) has returned to its original state, the surroundings have not, because the surroundings had to furnish a net amount of work as the battery was cycled. The *universe is different* after this cyclic process is performed, and this function is called an **irreversible process**. *All real processes are irreversible*.

In general, after any real cyclic process is carried out in a system, the surroundings have less ability to do work and contain more thermal energy. In other words, *in any real cyclic process in the system, work is changed to heat in the surroundings, and the entropy of the universe increases*. This is another way of stating the second law of thermodynamics.

Thus thermodynamics tells us the work potential of a process and then tells us that we can never achieve this potential. In this spirit, thermodynamicist Henry Bent has paraphrased the first two laws of thermodynamics as follows:

First law: You can't win, you can only break even.

Second law: You can't break even.

When energy is used to do work, it becomes less organized and less concentrated and thus less useful.

The ideas we have discussed in this section are applicable to the energy crisis that will probably increase in severity over the next 25 years. The crisis is obviously not one of supply; the first law tells us that the universe contains a constant supply of energy. The problem is the availability of *useful* energy. As we use energy, we degrade its usefulness. For example, when gasoline reacts with oxygen in the combustion reaction, the change in potential energy results in heat flow. Thus the energy concentrated in the bonds of the gasoline and oxygen molecules ends up spread over the surroundings as thermal energy, where it is much more difficult to harness for useful work. This is a way in which the entropy of the universe increases: Concentrated energy becomes spread out—more disordered and less useful. Thus the crux of the energy problem is that we are rapidly consuming the concentrated energy found in fossil fuels. It took millions of years to concentrate the sun's energy in these fuels, and we will consume these same fuels in a few hundred years. Thus we must use these energy sources as wisely as possible.

Key Terms

Section 16.1

spontaneous process
entropy
positional probability

Section 16.2

second law of thermodynamics

Section 16.4

free energy

Section 16.5

third law of thermodynamics

Section 16.6

standard free energy change
standard free energy of formation

Section 16.8

equilibrium point (thermodynamic definition)

Section 16.9

reversible process
irreversible process

For Review

First law of thermodynamics

- States that the energy of the universe is constant
- Provides a way to keep track of energy as it changes form
- Gives no information about why a particular process occurs in a given direction

Second law of thermodynamics

- States that for any spontaneous process there is always an increase in the entropy of the universe
- Entropy(S) is a thermodynamic function that describes the number of arrangements (positions and/or energy levels) available to a system existing in a given state
 - Nature spontaneously proceeds toward states that have the highest probability of occurring
 - Using entropy, thermodynamics can predict the direction in which a process will occur spontaneously

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

- For a spontaneous process, ΔS_{univ} must be positive
- For a process at constant temperature and pressure:
 - ΔS_{sys} is dominated by “positional” entropy
For a chemical reaction, ΔS_{sys} is dominated by changes in the number of gaseous molecules
 - ΔS_{surr} is determined by heat:

$$\Delta S_{\text{surr}} = -\frac{\Delta H}{T}$$

ΔS_{surr} is positive for an exothermic process (ΔH is negative)

Because ΔS_{surr} depends inversely on T , exothermicity becomes a more important driving force at low temperatures

- Thermodynamics cannot predict the rate at which a system will spontaneously change; the principles of kinetics are necessary to do this

Third law of thermodynamics

- States that the entropy of a perfect crystal at 0 K is zero

Free energy (G)

- Free energy is a state function:

$$G = H - TS$$

- A process occurring at constant temperature and pressure is spontaneous in the direction in which its free energy decreases ($\Delta G < 0$)
- For a reaction the standard free energy change (ΔG°) is the change in free energy that occurs when reactants in their standard states are converted to products in their standard states
- The standard free energy change for a reaction can be determined from the standard free energies of formation (ΔG_f°) of the reactants and products:

$$\Delta G^\circ = \sum n_p \Delta G_f^\circ(\text{products}) - \sum n_r \Delta G_f^\circ(\text{reactants})$$

- Free energy depends on temperature and pressure:

$$G = G^\circ + RT \ln P$$

- This relationship can be used to derive the relationship between ΔG° for a reaction and the value of its equilibrium constant K :

$$\Delta G^\circ = -RT \ln K$$

- For $\Delta G^\circ = 0, K = 1$
- For $\Delta G^\circ < 0, K > 1$
- For $\Delta G^\circ > 0, K < 1$
- The maximum possible useful work obtainable from a process at constant temperature and pressure is equal to the change in free energy:

$$w_{\max} = \Delta G$$

- In any real process, $w < w_{\max}$
- When energy is used to do work in a real process, the energy of the universe remains constant but the usefulness of the energy decreases
- Concentrated energy is spread out in the surroundings as thermal energy

REVIEW QUESTIONS

1. Define the following:
 - a. spontaneous process
 - b. entropy
 - c. positional probability
 - d. system
 - e. surroundings
 - f. universe
2. What is the second law of thermodynamics? For any process, there are four possible sign combinations for ΔS_{sys} and ΔS_{surr} . Which sign combination(s) always give a spontaneous process? Which sign combination(s) always give a nonspontaneous process? Which sign combination(s) may or may not give a spontaneous process?
3. What determines ΔS_{surr} for a process? To calculate ΔS_{surr} at constant pressure and temperature, we use the following equation: $\Delta S_{\text{surr}} = -\Delta H/T$. Why does a minus sign appear in the equation, and why is ΔS_{surr} inversely proportional to temperature?
4. The free energy change, ΔG , for a process at constant temperature and pressure is related to ΔS_{univ} and reflects the spontaneity of the process. How is ΔG related to ΔS_{univ} ? When is a process spontaneous? Nonspontaneous? At equilibrium? ΔG is a composite term composed of ΔH , T , and ΔS . What is the ΔG equation? Give the four possible sign combinations for ΔH and ΔS . What temperatures are required for each sign combination to yield a spontaneous process? If ΔG is positive, what does it say about the reverse process? How does the $\Delta G = \Delta H - T\Delta S$ equation reduce when at the melting-point temperature of a solid-to-liquid phase change or at the boiling-point temperature of a liquid-to-gas phase change? What is the sign of ΔG for the solid-to-liquid phase change at temperatures above the freezing point? What is the sign of ΔG for the liquid-to-gas phase change at temperatures below the boiling point?
5. What is the third law of thermodynamics? What are standard entropy values, S° , and how are these S° values (listed in Appendix 4) used to calculate ΔS° for a reaction? How would you use Hess's law to calculate ΔS° for a reaction? What does the superscript $^\circ$ indicate?

Predicting the sign of ΔS° for a reaction is an important skill to master. For a gas-phase reaction, what do you concentrate on to predict the sign of ΔS° ? For a phase change, what do you concentrate on to predict the sign of ΔS° ?

That is, how are S_{solid}° , S_{liquid}° , and S_{gas}° related to one another? When a solute dissolves in water, what is usually the sign of ΔS° for this process?

6. What is the standard free energy change, ΔG° , for a reaction? What is the standard free energy of formation, ΔG_f° , for a substance? How are ΔG_f° values used to calculate $\Delta G_{\text{rxn}}^\circ$? How can you use Hess's law to calculate $\Delta G_{\text{rxn}}^\circ$? How can you use ΔH° and ΔS° values to calculate $\Delta G_{\text{rxn}}^\circ$? Of the functions ΔH° , ΔS° , and ΔG° , which depends most strongly on temperature? When ΔG° is calculated at temperatures other than 25°C, what assumptions are generally made concerning ΔH° and ΔS° ?
7. If you calculate a value for ΔG° for a reaction using the values of ΔG_f° in Appendix 4 and get a negative number, is it correct to say that the reaction is always spontaneous? Why or why not? Free energy changes also depend on concentration. For gases, how is G related to the pressure of the gas? What are standard pressures for gases and standard concentrations for solutes? How do you calculate ΔG for a reaction at nonstandard conditions? The equation to determine ΔG at nonstandard conditions has Q in it: What is Q ? A reaction is spontaneous as long as ΔG is negative; that is, reactions always proceed as long as the products have a lower free energy than the reactants. What is so special about equilibrium? Why don't reactions move away from equilibrium?
8. Consider the equation $\Delta G = \Delta G^\circ + RT \ln(Q)$. What is the value of ΔG for a reaction at equilibrium? What does Q equal at equilibrium? At equilibrium, the previous equation reduces to $\Delta G^\circ = -RT \ln(K)$. When $\Delta G^\circ > 0$, what does it indicate about K ? When $\Delta G^\circ < 0$, what does it indicate about K ? When $\Delta G^\circ = 0$, what does it indicate about K ? ΔG predicts spontaneity for a reaction, whereas ΔG° predicts the equilibrium position. Explain what this statement means. Under what conditions can you use ΔG° to determine the spontaneity of a reaction?
9. Even if ΔG is negative, the reaction may not occur. Explain the interplay between the thermodynamics and the kinetics of a reaction. High temperatures are favorable to a reaction kinetically but may be unfavorable to a reaction thermodynamically. Explain.
10. Discuss the relationship between w_{max} and the magnitude and sign of the free energy change for a reaction. Also discuss w_{max} for real processes. What is a reversible process?

Active Learning Questions

These questions are designed to be used by groups of students in class. The questions allow students to explore their understanding of concepts through discussion and peer teaching. The real value of these questions is the learning that occurs while students talk to each other about chemical concepts.

1. For the process $A(l) \longrightarrow A(g)$, which direction is favored by changes in energy probability? Positional probability? Explain your answers. If you wanted to favor the process as written, would you raise or lower the temperature of the system? Explain.
2. For a liquid, which would you expect to be larger, ΔS_{fusion} or $\Delta S_{\text{evaporation}}$? Why?
3. Gas A_2 reacts with gas B_2 to form gas AB at a constant temperature. The bond energy of AB is much greater than that of either

reactant. What can be said about the sign of ΔH ? ΔS_{surr} ? ΔS ? Explain how potential energy changes for this process. Explain how random kinetic energy changes during the process.

4. What types of experiments can be carried out to determine whether a reaction is spontaneous? Does spontaneity have any relationship to the final equilibrium position of a reaction? Explain.
5. A friend tells you, "Free energy G and pressure P are related by the equation $G = G^\circ + RT \ln(P)$. Also, G is related to the equilibrium constant K in that when $G_{\text{products}} = G_{\text{reactants}}$, the system is at equilibrium. Therefore, it must be true that a system is at equilibrium when all the pressures are equal." Do you agree with this friend? Explain.
6. You remember that ΔG° is related to $RT \ln(K)$ but cannot remember if it's $RT \ln(K)$ or $-RT \ln(K)$. Realizing what ΔG° and K mean, how can you figure out the correct sign?

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide*.

Questions

7. The synthesis of glucose directly from CO₂ and H₂O and the synthesis of proteins directly from amino acids are both nonspontaneous processes under standard conditions. Yet it is necessary for these to occur for life to exist. In light of the second law of thermodynamics, how can life exist?
8. When the environment is contaminated by a toxic or potentially toxic substance (for example, from a chemical spill or the use of insecticides), the substance tends to disperse. How is this consistent with the second law of thermodynamics? In terms of the second law, which requires the least work: cleaning the environment after it has been contaminated or trying to prevent the contamination before it occurs? Explain.
9. A green plant synthesizes glucose by photosynthesis, as shown in the reaction

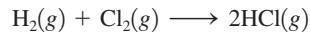


Animals use glucose as a source of energy:



If we were to assume that both these processes occur to the same extent in a cyclic process, what thermodynamic property must have a nonzero value?

10. Human DNA contains almost twice as much information as is needed to code for all the substances produced in the body. Likewise, the digital data sent from *Voyager II* contained one redundant bit out of every two bits of information. The Hubble space telescope transmits three redundant bits for every bit of information. How is entropy related to the transmission of information? What do you think is accomplished by having so many redundant bits of information in both DNA and the space probes?
11. Entropy has been described as “time’s arrow.” Interpret this view of entropy.
12. A mixture of hydrogen gas and chlorine gas remains unreacted until it is exposed to ultraviolet light from a burning magnesium strip. Then the following reaction occurs very rapidly:



Explain.

13. Table 16.1 shows the possible arrangements of four molecules in a two-bulbed flask. What are the possible arrangements if there is one molecule in this two-bulbed flask or two molecules or three molecules? For each, what arrangement is most likely?
14. ΔS_{surr} is sometime called the energy disorder term. Explain.
15. The third law of thermodynamics states that the entropy of a perfect crystal at 0 K is zero. In Appendix 4, F⁻(aq), OH⁻(aq), and S²⁻(aq) all have negative standard entropy values. How can S° values be less than zero?
16. The deciding factor on why HF is a weak acid and not a strong acid like the other hydrogen halides is entropy. What occurs when HF dissociates in water as compared to the other hydrogen halides?

17. List three different ways to calculate the standard free energy change, ΔG° , for a reaction at 25°C? How is ΔG° estimated at temperatures other than 25°C? What assumptions are made?
18. What information can be determined from ΔG for a reaction? Does one get the same information from ΔG° , the standard free energy change? ΔG° allows determination of the equilibrium constant K for a reaction. How? How can one estimate the value of K at temperatures other than 25°C for a reaction? How can one estimate the temperature where $K = 1$ for a reaction? Do all reactions have a specific temperature where $K = 1$?

Exercises

In this section similar exercises are paired.

Spontaneity, Entropy, and the Second Law of Thermodynamics: Free Energy

19. Which of the following processes are spontaneous?
 - a. Salt dissolves in H₂O.
 - b. A clear solution becomes a uniform color after a few drops of dye are added.
 - c. Iron rusts.
 - d. You clean your bedroom.
20. Which of the following processes are spontaneous?
 - a. A house is built.
 - b. A satellite is launched into orbit.
 - c. A satellite falls back to earth.
 - d. The kitchen gets cluttered.
21. Consider the following energy levels, each capable of holding two objects:

$E = 2 \text{ kJ}$	_____
$E = 1 \text{ kJ}$	_____
$E = 0$	XX

 Draw all the possible arrangements of the two identical particles (represented by X) in the three energy levels. What total energy is most likely, that is, occurs the greatest number of times? Assume that the particles are indistinguishable from each other.
22. Redo Exercise 21 with two particles A and B, which can be distinguished from each other.
23. Choose the compound with the greatest positional probability in each case.
 - a. 1 mol H₂ (at STP) or 1 mol H₂ (at 100°C, 0.5 atm)
 - b. 1 mol N₂ (at STP) or 1 mol N₂ (at 100 K, 2.0 atm)
 - c. 1 mol H₂O(s) (at 0°C) or 1 mol H₂O(l) (at 20°C)
24. Which of the following involve an increase in the entropy of the system?
 - a. melting of a solid
 - b. sublimation
 - c. freezing
 - d. mixing
 - e. separation
 - f. boiling
25. Predict the sign of ΔS_{surr} for the following processes.
 - a. H₂O(l) \longrightarrow H₂O(g)
 - b. CO₂(g) \longrightarrow CO₂(s)

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26. Calculate ΔS_{surf} for the following reactions at 25°C and 1 atm.
 a. $\text{C}_3\text{H}_8(g) + 5\text{O}_2(g) \rightarrow 3\text{CO}_2(g) + 4\text{H}_2\text{O}(l)$ $\Delta H^\circ = -2221 \text{ kJ}$
 b. $2\text{NO}_2(g) \rightarrow 2\text{NO}(g) + \text{O}_2(g)$ $\Delta H^\circ = 112 \text{ kJ}$

27. Given the values of ΔH and ΔS , which of the following changes will be spontaneous at constant T and P ?
 a. $\Delta H = +25 \text{ kJ}$, $\Delta S = +5.0 \text{ J/K}$, $T = 300 \text{ K}$
 b. $\Delta H = +25 \text{ kJ}$, $\Delta S = +100 \text{ J/K}$, $T = 300 \text{ K}$
 c. $\Delta H = -10 \text{ kJ}$, $\Delta S = +5.0 \text{ J/K}$, $T = 298 \text{ K}$
 d. $\Delta H = -10 \text{ kJ}$, $\Delta S = -40 \text{ J/K}$, $T = 200 \text{ K}$

28. At what temperatures will the following processes be spontaneous?
 a. $\Delta H = -18 \text{ kJ}$ and $\Delta S = -60 \text{ J/K}$
 b. $\Delta H = +18 \text{ kJ}$ and $\Delta S = +60 \text{ J/K}$
 c. $\Delta H = +18 \text{ kJ}$ and $\Delta S = -60 \text{ J/K}$
 d. $\Delta H = -18 \text{ kJ}$ and $\Delta S = +60 \text{ J/K}$

29. Ethanethiol ($\text{C}_2\text{H}_5\text{SH}$; also called ethyl mercaptan) is commonly added to natural gas to provide the “rotten egg” smell of a gas leak. The boiling point of ethanethiol is 35°C and its heat of vaporization is 27.5 kJ/mol. What is the entropy of vaporization for this substance?

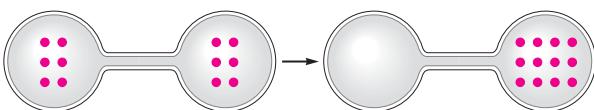
30. For mercury, the enthalpy of vaporization is 58.51 kJ/mol and the entropy of vaporization is 92.92 J/K · mol. What is the normal boiling point of mercury?

31. For ammonia (NH_3), the enthalpy of fusion is 5.65 kJ/mol and the entropy of fusion is 28.9 J/K · mol.
 a. Will $\text{NH}_3(s)$ spontaneously melt at 200. K?
 b. What is the approximate melting point of ammonia?

32. The enthalpy of vaporization of ethanol is 38.7 kJ/mol at its boiling point (78°C). Determine ΔS_{sys} , ΔS_{surf} , and ΔS_{univ} when 1.00 mol of ethanol is vaporized at 78°C and 1.00 atm.

Chemical Reactions: Entropy Changes and Free Energy

33. Predict the sign of ΔS° for each of the following changes.
 a.



- b. $\text{AgCl}(s) \rightarrow \text{Ag}^+(aq) + \text{Cl}^-(aq)$
 c. $2\text{H}_2(g) + \text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(l)$
 d. $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g)$

34. Predict the sign of ΔS° for each of the following changes.
 a. $\text{Na}(s) + \frac{1}{2}\text{Cl}_2(g) \rightarrow \text{NaCl}(s)$
 b. $\text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g)$
 c. $\text{NaCl}(s) \rightarrow \text{Na}^+(aq) + \text{Cl}^-(aq)$
 d. $\text{NaCl}(s) \rightarrow \text{NaCl}(l)$

35. For each of the following pairs of substances, which substance has the greater value of S° ?
 a. $\text{C}_{\text{graphite}}(s)$ or $\text{C}_{\text{diamond}}(s)$
 b. $\text{C}_2\text{H}_5\text{OH}(l)$ or $\text{C}_2\text{H}_5\text{OH}(g)$
 c. $\text{CO}_2(s)$ or $\text{CO}_2(g)$

36. For each of the following pairs, which substance has the greater value of S° ?
 a. N_2O (at 0 K) or He (at 10 K)
 b. $\text{N}_2\text{O}(g)$ (at 1 atm, 25°C) or He(g) (at 1 atm, 25°C)
 c. $\text{H}_2\text{O}(s)$ (at 0°C) or $\text{H}_2\text{O}(l)$ (at 0°C)

37. Predict the sign of ΔS° and then calculate ΔS° for each of the following reactions.
 a. $2\text{H}_2\text{S}(g) + \text{SO}_2(g) \rightarrow 3\text{S}_{\text{rhombic}}(s) + 2\text{H}_2\text{O}(g)$
 b. $2\text{SO}_3(g) \rightarrow 2\text{SO}_2(g) + \text{O}_2(g)$
 c. $\text{Fe}_2\text{O}_3(s) + 3\text{H}_2(g) \rightarrow 2\text{Fe}(s) + 3\text{H}_2\text{O}(g)$

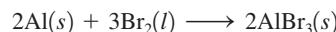
38. Predict the sign of ΔS° and then calculate ΔS° for each of the following reactions.
 a. $\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{H}_2\text{O}(l)$
 b. $2\text{CH}_3\text{OH}(g) + 3\text{O}_2(g) \rightarrow 2\text{CO}_2(g) + 4\text{H}_2\text{O}(g)$
 c. $\text{HCl}(g) \rightarrow \text{H}^+(aq) + \text{Cl}^-(aq)$

39. For the reaction



ΔS° is equal to -358 J/K . Use this value and data from Appendix 4 to calculate the value of S° for $\text{CF}_4(g)$.

40. For the reaction



ΔS° is equal to -144 J/K . Use this value and data from Appendix 4 to calculate the value of S° for solid aluminum bromide.

41. It is quite common for a solid to change from one structure to another at a temperature below its melting point. For example, sulfur undergoes a phase change from the rhombic crystal structure to the monoclinic crystal form at temperatures above 95°C.

- a. Predict the signs of ΔH and ΔS for the process $\text{S}_{\text{rhombic}} \rightarrow \text{S}_{\text{monoclinic}}$.
 b. Which form of sulfur has the more ordered crystalline structure?

42. When most biologic enzymes are heated they lose their catalytic activity. The change



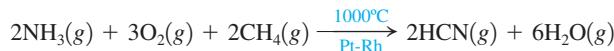
that occurs on heating is endothermic and spontaneous. Is the structure of the original enzyme or its new form more ordered? Explain.

43. Consider the reaction



- a. Predict the signs of ΔH and ΔS .
 b. Would the reaction be more spontaneous at high or low temperatures?

44. Hydrogen cyanide is produced industrially by the following exothermic reaction:



Is the high temperature needed for thermodynamic or kinetic reasons?

45. From data in Appendix 4, calculate ΔH° , ΔS° , and ΔG° for each of the following reactions at 25°C.

- a. $\text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g)$
 b. $6\text{CO}_2(g) + 6\text{H}_2\text{O}(l) \rightarrow \text{C}_6\text{H}_{12}\text{O}_6(s) + 6\text{O}_2(g)$
 Glucose
 c. $\text{P}_4\text{O}_{10}(s) + 6\text{H}_2\text{O}(l) \rightarrow 4\text{H}_3\text{PO}_4(s)$
 d. $\text{HCl}(g) + \text{NH}_3(g) \rightarrow \text{NH}_4\text{Cl}(s)$

46. The decomposition of ammonium dichromate $[(\text{NH}_4)_2\text{Cr}_2\text{O}_7]$ is called the “volcano” demonstration for its fiery display. The decomposition reaction involves breaking down ammonium dichromate into nitrogen gas, water vapor, and solid chromium(III) oxide. From the data in Appendix 4 and given $\Delta H_f^\circ = -23 \text{ kJ/mol}$ and $\Delta S^\circ = 114 \text{ J/K} \cdot \text{mol}$ for $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$, calculate ΔG° for the “volcano” reaction and calculate ΔG_f° for ammonium dichromate.

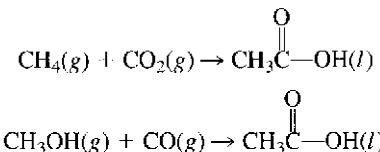
47. For the reaction at 298 K,



the values of ΔH° and ΔS° are -58.03 kJ and -176.6 J/K , respectively. What is the value of ΔG° at 298 K? Assuming that ΔH° and ΔS° do not depend on temperature, at what temperature is $\Delta G^\circ = 0$? Is ΔG° negative above or below this temperature?

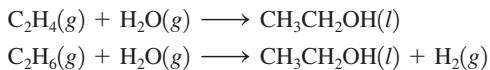
48. At $100.^\circ\text{C}$ and 1.00 atm , $\Delta H^\circ = 40.6 \text{ kJ/mol}$ for the vaporization of water. Estimate ΔG° for the vaporization of water at $90.^\circ\text{C}$ and $110.^\circ\text{C}$. Assume ΔH° and ΔS° at $100.^\circ\text{C}$ and 1.00 atm do not depend on temperature.

49. Using data from Appendix 4, calculate ΔH° , ΔS° , and ΔG° for the following reactions that produce acetic acid:



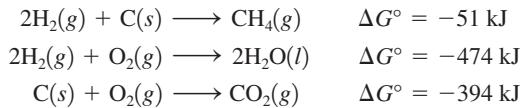
Which reaction would you choose as a commercial method for producing acetic acid ($\text{CH}_3\text{CO}_2\text{H}$) at standard conditions? What temperature conditions would you choose for the reaction? Assume ΔH° and ΔS° do not depend on temperature.

50. Consider two reactions for the production of ethanol:



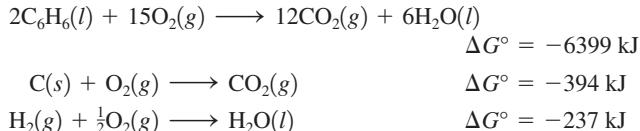
Which would be the more thermodynamically feasible at standard conditions? Why?

51. Given the following data:

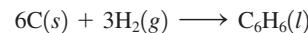


Calculate ΔG° for $\text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l)$.

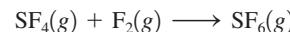
52. Given the following data:



calculate ΔG° for the reaction



53. For the reaction



the value of ΔG° is -374 kJ . Use this value and data from Appendix 4 to calculate the value of ΔG_f° for $\text{SF}_4(g)$.

54. The value of ΔG° for the reaction



is -5490 kJ . Use this value and data from Appendix 4 to calculate the standard free energy of formation for $\text{C}_4\text{H}_{10}(g)$.

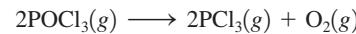
55. Assuming standard conditions, can the following reaction take place at room temperature?



$$\Delta G^\circ(\text{CH}_4) = -50.72 \text{ kJ/mol} \quad \Delta G^\circ(\text{CH}_3\text{Cl}) = -57.37 \text{ kJ/mol}$$

$$\Delta G^\circ(\text{CH}_2\text{Cl}_2) = -68.85 \text{ kJ/mol} \quad \Delta G^\circ(\text{HCl}) = -95.30 \text{ kJ/mol}$$

56. Consider the reaction



a. Calculate ΔG° for this reaction. The ΔG_f° values for $\text{POCl}_3(g)$ and $\text{PCl}_3(g)$ are -502 kJ/mol and -270 kJ/mol , respectively.

b. Is this reaction spontaneous under standard conditions at 298 K?

c. The value of ΔS° for this reaction is 179 J/K . At what temperatures is this reaction spontaneous at standard conditions? Assume that ΔH° and ΔS° do not depend on temperature.

Free Energy: Pressure Dependence and Equilibrium

57. Using data from Appendix 4, calculate ΔG for the reaction



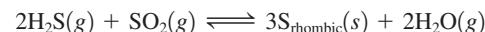
for these conditions:

$$T = 298 \text{ K}$$

$$P_{\text{NO}} = 1.00 \times 10^{-6} \text{ atm}, P_{\text{O}_3} = 2.00 \times 10^{-6} \text{ atm}$$

$$P_{\text{NO}_2} = 1.00 \times 10^{-7} \text{ atm}, P_{\text{O}_2} = 1.00 \times 10^{-3} \text{ atm}$$

58. Using data from Appendix 4, calculate ΔG for the reaction



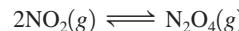
for the following conditions at 25°C :

$$P_{\text{H}_2\text{S}} = 1.0 \times 10^{-4} \text{ atm}$$

$$P_{\text{SO}_2} = 1.0 \times 10^{-2} \text{ atm}$$

$$P_{\text{H}_2\text{O}} = 3.0 \times 10^{-2} \text{ atm}$$

59. Consider the reaction



For each of the following mixtures of reactants and products at 25°C , predict the direction in which the reaction will shift to reach equilibrium.

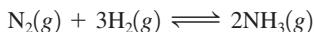
$$\text{a. } P_{\text{NO}_2} = P_{\text{N}_2\text{O}_4} = 1.0 \text{ atm}$$

$$\text{b. } P_{\text{NO}_2} = 0.21 \text{ atm}, P_{\text{N}_2\text{O}_4} = 0.50 \text{ atm}$$

$$\text{c. } P_{\text{NO}_2} = 0.29 \text{ atm}, P_{\text{N}_2\text{O}_4} = 1.6 \text{ atm}$$

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60. Consider the following reaction:



Calculate ΔG for this reaction under the following conditions (assume an uncertainty of ± 1 in all quantities):

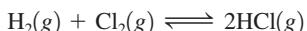
- a. $T = 298 \text{ K}$, $P_{\text{N}_2} = P_{\text{H}_2} = 200 \text{ atm}$, $P_{\text{NH}_3} = 50 \text{ atm}$
- b. $T = 298 \text{ K}$, $P_{\text{N}_2} = 200 \text{ atm}$, $P_{\text{H}_2} = 600 \text{ atm}$, $P_{\text{NH}_3} = 200 \text{ atm}$

61. Consider the following reaction at 25.0°C :



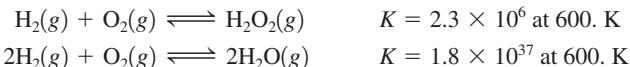
The values of ΔH° and ΔS° are -58.03 kJ/mol and $-176.6 \text{ J/K} \cdot \text{mol}$, respectively. Calculate the value of K at 25.0°C . Assuming ΔH° and ΔS° are temperature independent, estimate the value of K at 100.0°C .

62. Consider the reaction

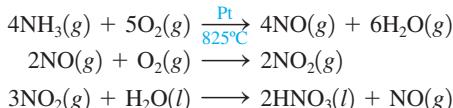


- a. Calculate ΔH° , ΔS° , ΔG° , and K (at 298 K) using data in Appendix 4.
- b. If $\text{H}_2(g)$, $\text{Cl}_2(g)$, and $\text{HCl}(g)$ are placed in a flask such that the pressure of each gas is 1 atm, in which direction will the system shift to reach equilibrium at 25°C ?

63. Calculate ΔG° for $\text{H}_2\text{O}(g) + \frac{1}{2}\text{O}_2(g) \rightleftharpoons \text{H}_2\text{O}_2(g)$ at $600. \text{ K}$, using the following data:

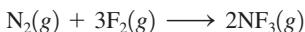


64. The Ostwald process for the commercial production of nitric acid involves three steps:



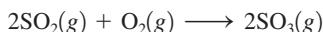
- a. Calculate ΔH° , ΔS° , ΔG° , and K (at 298 K) for each of the three steps in the Ostwald process (see Appendix 4).
- b. Calculate the equilibrium constant for the first step at 825°C , assuming ΔH° and ΔS° do not depend on temperature.
- c. Is there a thermodynamic reason for the high temperature in the first step assuming standard conditions?

65. Consider the following reaction at $800. \text{ K}$:



An equilibrium mixture contains the following partial pressures: $P_{\text{N}_2} = 0.021 \text{ atm}$, $P_{\text{F}_2} = 0.063 \text{ atm}$, $P_{\text{NF}_3} = 0.48 \text{ atm}$. Calculate ΔG° for the reaction at $800. \text{ K}$.

66. Consider the following reaction at 298 K :

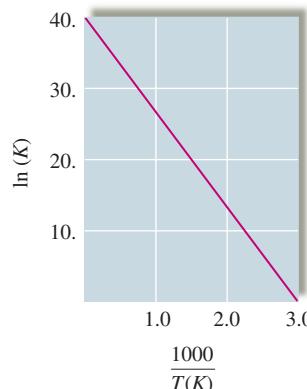


An equilibrium mixture contains $\text{O}_2(g)$ and $\text{SO}_3(g)$ at partial pressures of 0.50 atm and 2.0 atm , respectively. Using data from Appendix 4, determine the equilibrium partial pressure of SO_2 in the mixture. Will this reaction be most favored at a high or a low temperature, assuming standard conditions?

67. Consider the relationship:

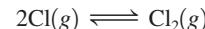
$$\ln(K) = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

The equilibrium constant for some hypothetical process was determined as a function of temperature (in Kelvin) with the results plotted below.



From the plot, determine the values of ΔH° and ΔS° for this process. What would be the major difference in the $\ln(K)$ versus $1/T$ plot for an endothermic process as compared to an exothermic process?

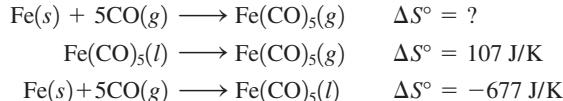
68. The equilibrium constant K for the reaction



was measured as a function of temperature (Kelvin). A graph of $\ln K$ versus $1/T$ for this reaction gives a straight line with a slope of $1.352 \times 10^4 \text{ K}$ and a y -intercept of -14.51 . Determine the values of ΔH° and ΔS° for this reaction. Reference Exercise 67.

Additional Exercises

69. Using Appendix 4 and the following data, determine S° for $\text{Fe}(\text{CO})_5(g)$.



70. Some water is placed in a coffee-cup calorimeter. When 1.0 g of an ionic solid is added, the temperature of the solution increases from 21.5°C to 24.2°C as the solid dissolves. For the dissolving process, what are the signs for ΔS_{sys} , ΔS_{surr} , and ΔS_{univ} ?

71. Consider the following system at equilibrium at 25°C :



What will happen to the ratio of partial pressure of PCl_5 to partial pressure of PCl_3 if the temperature is raised? Explain completely.

72. Calculate the entropy change for the vaporization of liquid methane and liquid hexane using the following data.

	Boiling Point (1 atm)	ΔH_{vap}
Methane	112 K	8.20 kJ/mol
Hexane	342 K	28.9 kJ/mol

Compare the molar volume of gaseous methane at 112 K with that of gaseous hexane at 342 K. How do the differences in molar volume affect the values of ΔS_{vap} for these liquids?

73. As $\text{O}_2(l)$ is cooled at 1 atm, it freezes at 54.5 K to form solid I. At a lower temperature, solid I rearranges to solid II, which has a different crystal structure. Thermal measurements show that ΔH for the I \rightarrow II phase transition is -743.1 J/mol , and ΔS for the same transition is $-17.0 \text{ J/K} \cdot \text{mol}$. At what temperature are solids I and II in equilibrium?

74. Consider the following reaction:



For $\text{Cl}_2\text{O}(g)$,

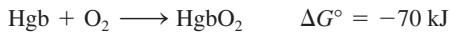
$$\Delta G_f^\circ = 97.9 \text{ kJ/mol}$$

$$\Delta H_f^\circ = 80.3 \text{ kJ/mol}$$

$$S^\circ = 266.1 \text{ J/K} \cdot \text{mol}$$

- Calculate ΔG° for the reaction using the equation $\Delta G^\circ = -RT \ln(K)$.
- Use bond energy values (Table 8.4) to estimate ΔH° for the reaction.
- Use the results from parts a and b to estimate ΔS° for the reaction.
- Estimate ΔH_f° and S° for $\text{HOCl}(g)$.
- Estimate the value of K at 500. K.
- Calculate ΔG at 25°C when $P_{\text{H}_2\text{O}} = 18 \text{ torr}$, $P_{\text{Cl}_2\text{O}} = 2.0 \text{ torr}$, and $P_{\text{HOCl}} = 0.10 \text{ torr}$.

75. Carbon monoxide is toxic because it bonds much more strongly to the iron in hemoglobin (Hgb) than does O_2 . Consider the following reactions and approximate standard free energy changes:



Using these data, estimate the equilibrium constant value at 25°C for the following reaction:



76. Using the following data, calculate the value of K_{sp} for $\text{Ba}(\text{NO}_3)_2$, one of the *least* soluble of the common nitrate salts.

Species	ΔG_f°
$\text{Ba}^{2+}(aq)$	-561 kJ/mol
$\text{NO}_3^-(aq)$	-109 kJ/mol
$\text{Ba}(\text{NO}_3)_2(s)$	-797 kJ/mol

77. In the text the equation

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

was derived for gaseous reactions where the quantities in Q were expressed in units of pressure. We also can use units of mol/L for the quantities in Q , specifically for aqueous reactions. With this in mind, consider the reaction



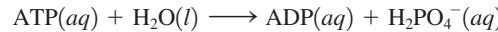
for which $K_a = 7.2 \times 10^{-4}$ at 25°C. Calculate ΔG for the reaction under the following conditions at 25°C.

- $[\text{HF}] = [\text{H}^+] = [\text{F}^-] = 1.0 \text{ M}$
- $[\text{HF}] = 0.98 \text{ M}$, $[\text{H}^+] = [\text{F}^-] = 2.7 \times 10^{-2} \text{ M}$
- $[\text{HF}] = [\text{H}^+] = [\text{F}^-] = 1.0 \times 10^{-5} \text{ M}$
- $[\text{HF}] = [\text{F}^-] = 0.27 \text{ M}$, $[\text{H}^+] = 7.2 \times 10^{-4} \text{ M}$
- $[\text{HF}] = 0.52 \text{ M}$, $[\text{F}^-] = 0.67 \text{ M}$, $[\text{H}^+] = 1.0 \times 10^{-3} \text{ M}$

Based on the calculated ΔG values, in what direction will the reaction shift to reach equilibrium for each of the five sets of conditions?

78. Many biochemical reactions that occur in cells require relatively high concentrations of potassium ion (K^+). The concentration of K^+ in muscle cells is about 0.15 M. The concentration of K^+ in blood plasma is about 0.0050 M. The high internal concentration in cells is maintained by pumping K^+ from the plasma. How much work must be done to transport 1.0 mol K^+ from the blood to the inside of a muscle cell at 37°C, normal body temperature? When 1.0 mol K^+ is transferred from blood to the cells, do any other ions have to be transported? Why or why not?

79. Cells use the hydrolysis of adenosine triphosphate, abbreviated as ATP, as a source of energy. Symbolically, this reaction can be written as



where ADP represents adenosine diphosphate. For this reaction, $\Delta G^\circ = -30.5 \text{ kJ/mol}$.

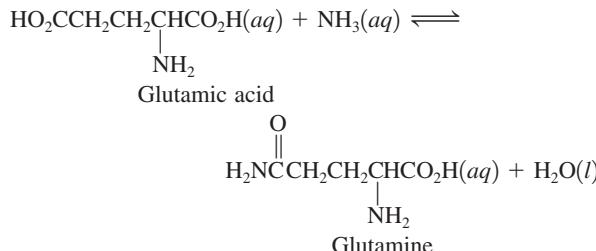
- Calculate K at 25°C.
- If all the free energy from the metabolism of glucose



goes into forming ATP from ADP, how many ATP molecules can be produced for every molecule of glucose?

- Much of the ATP formed from metabolic processes is used to provide energy for transport of cellular components. What amount (mol) of ATP must be hydrolyzed to provide the energy for the transport of 1.0 mol of K^+ from the blood to the inside of a muscle cell at 37°C as described in Exercise 78?

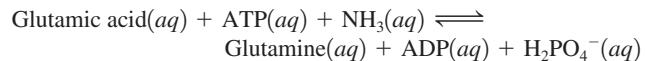
80. One reaction that occurs in human metabolism is



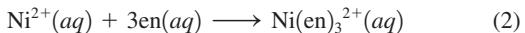
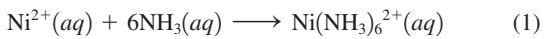
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For this reaction $\Delta G^\circ = 14 \text{ kJ}$ at 25°C .

- Calculate K for this reaction at 25°C .
- In a living cell this reaction is coupled with the hydrolysis of ATP. (See Exercise 79.) Calculate ΔG° and K at 25°C for the following reaction:



- 81.** Consider the reactions

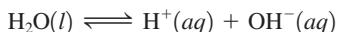


where



The ΔH values for the two reactions are quite similar, yet $K_{\text{reaction } 2} > K_{\text{reaction } 1}$. Explain.

- 82.** Use the equation in Exercise 67 to determine ΔH° and ΔS° for the autoionization of water:



$T(^{\circ}\text{C})$	K_w
0	1.14×10^{-15}
25	1.00×10^{-14}
35	2.09×10^{-14}
40.	2.92×10^{-14}
50.	5.47×10^{-14}

- 83.** Consider the reaction



Assuming ΔH° and ΔS° do not depend on temperature, calculate the temperature where $K = 1.00$ for this reaction.

Challenge Problems

- 84.** Liquid water at 25°C is introduced into an evacuated, insulated vessel. Identify the signs of the following thermodynamic functions for the process that occurs: ΔH , ΔS , ΔT_{water} , ΔS_{surr} , ΔS_{univ} .
- 85.** Using data from Appendix 4, calculate ΔH° , ΔG° , and K (at 298 K) for the production of ozone from oxygen:



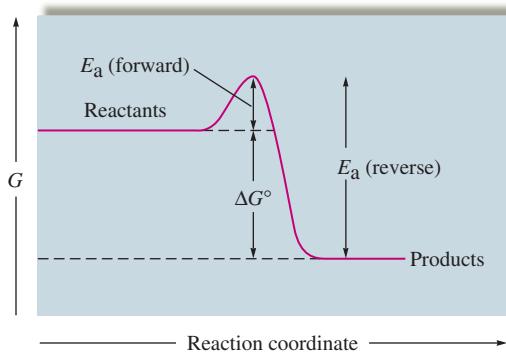
At 30 km above the surface of the earth, the temperature is about 230 K and the partial pressure of oxygen is about $1.0 \times 10^{-3} \text{ atm}$. Estimate the partial pressure of ozone in equilibrium with oxygen at 30 km above the earth's surface. Is it reasonable to assume that the equilibrium between oxygen and ozone is maintained under these conditions? Explain.

- 86.** Entropy can be calculated by a relationship proposed by Ludwig Boltzmann:

$$S = k \ln(W)$$

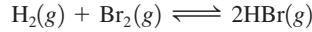
where $k = 1.38 \times 10^{-23} \text{ J/K}$ and W is the number of ways a particular state can be obtained. (This equation is engraved on Boltzmann's tombstone.) Calculate S for the three arrangements of particles in Table 16.1.

- 87.** a. Using the free energy profile for a simple one-step reaction, show that at equilibrium $K = k_f/k_r$, where k_f and k_r are the rate constants for the forward and reverse reactions. Hint: Use the relationship $\Delta G^\circ = -RT \ln(K)$ and represent k_f and k_r using the Arrhenius equation ($k = Ae^{-E_a/RT}$).



- b. Why is the following statement false? "A catalyst can increase the rate of a forward reaction but not the rate of the reverse reaction."

- 88.** Consider the reaction



where $\Delta H^\circ = -103.8 \text{ kJ/mol}$. In a particular experiment, equal moles of $\text{H}_2(g)$ at 1.00 atm and $\text{Br}_2(g)$ at 1.00 atm were mixed in a 1.00-L flask at 25°C and allowed to reach equilibrium. Then the molecules of H_2 at equilibrium were counted using a very sensitive technique, and 1.10×10^{13} molecules were found. For this reaction, calculate the values of K , ΔG° , and ΔS° .

- 89.** Consider the system

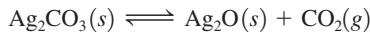


at 25°C .

- a. Assuming that $G_A^\circ = 8996 \text{ J/mol}$ and $G_B^\circ = 11,718 \text{ J/mol}$, calculate the value of the equilibrium constant for this reaction.
- b. Calculate the equilibrium pressures that result if $1.00 \text{ mol A}(g)$ at 1.00 atm and $1.00 \text{ mol B}(g)$ at 1.00 atm are mixed at 25°C .
- c. Show by calculations that $\Delta G = 0$ at equilibrium.

- 90.** The equilibrium constant for a certain reaction decreases from 8.84 to 3.25×10^{-2} when the temperature increases from 25°C to 75°C . Estimate the temperature where $K = 1.00$ for this reaction. Estimate the value of ΔS° for this reaction. Hint: Manipulate the equation in Exercise 67.

- 91.** If wet silver carbonate is dried in a stream of hot air, the air must have a certain concentration level of carbon dioxide to prevent silver carbonate from decomposing by the reaction



ΔH° for this reaction is 79.14 kJ/mol in the temperature range of 25 to 125°C . Given that the partial pressure of carbon dioxide in

equilibrium with pure solid silver carbonate is 6.23×10^{-3} torr at 25°C, calculate the partial pressure of CO₂ necessary to prevent decomposition of Ag₂CO₃ at 110°C. Hint: Manipulate the equation in Exercise 67.

92. Carbon tetrachloride (CCl₄) and benzene (C₆H₆) form ideal solutions. Consider an equimolar solution of CCl₄ and C₆H₆ at 25°C. The vapor above the solution is collected and condensed. Using the following data, determine the composition in mole fraction of the condensed vapor.

Substance	ΔG_f°
C ₆ H ₆ (l)	124.50 kJ/mol
C ₆ H ₆ (g)	129.66 kJ/mol
CCl ₄ (l)	-65.21 kJ/mol
CCl ₄ (g)	-60.59 kJ/mol

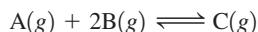
93. Some nonelectrolyte solute (molar mass = 142 g/mol) was dissolved in 150. mL of a solvent (density = 0.879 g/cm³). The elevated boiling point of the solution was 355.4 K. What mass of solute was dissolved in the solvent? For the solvent, the enthalpy of vaporization is 33.90 kJ/mol, the entropy of vaporization is 95.95 J/K · mol, and the boiling-point elevation constant is 2.5 K · kg/mol.
94. You have a 1.00-L sample of hot water (90.0°C) sitting open in a 25.0°C room. Eventually the water cools to 25.0°C while the temperature of the room remains unchanged. Calculate ΔS_{sur} for this process. Assume the density of water is 1.00 g/cm³ over this temperature range, and the heat capacity of water is constant over this temperature range and equal to 75.4 J/K · mol.
95. Consider a weak acid, HX. If a 0.10 M solution of HX has a pH of 5.83 at 25°C, what is ΔG° for the acid's dissociation reaction at 25°C?
96. Sodium chloride is added to water (at 25°C) until it is saturated. Calculate the Cl⁻ concentration in such a solution.

Species	$\Delta G^\circ(\text{kJ/mol})$
NaCl(s)	-384
Na ⁺ (aq)	-262
Cl ⁻ (aq)	-131

Integrative Problems

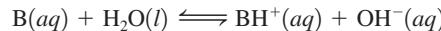
These problems require the integration of multiple concepts to find the solutions.

97. For the equilibrium



the initial concentrations are [A] = [B] = [C] = 0.100 atm. Once equilibrium has been established, it is found that [C] = 0.040 atm. What is ΔG° for this reaction at 25°C?

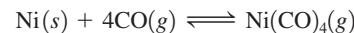
98. What is the pH of a 0.125 M solution of the weak base B if $\Delta H^\circ = -28.0$ kJ and $\Delta S^\circ = -175$ J/K for the following equilibrium reaction at 25°C?



Marathon Problem

This problem is designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

99. Impure nickel, refined by smelting sulfide ores in a blast furnace, can be converted into metal from 99.90% to 99.99% purity by the Mond process. The primary reaction involved in the Mond process is



- Without referring to Appendix 4, predict the sign of ΔS° for the above reaction. Explain.
- The spontaneity of the above reaction is temperature dependent. Predict the sign of ΔS_{sur} for this reaction. Explain.
- For Ni(CO)₄(g), $\Delta H_f^\circ = -607$ kJ/mol and $S^\circ = 417$ J/K · mol at 298 K. Using these values and data in Appendix 4, calculate ΔH° and ΔS° for the above reaction.
- Calculate the temperature at which $\Delta G^\circ = 0$ ($K = 1$) for the above reaction, assuming that ΔH° and ΔS° do not depend on temperature.
- The first step of the Mond process involves equilibrating impure nickel with CO(g) and Ni(CO)₄(g) at about 50°C. The purpose of this step is to convert as much nickel as possible into the gas phase. Calculate the equilibrium constant for the above reaction at 50°C.
- In the second step of the Mond process, the gaseous Ni(CO)₄ is isolated and heated to 227°C. The purpose of this step is to deposit as much nickel as possible as pure solid (the reverse of the above reaction). Calculate the equilibrium constant for the above reaction at 227°C.
- Why is temperature increased for the second step of the Mond process?
- The Mond process relies on the volatility of Ni(CO)₄ for its success. Only pressures and temperatures at which Ni(CO)₄ is a gas are useful. A recently developed variation of the Mond process carries out the first step at higher pressures and a temperature of 152°C. Estimate the maximum pressure of Ni(CO)₄(g) that can be attained before the gas will liquefy at 152°C. The boiling point for Ni(CO)₄ is 42°C and the enthalpy of vaporization is 29.0 kJ/mol.

[Hint: The phase change reaction and the corresponding equilibrium expression are



Ni(CO)₄(g) will liquefy when the pressure of Ni(CO)₄ is greater than the K value.]

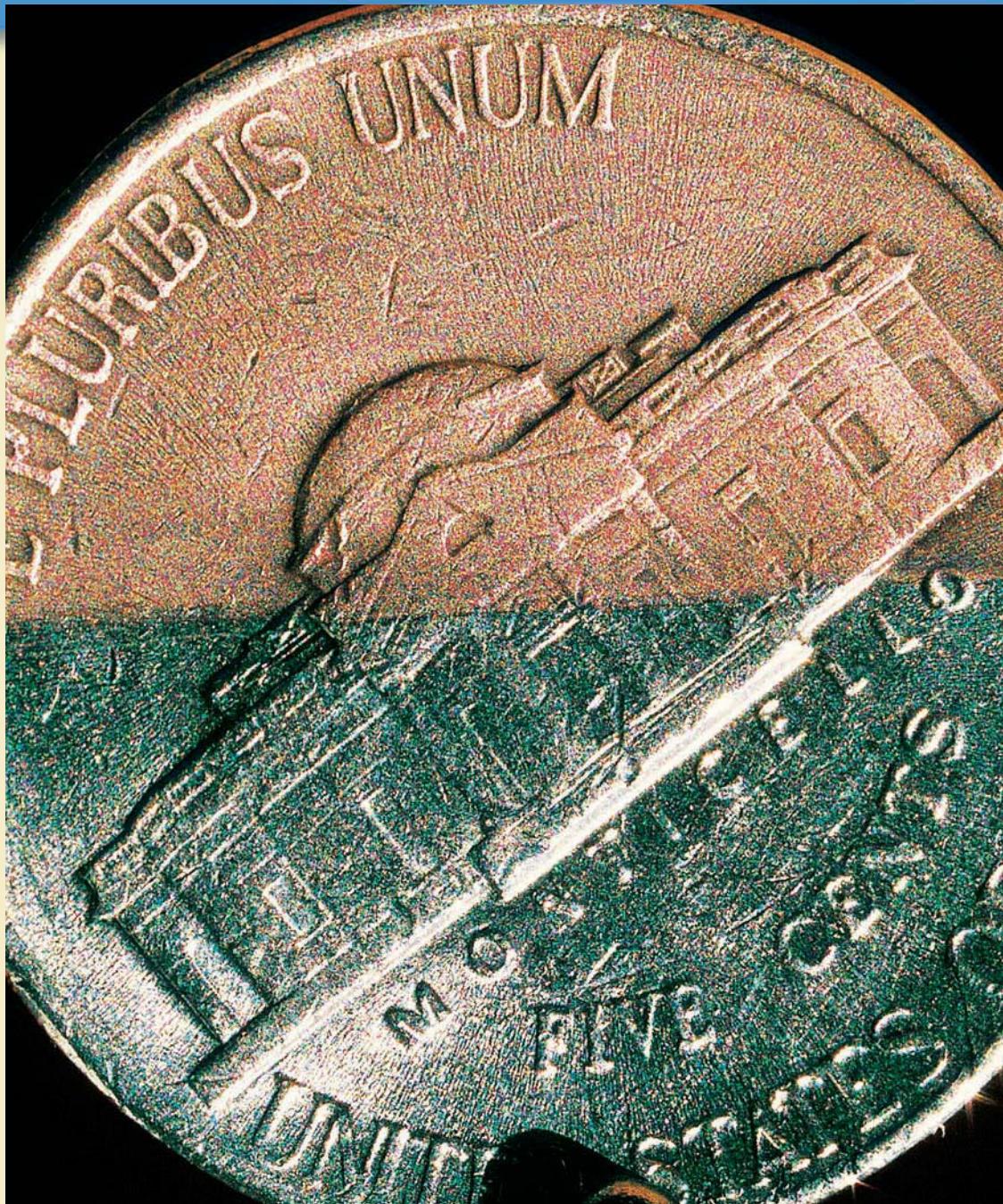


Get help understanding core concepts and visualizing molecular-level interactions, and practice problem solving, by visiting the Online Study Center at college.hmco.com/PIC/zumdahl17e.

17 Electrochemistry

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A nickel half-electroplated with copper.

E

lectrochemistry constitutes one of the most important interfaces between chemistry and everyday life. Every time you start your car, turn on your calculator, look at your digital watch, or listen to a radio at the beach, you are depending on electrochemical reactions. Our society sometimes seems to run almost entirely on batteries. Certainly the advent of small, dependable batteries along with silicon-chip technology has made possible the tiny calculators, tape recorders, and clocks that we take for granted.

Electrochemistry is important in other less obvious ways. For example, the corrosion of iron, which has tremendous economic implications, is an electrochemical process. In addition, many important industrial materials such as aluminum, chlorine, and sodium hydroxide are prepared by electrolytic processes. In analytical chemistry, electrochemical techniques employ electrodes that are specific for a given molecule or ion, such as H^+ (pH meters), F^- , Cl^- , and many others. These increasingly important methods are used to analyze for trace pollutants in natural waters or for the tiny quantities of chemicals in human blood that may signal the development of a specific disease.

Electrochemistry is best defined as *the study of the interchange of chemical and electrical energy*. It is primarily concerned with two processes that involve oxidation–reduction reactions: the generation of an electric current from a spontaneous chemical reaction and the opposite process, the use of a current to produce chemical change.

17.1 Galvanic Cells

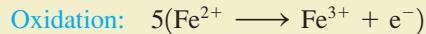
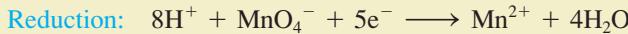
As we discussed in detail in Section 4.9, an **oxidation–reduction (redox) reaction** involves a transfer of electrons from the **reducing agent** to the **oxidizing agent**. Recall that **oxidation** involves a *loss of electrons* (an increase in oxidation number) and that **reduction** involves a *gain of electrons* (a decrease in oxidation number).

To understand how a redox reaction can be used to generate a current, let's consider the reaction between MnO_4^- and Fe^{2+} :



In this reaction, Fe^{2+} is oxidized and MnO_4^- is reduced; electrons are transferred from Fe^{2+} (the reducing agent) to MnO_4^- (the oxidizing agent).

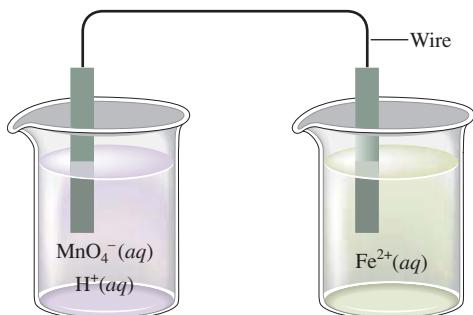
It is useful to break a redox reaction into **half-reactions**, one involving oxidation and one involving reduction. For the reaction above, the half-reactions are



The multiplication of the second half-reaction by 5 indicates that this reaction must occur five times for each time the first reaction occurs. The balanced overall reaction is the sum of the half-reactions.

When MnO_4^- and Fe^{2+} are present in the same solution, the electrons are transferred directly when the reactants collide. Under these conditions, no useful work is obtained from the chemical energy involved in the reaction, which instead is released as heat. How can we harness this energy? The key is to separate the oxidizing agent from the reducing agent, thus requiring the electron transfer to occur through a wire. The current produced in the wire by the electron flow can then be directed through a device, such as an electric motor, to provide useful work.

Balancing half-reactions is discussed in Section 4.10.

**FIGURE 17.1**

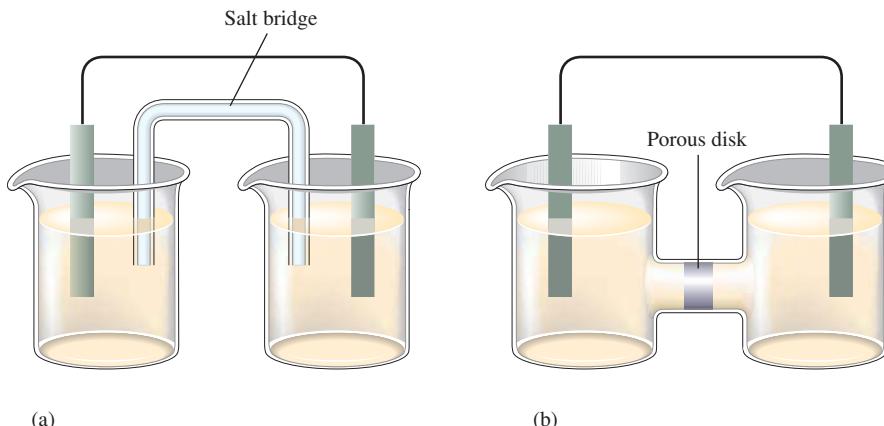
Schematic of a method to separate the oxidizing and reducing agents of a redox reaction. (The solutions also contain counterions to balance the charge.)

For example, consider the system illustrated in Fig. 17.1. If our reasoning has been correct, electrons should flow through the wire from Fe^{2+} to MnO_4^- . However, when we construct the apparatus as shown, no flow of electrons is apparent. Why? Careful observation shows that when we connect the wires from the two compartments, current flows for an instant and then ceases. The current stops flowing because of charge buildups in the two compartments. If electrons flowed from the right to the left compartment in the apparatus as shown, the left compartment (receiving electrons) would become negatively charged, and the right compartment (losing electrons) would become positively charged. Creating a charge separation of this type requires a large amount of energy. Thus sustained electron flow cannot occur under these conditions.

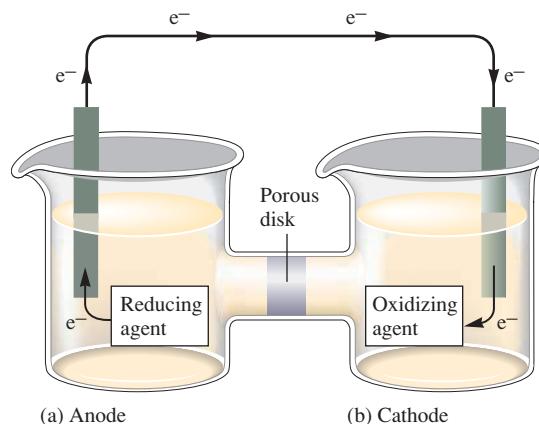
However, we can solve this problem very simply. The solutions must be connected so that ions can flow to keep the net charge in each compartment zero. This connection might involve a **salt bridge** (a U-tube filled with an electrolyte) or a **porous disk** in a tube connecting the two solutions (see Fig. 17.2). Either of these devices allows ions to flow without extensive mixing of the solutions. When we make the provision for ion flow, the circuit is complete. Electrons flow through the wire from reducing agent to oxidizing agent, and ions flow from one compartment to the other to keep the net charge zero.

We now have covered all the essential characteristics of a **galvanic cell**, a device in which chemical energy is changed to electrical energy. (The opposite process is called **electrolysis** and will be considered in Section 17.7.)

The reaction in an electrochemical cell occurs at the interface between the electrode and the solution where the electron transfer occurs. The electrode compartment in which oxidation occurs is called the **anode**; the electrode compartment in which reduction occurs is called the **cathode** (see Fig. 17.3).

**FIGURE 17.2**

Galvanic cells can contain a salt bridge as in (a) or a porous-disk connection as in (b). A salt bridge contains a strong electrolyte held in a Jello-like matrix. A porous disk contains tiny passages that allow hindered flow of ions.

**FIGURE 17.3**

An electrochemical process involves electron transfer at the interface between the electrode and the solution. (a) The species in the solution acting as the reducing agent supplies electrons to the anode. (b) The species in the solution acting as the oxidizing agent receives electrons from the cathode.



[Visualization: Voltaic Cell: Cathode Reaction](#)



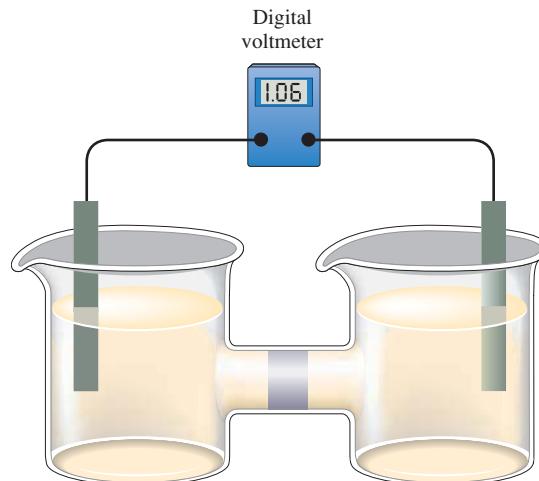
[Visualization: Voltaic Cell: Anode Reaction](#)

A volt is 1 joule of work per coulomb of charge transferred: $1\text{ V} = 1\text{ J/C}$.

Cell Potential

A galvanic cell consists of an oxidizing agent in one compartment that pulls electrons through a wire from a reducing agent in the other compartment. The “pull,” or driving force, on the electrons is called the **cell potential** ($\mathcal{E}_{\text{cell}}$), or the **electromotive force** (emf) of the cell. The unit of electrical potential is the **volt** (abbreviated V), which is defined as 1 joule of work per coulomb of charge transferred.

How can we measure the cell potential? One possible instrument is a crude **voltmeter**, which works by drawing current through a known resistance. However, when current flows through a wire, the frictional heating that occurs wastes some of the potentially useful energy of the cell. A traditional voltmeter will therefore measure a potential that is less than the maximum cell potential. The key to determining the maximum potential is to do the measurement under conditions of zero current so that no energy is wasted. Traditionally, this has been accomplished by inserting a variable-voltage device (powered from an external source) in *opposition* to the cell potential. The voltage on this instrument (called a **potentiometer**) is adjusted until no current flows in the cell circuit. Under such conditions, the cell potential is equal in magnitude and opposite in sign to the voltage setting of the potentiometer. This value represents the *maximum* cell potential, since no energy is wasted heating the wire. More recently, advances in electronic technology have allowed the design of *digital voltmeters* that draw only a negligible amount of current (see Fig. 17.4). Since these instruments are more convenient to use, they have replaced potentiometers in the modern laboratory.

**FIGURE 17.4**

Digital voltmeters draw only a negligible current and are convenient to use.

17.2 Standard Reduction Potentials

The name *galvanic cell* honors Luigi Galvani (1737–1798), an Italian scientist generally credited with the discovery of electricity. These cells are sometimes called *voltaic cells* after Alessandro Volta (1745–1827), another Italian, who first constructed cells of this type around 1800.



An electrochemical cell with a measured potential of 1.10 V.

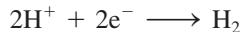
The reaction in a galvanic cell is always an oxidation–reduction reaction that can be broken down into two half-reactions. It would be convenient to assign a potential to *each* half-reaction so that when we construct a cell from a given pair of half-reactions we can obtain the cell potential by summing the half-cell potentials. For example, the observed potential for the cell shown in Fig. 17.5(a) is 0.76 V, and the cell reaction* is



For this cell, the anode compartment contains a zinc metal electrode with Zn^{2+} and SO_4^{2-} ions in aqueous solution. The anode reaction is the oxidation half-reaction:



The zinc metal, in producing Zn^{2+} ions that go into solution, is giving up electrons, which flow through the wire. For now, we will assume that all cell components are in their standard states, so in this case the solution in the anode compartment will contain 1 M Zn^{2+} . The cathode reaction of this cell is the reduction half-reaction:



The cathode consists of a platinum electrode (used because it is a chemically inert conductor) in contact with 1 M H^+ ions and bathed by hydrogen gas at 1 atm. Such an electrode, called the **standard hydrogen electrode**, is shown in Fig. 17.5(b).

Although we can measure the *total* potential of this cell (0.76 V), there is no way to measure the potentials of the individual electrode processes. Thus, if we want potentials for the half-reactions (half-cells), we must arbitrarily divide the total cell potential. For example, if we assign the reaction

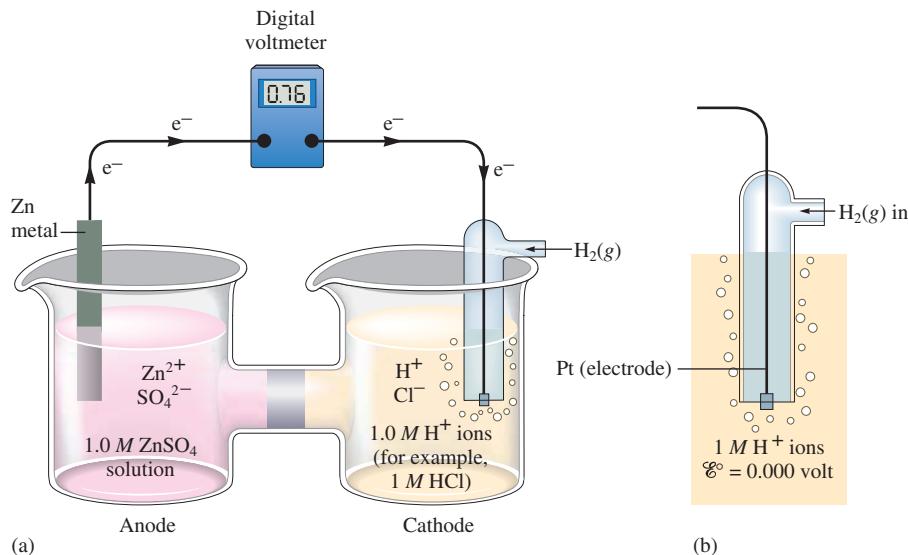
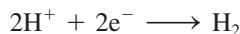


FIGURE 17.5

(a) A galvanic cell involving the reactions $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$ (at the anode) and $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ (at the cathode) has a potential of 0.76 V. (b) The standard hydrogen electrode where $\text{H}_2(\text{g})$ at 1 atm is passed over a platinum electrode in contact with 1 M H^+ ions. This electrode process (assuming ideal behavior) is arbitrarily assigned a value of exactly zero volts.

*In this text we will follow the convention of indicating the physical states of the reactants and products only in the overall redox reaction. For simplicity, half-reactions will *not* include the physical states.

where $[H^+] = 1 M$ and $P_{H_2} = 1 \text{ atm}$

a potential of exactly zero volts, then the reaction



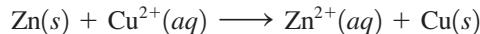
will have a potential of 0.76 V because

$$\mathcal{E}_{\text{cell}}^{\circ} = \mathcal{E}_{\text{H}^+ \rightarrow \text{H}_2}^{\circ} + \mathcal{E}_{\text{Zn} \rightarrow \text{Zn}^{2+}}^{\circ}$$

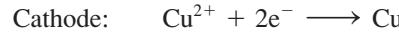
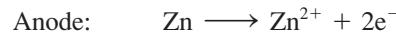
↑ ↑ ↑
0.76 V 0 V 0.76 V

where the superscript \circ indicates that *standard states* are employed. In fact, by setting the standard potential for the half-reaction $2\text{H}^+ + 2e^- \rightarrow \text{H}_2$ equal to zero, we can assign values to all other half-reactions.

For example, the measured potential for the cell shown in Fig. 17.6 is 1.10 V. The cell reaction is

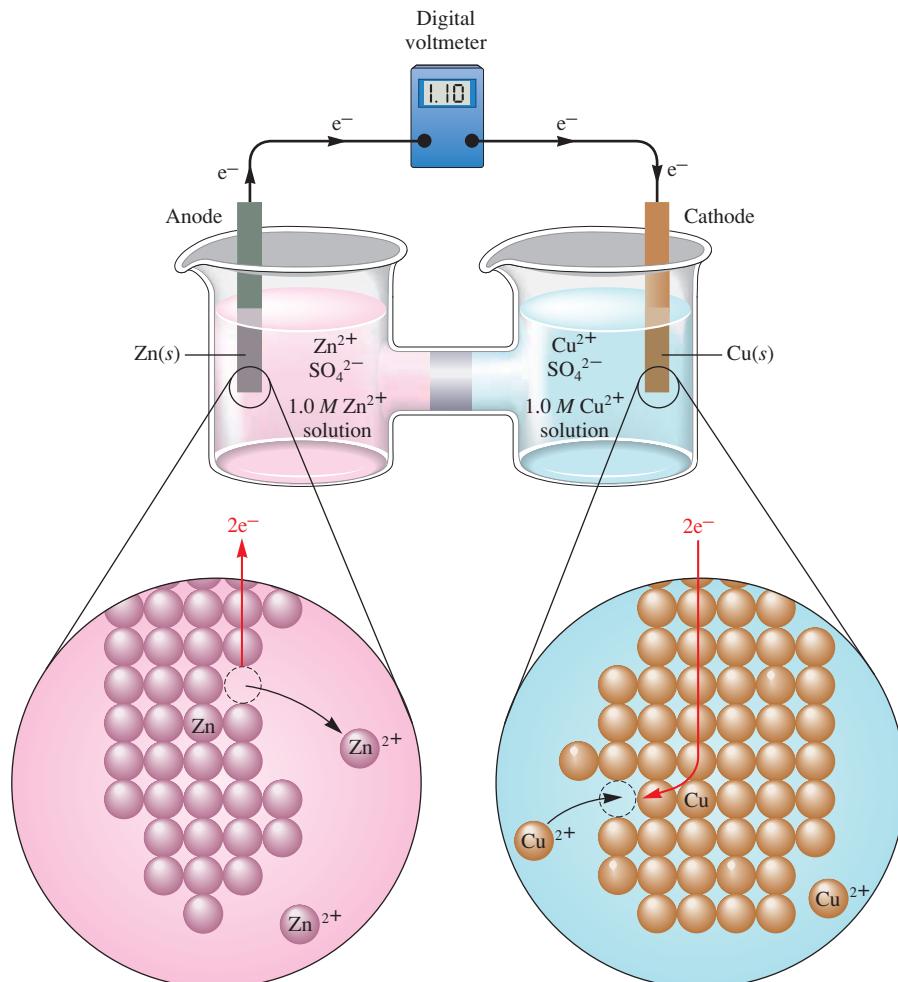


which can be divided into the half-reactions



Then

$$\mathcal{E}_{\text{cell}}^{\circ} = \mathcal{E}_{\text{Zn} \rightarrow \text{Zn}^{2+}}^{\circ} + \mathcal{E}_{\text{Cu}^{2+} \rightarrow \text{Cu}}^{\circ}$$



Standard states were discussed in Section 6.4.

 **Visualization: Zinc/Copper Cells with Lemons**

FIGURE 17.6

A galvanic cell involving the half-reactions $\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^-$ (anode) and $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$ (cathode), with $\mathcal{E}_{\text{cell}}^{\circ} = 1.10 \text{ V}$.

Since $\mathcal{E}_{\text{Zn} \rightarrow \text{Zn}^{2+}}^{\circ}$ was earlier assigned a value of 0.76 V, the value of $\mathcal{E}_{\text{Cu}^{2+} \rightarrow \text{Cu}}^{\circ}$ must be 0.34 V because

$$1.10 \text{ V} = 0.76 \text{ V} + 0.34 \text{ V}$$

The standard hydrogen potential is the reference potential against which all half-reaction potentials are assigned.

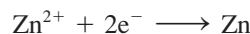
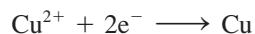
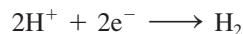


Visualization: Galvanic (Voltaic) Cells

All half-reactions are given as reduction processes in standard tables.

The scientific community has universally accepted the half-reaction potentials based on the assignment of zero volts to the process $2\text{H}^{+} + 2\text{e}^{-} \rightarrow \text{H}_2$ (under standard conditions where ideal behavior is assumed). However, before we can use these values to calculate cell potentials, we need to understand several essential characteristics of half-cell potentials.

The accepted convention is to give the potentials of half-reactions as *reduction* processes. For example:



The \mathcal{E}° values corresponding to reduction half-reactions with all solutes at 1 M and all gases at 1 atm are called **standard reduction potentials**. Standard reduction potentials for the most common half-reactions are given in Table 17.1 and Appendix 5.5.

Combining two half-reactions to obtain a balanced oxidation–reduction reaction often requires two manipulations:

1. One of the reduction half-reactions must be reversed (since redox reactions must involve a substance being oxidized and a substance being reduced). The half-reaction with the largest positive potential will run as written (as a reduction), and the other

TABLE 17.1 Standard Reduction Potentials at 25°C (298 K) for Many Common Half-Reactions

Half-Reaction	\mathcal{E}° (V)	Half-Reaction	\mathcal{E}° (V)
$\text{F}_2 + 2\text{e}^{-} \rightarrow 2\text{F}^{-}$	2.87	$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^{-} \rightarrow 4\text{OH}^{-}$	0.40
$\text{Ag}^{2+} + \text{e}^{-} \rightarrow \text{Ag}^{+}$	1.99	$\text{Cu}^{2+} + 2\text{e}^{-} \rightarrow \text{Cu}$	0.34
$\text{Co}^{3+} + \text{e}^{-} \rightarrow \text{Co}^{2+}$	1.82	$\text{Hg}_2\text{Cl}_2 + 2\text{e}^{-} \rightarrow 2\text{Hg} + 2\text{Cl}^{-}$	0.27
$\text{H}_2\text{O}_2 + 2\text{H}^{+} + 2\text{e}^{-} \rightarrow 2\text{H}_2\text{O}$	1.78	$\text{AgCl} + \text{e}^{-} \rightarrow \text{Ag} + \text{Cl}^{-}$	0.22
$\text{Ce}^{4+} + \text{e}^{-} \rightarrow \text{Ce}^{3+}$	1.70	$\text{SO}_4^{2-} + 4\text{H}^{+} + 2\text{e}^{-} \rightarrow \text{H}_2\text{SO}_3 + \text{H}_2\text{O}$	0.20
$\text{PbO}_2 + 4\text{H}^{+} + \text{SO}_4^{2-} + 2\text{e}^{-} \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O}$	1.69	$\text{Cu}^{2+} + \text{e}^{-} \rightarrow \text{Cu}^{+}$	0.16
$\text{MnO}_4^{-} + 4\text{H}^{+} + 3\text{e}^{-} \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$	1.68	$2\text{H}^{+} + 2\text{e}^{-} \rightarrow \text{H}_2$	0.00
$2\text{e}^{-} + 2\text{H}^{+} + \text{IO}_4^{-} \rightarrow \text{IO}_3^{-} + \text{H}_2\text{O}$	1.60	$\text{Fe}^{3+} + 3\text{e}^{-} \rightarrow \text{Fe}$	-0.036
$\text{MnO}_4^{-} + 8\text{H}^{+} + 5\text{e}^{-} \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	1.51	$\text{Pb}^{2+} + 2\text{e}^{-} \rightarrow \text{Pb}$	-0.13
$\text{Au}^{3+} + 3\text{e}^{-} \rightarrow \text{Au}$	1.50	$\text{Sn}^{2+} + 2\text{e}^{-} \rightarrow \text{Sn}$	-0.14
$\text{PbO}_2 + 4\text{H}^{+} + 2\text{e}^{-} \rightarrow \text{Pb}^{2+} + 2\text{H}_2\text{O}$	1.46	$\text{Ni}^{2+} + 2\text{e}^{-} \rightarrow \text{Ni}$	-0.23
$\text{Cl}_2 + 2\text{e}^{-} \rightarrow 2\text{Cl}^{-}$	1.36	$\text{PbSO}_4 + 2\text{e}^{-} \rightarrow \text{Pb} + \text{SO}_4^{2-}$	-0.35
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^{+} + 6\text{e}^{-} \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	1.33	$\text{Cd}^{2+} + 2\text{e}^{-} \rightarrow \text{Cd}$	-0.40
$\text{O}_2 + 4\text{H}^{+} + 4\text{e}^{-} \rightarrow 2\text{H}_2\text{O}$	1.23	$\text{Fe}^{2+} + 2\text{e}^{-} \rightarrow \text{Fe}$	-0.44
$\text{MnO}_2 + 4\text{H}^{+} + 2\text{e}^{-} \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}$	1.21	$\text{Cr}^{3+} + \text{e}^{-} \rightarrow \text{Cr}^{2+}$	-0.50
$\text{IO}_3^{-} + 6\text{H}^{+} + 5\text{e}^{-} \rightarrow \frac{1}{2}\text{I}_2 + 3\text{H}_2\text{O}$	1.20	$\text{Cr}^{3+} + 3\text{e}^{-} \rightarrow \text{Cr}$	-0.73
$\text{Br}_2 + 2\text{e}^{-} \rightarrow 2\text{Br}^{-}$	1.09	$\text{Zn}^{2+} + 2\text{e}^{-} \rightarrow \text{Zn}$	-0.76
$\text{VO}_2^{+} + 2\text{H}^{+} + \text{e}^{-} \rightarrow \text{VO}^{2+} + \text{H}_2\text{O}$	1.00	$2\text{H}_2\text{O} + 2\text{e}^{-} \rightarrow \text{H}_2 + 2\text{OH}^{-}$	-0.83
$\text{AuCl}_4^{-} + 3\text{e}^{-} \rightarrow \text{Au} + 4\text{Cl}^{-}$	0.99	$\text{Mn}^{2+} + 2\text{e}^{-} \rightarrow \text{Mn}$	-1.18
$\text{NO}_3^{-} + 4\text{H}^{+} + 3\text{e}^{-} \rightarrow \text{NO} + 2\text{H}_2\text{O}$	0.96	$\text{Al}^{3+} + 3\text{e}^{-} \rightarrow \text{Al}$	-1.66
$\text{ClO}_2 + \text{e}^{-} \rightarrow \text{ClO}_2^{-}$	0.954	$\text{H}_2 + 2\text{e}^{-} \rightarrow 2\text{H}^{-}$	-2.23
$2\text{Hg}^{2+} + 2\text{e}^{-} \rightarrow \text{Hg}_2^{2+}$	0.91	$\text{Mg}^{2+} + 2\text{e}^{-} \rightarrow \text{Mg}$	-2.37
$\text{Ag}^{+} + \text{e}^{-} \rightarrow \text{Ag}$	0.80	$\text{La}^{3+} + 3\text{e}^{-} \rightarrow \text{La}$	-2.37
$\text{Hg}_2^{2+} + 2\text{e}^{-} \rightarrow 2\text{Hg}$	0.80	$\text{Na}^{+} + \text{e}^{-} \rightarrow \text{Na}$	-2.71
$\text{Fe}^{3+} + \text{e}^{-} \rightarrow \text{Fe}^{2+}$	0.77	$\text{Ca}^{2+} + 2\text{e}^{-} \rightarrow \text{Ca}$	-2.76
$\text{O}_2 + 2\text{H}^{+} + 2\text{e}^{-} \rightarrow \text{H}_2\text{O}_2$	0.68	$\text{Ba}^{2+} + 2\text{e}^{-} \rightarrow \text{Ba}$	-2.90
$\text{MnO}_4^{-} + \text{e}^{-} \rightarrow \text{MnO}_4^{2-}$	0.56	$\text{K}^{+} + \text{e}^{-} \rightarrow \text{K}$	-2.92
$\text{I}_2 + 2\text{e}^{-} \rightarrow 2\text{I}^{-}$	0.54	$\text{Li}^{+} + \text{e}^{-} \rightarrow \text{Li}$	-3.05
$\text{Cu}^{+} + \text{e}^{-} \rightarrow \text{Cu}$	0.52		

When a half-reaction is reversed, the sign of \mathcal{E}° is reversed.

When a half-reaction is multiplied by an integer, \mathcal{E}° remains the same.



- Visualization: Copper Metal in Water
- Visualization: Copper Metal in Sulfuric Acid
- Visualization: Copper Metal in Hydrochloric Acid
- Visualization: Copper Metal in Nitric Acid

half-reaction will be forced to run in reverse (will be the oxidation reaction). The net potential of the cell will be the *difference* between the two. Since the reduction process occurs at the cathode and the oxidation process occurs at the anode, we can write

$$\mathcal{E}_{\text{cell}}^\circ = \mathcal{E}^\circ(\text{cathode}) - \mathcal{E}^\circ(\text{anode})$$

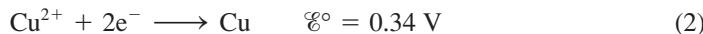
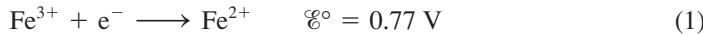
Because subtraction means “change the sign and add,” in the examples done here we will change the sign of the oxidation (anode) reaction when we reverse it and add it to the reduction (cathode) reaction.

- Since the number of electrons lost must equal the number gained, the half-reactions must be multiplied by integers as necessary to achieve the balanced equation. However, the *value* of \mathcal{E}° is *not changed* when a half-reaction is multiplied by an integer. Since a standard reduction potential is an *intensive property* (it does not depend on how many times the reaction occurs), the potential is *not* multiplied by the integer required to balance the cell reaction.

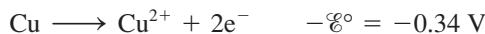
Consider a galvanic cell based on the redox reaction



The pertinent half-reactions are



To balance the cell reaction and calculate the standard cell potential, reaction (2) must be reversed:

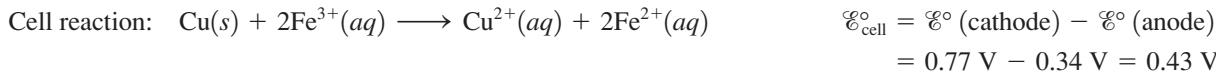


Note the change in sign for the \mathcal{E}° value. Now, since each Cu atom produces two electrons but each Fe^{3+} ion accepts only one electron, reaction (1) must be multiplied by 2:



Note that \mathcal{E}° is not changed in this case.

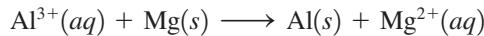
Now we can obtain the balanced cell reaction by summing the appropriately modified half-reactions:



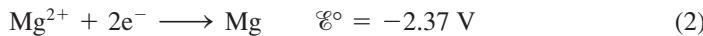
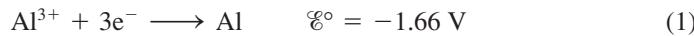
Sample Exercise 17.1

Galvanic Cells

- Consider a galvanic cell based on the reaction



The half-reactions are

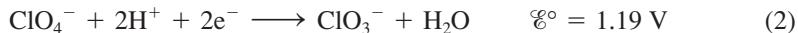
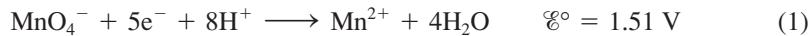


Give the balanced cell reaction and calculate \mathcal{E}° for the cell.

- A galvanic cell is based on the reaction



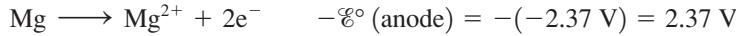
The half-reactions are



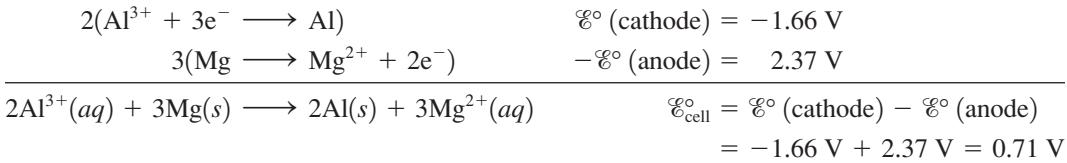
Give the balanced cell reaction and calculate \mathcal{E}° for the cell.

Solution

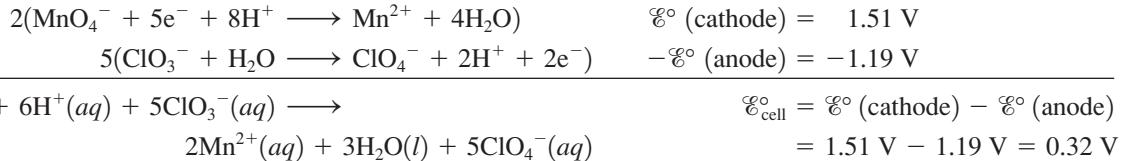
- a. The half-reaction involving magnesium must be reversed and since this is the oxidation process, it is the anode:



Also, since the two half-reactions involve different numbers of electrons, they must be multiplied by integers as follows:



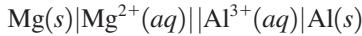
- b. Half-reaction (2) must be reversed (it is the anode), and both half-reactions must be multiplied by integers to make the number of electrons equal:



See Exercises 17.27 and 17.28.

Line Notation

We now will introduce a handy line notation used to describe electrochemical cells. In this notation the anode components are listed on the left and the cathode components are listed on the right, separated by double vertical lines (indicating the salt bridge or porous disk). For example, the line notation for the cell described in Sample Exercise 17.1(a) is



In this notation a phase difference (boundary) is indicated by a single vertical line. Thus, in this case, vertical lines occur between the solid Mg metal and the Mg^{2+} in aqueous solution and between solid Al and Al^{3+} in aqueous solution. Also note that the substance constituting the anode is listed at the far left and the substance constituting the cathode is listed at the far right.

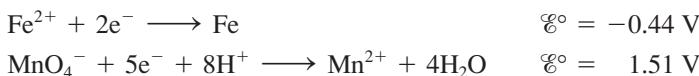
For the cell described in Sample Exercise 17.1(b), all the components involved in the oxidation–reduction reaction are ions. Since none of these dissolved ions can serve as an electrode, a nonreacting (inert) conductor must be used. The usual choice is platinum. Thus, for the cell described in Sample Exercise 17.1(b), the line notation is



Complete Description of a Galvanic Cell

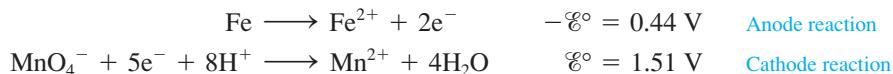
Next we want to consider how to describe a galvanic cell fully, given just its half-reactions. This description will include the cell reaction, the cell potential, and the

physical setup of the cell. Let's consider a galvanic cell based on the following half-reactions:



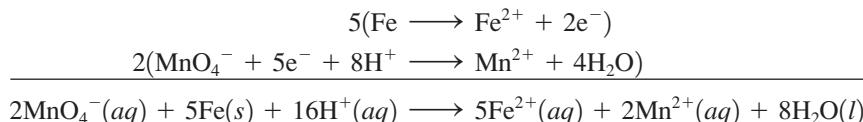
In a working galvanic cell, one of these reactions must run in reverse. Which one?

We can answer this question by considering the sign of the potential of a working cell: *A cell will always run spontaneously in the direction that produces a positive cell potential.* Thus, in the present case, it is clear that the half-reaction involving iron must be reversed, since this choice leads to a positive cell potential:



where $E_{\text{cell}}^\circ = E^\circ(\text{cathode}) - E^\circ(\text{anode}) = 1.51 \text{ V} + 0.44 \text{ V} = 1.95 \text{ V}$

The balanced cell reaction is obtained as follows:

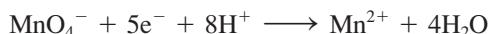


Now consider the physical setup of the cell, shown schematically in Fig. 17.7. In the left compartment the active components in their standard states are pure metallic iron (Fe) and 1.0 M Fe^{2+} . The anion present depends on the iron salt used. In this compartment the anion does not participate in the reaction but simply balances the charge. The half-reaction that takes place at this electrode is



which is an oxidation reaction, so this compartment is the anode. The electrode consists of pure iron metal.

In the right compartment the active components in their standard states are 1.0 M MnO_4^- , 1.0 M H^+ , and 1.0 M Mn^{2+} , with appropriate unreacting ions (often called *countercations*) to balance the charge. The half-reaction in this compartment is



which is a reduction reaction, so this compartment is the cathode. Since neither MnO_4^- nor Mn^{2+} ions can serve as the electrode, a nonreacting conductor such as platinum must be employed.

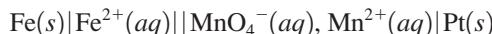
The next step is to determine the direction of electron flow. In the left compartment the half-reaction involves the oxidation of iron:



In the right compartment the half-reaction is the reduction of MnO_4^- :



Thus the electrons flow from Fe to MnO_4^- in this cell, or from the anode to the cathode, as is always the case. The line notation for this cell is



A complete description of a galvanic cell usually includes four items:

- The cell potential (always positive for a galvanic cell where $E_{\text{cell}}^\circ = E^\circ(\text{cathode}) - E^\circ(\text{anode})$ and the balanced cell reaction).
- The direction of electron flow, obtained by inspecting the half-reactions and using the direction that gives a positive E_{cell}° .

A galvanic cell runs spontaneously in the direction that gives a positive value for E_{cell}° .

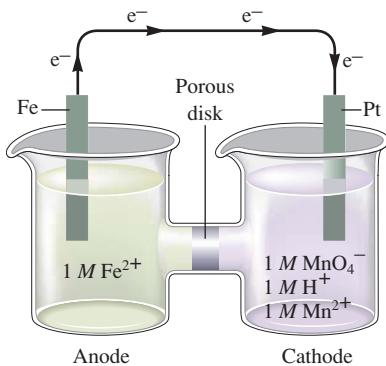
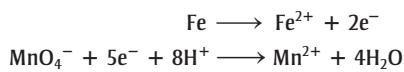


FIGURE 17.7

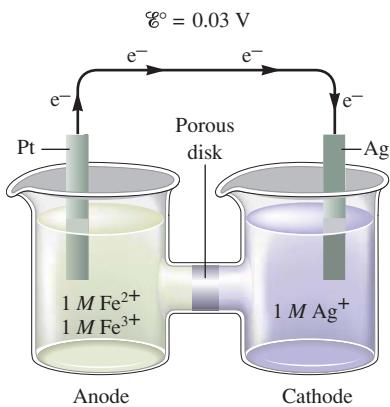
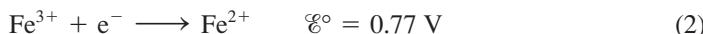
The schematic of a galvanic cell based on the half-reactions:



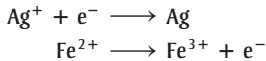
- Designation of the anode and cathode.
- The nature of each electrode and the ions present in each compartment. A chemically inert conductor is required if none of the substances participating in the half-reaction is a conducting solid.

Sample Exercise 17.2**Description of a Galvanic Cell**

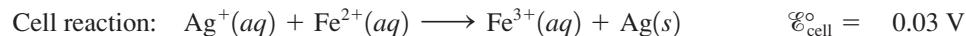
Describe completely the galvanic cell based on the following half-reactions under standard conditions:

**FIGURE 17.8**

Schematic diagram for the galvanic cell based on the half-reactions

**Solution**

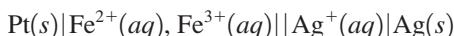
Item 1 Since a positive $\mathcal{E}_{\text{cell}}^\circ$ value is required, reaction (2) must run in reverse:



Item 2 Since Ag^+ receives electrons and Fe^{2+} loses electrons in the cell reaction, the electrons will flow from the compartment containing Fe^{2+} to the compartment containing Ag^+ .

Item 3 Oxidation occurs in the compartment containing Fe^{2+} (electrons flow from Fe^{2+} to Ag^+). Hence this compartment functions as the anode. Reduction occurs in the compartment containing Ag^+ , so this compartment functions as the cathode.

Item 4 The electrode in the Ag/Ag^+ compartment is silver metal, and an inert conductor, such as platinum, must be used in the $\text{Fe}^{2+}/\text{Fe}^{3+}$ compartment. Appropriate counterions are assumed to be present. The diagram for this cell is shown in Fig. 17.8. The line notation for this cell is



See Exercises 17.29 and 17.30.

17.3 Cell Potential, Electrical Work, and Free Energy

So far we have considered electrochemical cells in a very practical fashion without much theoretical background. The next step will be to explore the relationship between thermodynamics and electrochemistry.

The work that can be accomplished when electrons are transferred through a wire depends on the “push” (the thermodynamic driving force) behind the electrons. This driving force (the emf) is defined in terms of a *potential difference* (in volts) between two points in the circuit. Recall that a volt represents a joule of work per coulomb of charge transferred:

$$\text{emf} = \text{potential difference (V)} = \frac{\text{work (J)}}{\text{charge (C)}}$$

Thus 1 joule of work is produced or required (depending on the direction) when 1 coulomb of charge is transferred between two points in the circuit that differ by a potential of 1 volt.

In this book, *work is viewed from the point of view of the system*. Thus work flowing out of the system is indicated by a minus sign. When a cell produces a current, the cell



Using a battery-powered drill to insert a screw.

potential is positive, and the current can be used to do work—to run a motor, for instance. Thus the cell potential \mathcal{E} and the work w have opposite signs:

$$\mathcal{E} = \frac{-w}{q} \begin{array}{l} \leftarrow \text{Work} \\ \leftarrow \text{Charge} \end{array}$$

Therefore,

$$-w = q\mathcal{E}$$

From this equation it can be seen that the maximum work in a cell would be obtained at the maximum cell potential:

$$-w_{\max} = q\mathcal{E}_{\max} \quad \text{or} \quad w_{\max} = -q\mathcal{E}_{\max}$$

Work is never the maximum possible if any current is flowing.

However, there is a problem. To obtain electrical work, current must flow. When current flows, some energy is inevitably wasted through frictional heating, and the maximum work is not obtained. This reflects the important general principle introduced in Section 16.9: *In any real, spontaneous process some energy is always wasted—the actual work realized is always less than the calculated maximum.* This is a consequence of the fact that the entropy of the universe must increase in any spontaneous process. Recall from Section 16.9 that the only process from which maximum work could be realized is the hypothetical reversible process. For a galvanic cell this would involve an infinitesimally small current flow and thus an infinite amount of time to do the work. Even though we can never achieve the maximum work through the actual discharge of a galvanic cell, we can measure the maximum potential. There is negligible current flow when a cell potential is measured with a potentiometer or an efficient digital voltmeter. No current flow implies no waste of energy, so the potential measured is the maximum.

Although we can never actually realize the maximum work from a cell reaction, the value for it is still useful in evaluating the efficiency of a real process based on the cell reaction. For example, suppose a certain galvanic cell has a maximum potential (at zero current) of 2.50 V. In a particular experiment 1.33 moles of electrons were passed through this cell at an average actual potential of 2.10 V. The actual work done is

$$w = -q\mathcal{E}$$

where \mathcal{E} represents the actual potential difference at which the current flowed (2.10 V or 2.10 J/C) and q is the quantity of charge in coulombs transferred. The charge on 1 mole of electrons is a constant called the **faraday** (abbreviated F), which has the value $96,485 \text{ coulombs of charge per mole of electrons}$. Thus q equals the number of moles of electrons times the charge per mole of electrons:

$$q = nF = 1.33 \text{ mol e}^- \times 96,485 \text{ C/mol e}^-$$

Then, for the preceding experiment, the actual work is

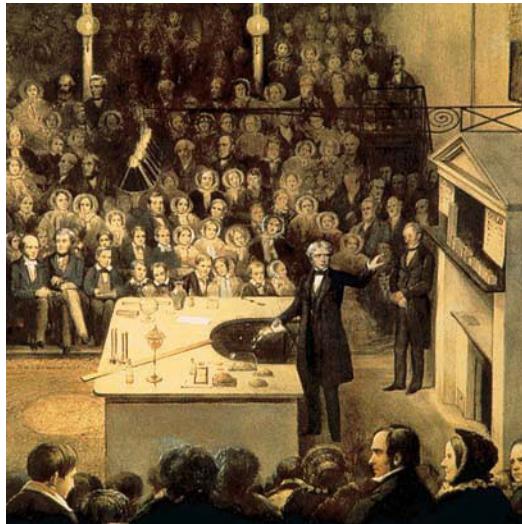
$$\begin{aligned} w &= -q\mathcal{E} = -(1.33 \text{ mol e}^- \times 96,485 \text{ C/mol e}^-) \times (2.10 \text{ J/C}) \\ &= -2.69 \times 10^5 \text{ J} \end{aligned}$$

For the maximum possible work, the calculation is similar, except that the maximum potential is used:

$$\begin{aligned} w_{\max} &= -q\mathcal{E} \\ &= -\left(1.33 \text{ mol e}^- \times 96,485 \frac{\text{C}}{\text{mol e}^-}\right)\left(2.50 \frac{\text{J}}{\text{C}}\right) \\ &= -3.21 \times 10^5 \text{ J} \end{aligned}$$

Thus, in its actual operation, the efficiency of this cell is

$$\frac{w}{w_{\max}} \times 100\% = \frac{-2.69 \times 10^5 \text{ J}}{-3.21 \times 10^5 \text{ J}} \times 100\% = 83.8\%$$



Michael Faraday lecturing at the Royal Institution before Prince Albert and others (1855). The faraday was named in honor of Michael Faraday (1791–1867), an Englishman who may have been the greatest experimental scientist of the nineteenth century. Among his many achievements were the invention of the electric motor and generator and the development of the principles of electrolysis.

Next we want to relate the potential of a galvanic cell to free energy. In Section 16.9 we saw that for a process carried out at constant temperature and pressure, the change in free energy equals the maximum useful work obtainable from that process:

$$w_{\max} = \Delta G$$

For a galvanic cell,

$$w_{\max} = -q\mathcal{E}_{\max} = \Delta G$$

Since

$$q = nF$$

we have

$$\Delta G = -q\mathcal{E}_{\max} = -nF\mathcal{E}_{\max}$$

From now on the subscript on \mathcal{E}_{\max} will be deleted, with the understanding that any potential given in this book is the maximum potential. Thus

$$\Delta G = -nF\mathcal{E}$$

For standard conditions,

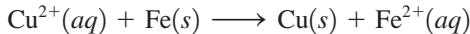
$$\Delta G^\circ = -nF\mathcal{E}^\circ$$

This equation states that *the maximum cell potential is directly related to the free energy difference between the reactants and the products in the cell.* This relationship is important because it provides an experimental means to obtain ΔG for a reaction. It also confirms that a galvanic cell will run in the direction that gives a positive value for $\mathcal{E}_{\text{cell}}$; a positive $\mathcal{E}_{\text{cell}}$ value corresponds to a negative ΔG value, which is the condition for spontaneity.

Sample Exercise 17.3

Calculating ΔG° for a Cell Reaction

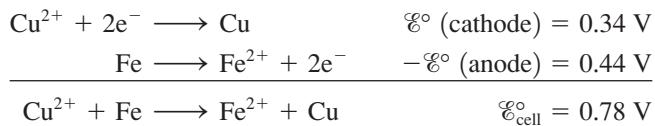
Using the data in Table 17.1, calculate ΔG° for the reaction



Is this reaction spontaneous?

Solution

The half-reactions are



We can calculate ΔG° from the equation

$$\Delta G^\circ = -nF\mathcal{E}^\circ$$

Since two electrons are transferred per atom in the reaction, 2 moles of electrons are required per mole of reactants and products. Thus $n = 2 \text{ mol e}^-$, $F = 96,485 \text{ C/mol e}^-$, and $\mathcal{E}^\circ = 0.78 \text{ V} = 0.78 \text{ J/C}$. Therefore,

$$\begin{aligned}\Delta G^\circ &= -(2 \text{ mol e}^-) \left(96,485 \frac{\text{C}}{\text{mol e}^-} \right) \left(0.78 \frac{\text{J}}{\text{C}} \right) \\ &= -1.5 \times 10^5 \text{ J}\end{aligned}$$

The process is spontaneous, as indicated by both the negative sign of ΔG° and the positive sign of $\mathcal{E}_{\text{cell}}^\circ$.

This reaction is used industrially to deposit copper metal from solutions resulting from the dissolving of copper ores.

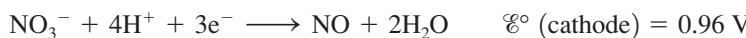
See Exercises 17.37 and 17.38.

Sample Exercise 17.4**Predicting Spontaneity**

Using the data from Table 17.1, predict whether 1 M HNO₃ will dissolve gold metal to form a 1 M Au³⁺ solution.

Solution

The half-reaction for HNO₃ acting as an oxidizing agent is



The reaction for the oxidation of solid gold to Au³⁺ ions is



The sum of these half-reactions gives the required reaction:



and $\mathcal{E}_{\text{cell}}^\circ = \mathcal{E}^\circ \text{ (cathode)} - \mathcal{E}^\circ \text{ (anode)} = 0.96 \text{ V} - 1.50 \text{ V} = -0.54 \text{ V}$

Since the \mathcal{E}° value is negative, the process will *not* occur under standard conditions. That is, gold will not dissolve in 1 M HNO₃ to give 1 M Au³⁺. In fact, a mixture (1:3 by volume) of concentrated nitric and hydrochloric acids, called *aqua regia*, is required to dissolve gold.

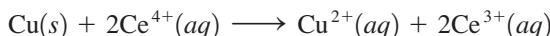
See Exercises 17.37 and 17.38.



A gold ring does not dissolve in nitric acid.

17.4 Dependence of Cell Potential on Concentration

So far we have described cells under standard conditions. In this section we consider the dependence of the cell potential on concentration. Under standard conditions (all concentrations 1 M), the cell with the reaction

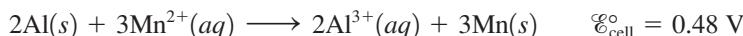


has a potential of 1.36 V. What will the cell potential be if [Ce⁴⁺] is greater than 1.0 M? This question can be answered qualitatively in terms of Le Châtelier's principle. An increase in the concentration of Ce⁴⁺ will favor the forward reaction and thus increase the driving force on the electrons. The cell potential will increase. On the other hand, an increase in the concentration of a product (Cu²⁺ or Ce³⁺) will oppose the forward reaction, thus decreasing the cell potential.

These ideas are illustrated in Sample Exercise 17.5.

Sample Exercise 17.5**The Effects of Concentration on \mathcal{E}**

For the cell reaction



predict whether $\mathcal{E}_{\text{cell}}$ is larger or smaller than $\mathcal{E}_{\text{cell}}^\circ$ for the following cases.

- a. $[\text{Al}^{3+}] = 2.0 \text{ M}$, $[\text{Mn}^{2+}] = 1.0 \text{ M}$
- b. $[\text{Al}^{3+}] = 1.0 \text{ M}$, $[\text{Mn}^{2+}] = 3.0 \text{ M}$

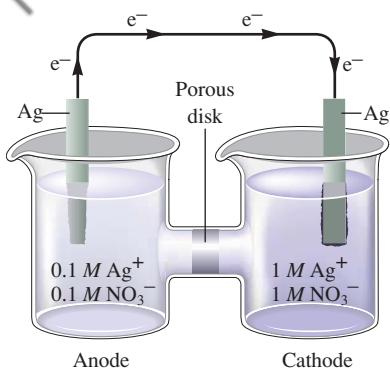
Solution

- a. A product concentration has been raised above 1.0 M. This will oppose the cell reaction and will cause $\mathcal{E}_{\text{cell}}$ to be less than $\mathcal{E}_{\text{cell}}^\circ$ ($\mathcal{E}_{\text{cell}} < 0.48 \text{ V}$).
- b. A reactant concentration has been increased above 1.0 M, and $\mathcal{E}_{\text{cell}}$ will be greater than $\mathcal{E}_{\text{cell}}^\circ$ ($\mathcal{E}_{\text{cell}} > 0.48 \text{ V}$).

See Exercise 17.51.



A concentration cell with 1.0 M Cu²⁺ on the right and 0.010 M Cu²⁺ on the left.

**FIGURE 17.9**

A concentration cell that contains a silver electrode and aqueous silver nitrate in both compartments. Because the right compartment contains 1 M Ag^+ and the left compartment contains 0.1 M Ag^+ , there will be a driving force to transfer electrons from left to right. Silver will be deposited on the right electrode, thus lowering the concentration of Ag^+ in the right compartment. In the left compartment the silver electrode dissolves (producing Ag^+ ions) to raise the concentration of Ag^+ in solution.

Concentration Cells

Because cell potentials depend on concentration, we can construct galvanic cells where both compartments contain the same components but at different concentrations. For example, in the cell in Fig. 17.9, both compartments contain aqueous AgNO_3 , but with different molarities. Let's consider the potential of this cell and the direction of electron flow. The half-reaction relevant to both compartments of this cell is



If the cell had 1 M Ag^+ in both compartments,

$$\mathcal{E}_{\text{cell}}^\circ = 0.80\text{ V} - 0.80\text{ V} = 0\text{ V}$$

However, in the cell described here, the concentrations of Ag^+ in the two compartments are 1 M and 0.1 M . Because the concentrations of Ag^+ are unequal, the half-cell potentials will not be identical, and the cell will exhibit a positive voltage. In which direction will the electrons flow in this cell? The best way to think about this question is to recognize that nature will try to equalize the concentrations of Ag^+ in the two compartments. This can be done by transferring electrons from the compartment containing 0.1 M Ag^+ to the one containing 1 M Ag^+ (left to right in Fig. 17.9). This electron transfer will produce more Ag^+ in the left compartment and consume Ag^+ (to form Ag) in the right compartment.

A cell in which both compartments have the same components but at different concentrations is called a **concentration cell**. The difference in concentration is the only factor that produces a cell potential in this case, and the voltages are typically small.

Sample Exercise 17.6

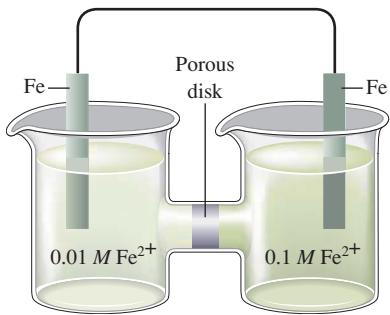
Concentration Cells

Determine the direction of electron flow and designate the anode and cathode for the cell represented in Fig. 17.10.

Solution

The concentrations of Fe^{2+} ion in the two compartments can (eventually) be equalized by transferring electrons from the left compartment to the right. This will cause Fe^{2+} to be formed in the left compartment, and iron metal will be deposited (by reducing Fe^{2+} ions to Fe) on the right electrode. Since electron flow is from left to right, oxidation occurs in the left compartment (the anode) and reduction occurs in the right (the cathode).

See Exercise 17.52.

**FIGURE 17.10**

A concentration cell containing iron electrodes and different concentrations of Fe^{2+} ion in the two compartments.

The Nernst Equation

The dependence of the cell potential on concentration results directly from the dependence of free energy on concentration. Recall from Chapter 16 that the equation

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

where Q is the reaction quotient, was used to calculate the effect of concentration on ΔG . Since $\Delta G = -nF\mathcal{E}$ and $\Delta G^\circ = -nF\mathcal{E}^\circ$, the equation becomes

$$-nF\mathcal{E} = -nF\mathcal{E}^\circ + RT \ln(Q)$$

Dividing each side of the equation by $-nF$ gives

$$\mathcal{E} = \mathcal{E}^\circ - \frac{RT}{nF} \ln(Q) \quad (17.1)$$

Nernst was one of the pioneers in the development of electrochemical theory and is generally given credit for first stating the third law of thermodynamics. He won the Nobel Prize in chemistry in 1920.

Equation (17.1), which gives the relationship between the cell potential and the concentrations of the cell components, is commonly called the **Nernst equation**, after the German chemist Walther Hermann Nernst (1864–1941).

The Nernst equation is often given in a form that is valid at 25°C:

$$\mathcal{E} = \mathcal{E}^\circ - \frac{0.0591}{n} \log(Q)$$

Using this relationship, we can calculate the potential of a cell in which some or all of the components are not in their standard states.

For example, $\mathcal{E}_{\text{cell}}^\circ$ is 0.48 V for the galvanic cell based on the reaction



Consider a cell in which

$$[\text{Mn}^{2+}] = 0.50 \text{ M} \quad \text{and} \quad [\text{Al}^{3+}] = 1.50 \text{ M}$$

The cell potential at 25°C for these concentrations can be calculated using the Nernst equation:

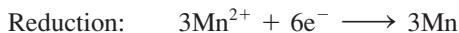
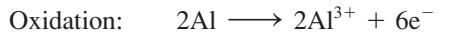
$$\mathcal{E}_{\text{cell}} = \mathcal{E}_{\text{cell}}^\circ - \frac{0.0591}{n} \log(Q)$$

We know that

$$\mathcal{E}_{\text{cell}}^\circ = 0.48 \text{ V}$$

$$\text{and} \quad Q = \frac{[\text{Al}^{3+}]^2}{[\text{Mn}^{2+}]^3} = \frac{(1.50)^2}{(0.50)^3} = 18$$

Since the half-reactions are



we know that

$$n = 6$$

$$\begin{aligned} \text{Thus} \quad \mathcal{E}_{\text{cell}} &= 0.48 - \frac{0.0591}{6} \log(18) \\ &= 0.48 - \frac{0.0591}{6} (1.26) = 0.48 - 0.01 = 0.47 \text{ V} \end{aligned}$$

Note that the cell voltage decreases slightly because of the nonstandard concentrations. This change is consistent with the predictions of Le Châtelier's principle (see Sample Exercise 17.5). In this case, since the reactant concentration is lower than 1.0 M and the product concentration is higher than 1.0 M, $\mathcal{E}_{\text{cell}}$ is less than $\mathcal{E}_{\text{cell}}^\circ$.

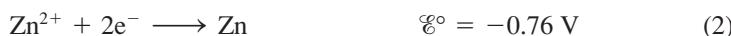
The potential calculated from the Nernst equation is the maximum potential before any current flow has occurred. As the cell discharges and current flows from anode to cathode, the concentrations will change, and as a result, $\mathcal{E}_{\text{cell}}$ will change. In fact, *the cell will spontaneously discharge until it reaches equilibrium*, at which point

$$Q = K \text{ (the equilibrium constant)} \quad \text{and} \quad \mathcal{E}_{\text{cell}} = 0$$

A “dead” battery is one in which the cell reaction has reached equilibrium, and there is no longer any chemical driving force to push electrons through the wire. In other words, *at equilibrium, the components in the two cell compartments have the same free energy*, and $\Delta G = 0$ for the cell reaction at the equilibrium concentrations. The cell no longer has the ability to do work.

Sample Exercise 17.7**The Nernst Equation**

Describe the cell based on the following half-reactions:



where

$$T = 25^\circ\text{C}$$

$$[\text{VO}_2^+] = 2.0 \text{ M}$$

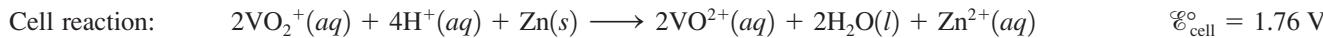
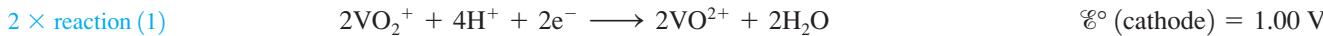
$$[\text{H}^+] = 0.50 \text{ M}$$

$$[\text{VO}^{2+}] = 1.0 \times 10^{-2} \text{ M}$$

$$[\text{Zn}^{2+}] = 1.0 \times 10^{-1} \text{ M}$$

Solution

The balanced cell reaction is obtained by reversing reaction (2) and multiplying reaction (1) by 2:



Since the cell contains components at concentrations other than 1 M, we must use the Nernst equation, where $n = 2$ (since two electrons are transferred), to calculate the cell potential. At 25°C we can use the equation

$$\begin{aligned} \mathcal{E} &= \mathcal{E}_{\text{cell}}^\circ - \frac{0.0591}{n} \log(Q) \\ &= 1.76 - \frac{0.0591}{2} \log\left(\frac{[\text{Zn}^{2+}][\text{VO}^{2+}]^2}{[\text{VO}_2^+]^2[\text{H}^+]^4}\right) \\ &= 1.76 - \frac{0.0591}{2} \log\left(\frac{(1.0 \times 10^{-1})(1.0 \times 10^{-2})^2}{(2.0)^2(0.50)^4}\right) \\ &= 1.76 - \frac{0.0591}{2} \log(4 \times 10^{-5}) = 1.76 + 0.13 = 1.89 \text{ V} \end{aligned}$$

The cell diagram is given in Fig. 17.11.

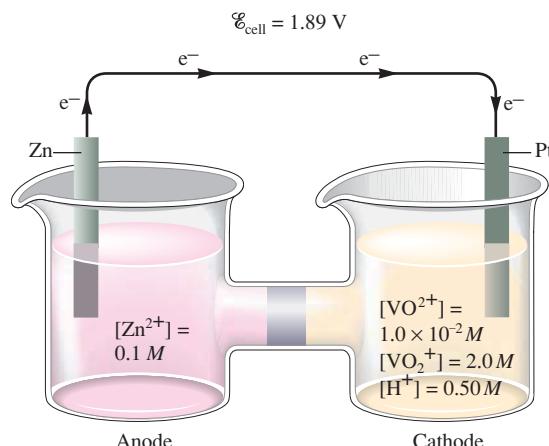


FIGURE 17.11

Schematic diagram of the cell described in Sample Exercise 17.7.

See Exercises 17.55 through 17.58.

FIGURE 17.12

A glass electrode contains a reference solution of dilute hydrochloric acid in contact with a thin glass membrane in which a silver wire coated with silver chloride has been embedded. When the electrode is dipped into a solution containing H^+ ions, the electrode potential is determined by the difference in $[\text{H}^+]$ between the two solutions.



Ion-Selective Electrodes

Because the cell potential is sensitive to the concentrations of the reactants and products involved in the cell reaction, measured potentials can be used to determine the concentration of an ion. A pH meter (see Fig. 14.9) is a familiar example of an instrument that measures concentration using an observed potential. The pH meter has three main components: a standard electrode of known potential, a special **glass electrode** that changes potential depending on the concentration of H^+ ions in the solution into which it is dipped, and a potentiometer that measures the potential between the electrodes. The potentiometer reading is automatically converted electronically to a direct reading of the pH of the solution being tested.

The glass electrode (see Fig. 17.12) contains a reference solution of dilute hydrochloric acid in contact with a thin glass membrane. The electrical potential of the glass electrode depends on the difference in $[\text{H}^+]$ between the reference solution and the solution into which the electrode is dipped. Thus the electrical potential varies with the pH of the solution being tested.

Electrodes that are sensitive to the concentration of a particular ion are called **ion-selective electrodes**, of which the glass electrode for pH measurement is just one example. Glass electrodes can be made sensitive to such ions as Na^+ , K^+ , or NH_4^+ by changing the composition of the glass. Other ions can be detected if an appropriate crystal replaces the glass membrane. For example, a crystal of lanthanum(III) fluoride (LaF_3) can be used in an electrode to measure $[\text{F}^-]$. Solid silver sulfide (Ag_2S) can be used to measure $[\text{Ag}^+]$ and $[\text{S}^{2-}]$. Some of the ions that can be detected by ion-selective electrodes are listed in Table 17.2.

TABLE 17.2 Some Ions Whose Concentrations Can Be Detected by Ion-Selective Electrodes

Cations	Anions
H^+	Br^-
Cd^{2+}	Cl^-
Ca^{2+}	CN^-
Cu^{2+}	F^-
K^+	NO_3^-
Ag^+	S^{2-}
Na^+	

Calculation of Equilibrium Constants for Redox Reactions

The quantitative relationship between \mathcal{E}° and ΔG° allows calculation of equilibrium constants for redox reactions. For a cell at equilibrium,

$$\mathcal{E}_{\text{cell}} = 0 \quad \text{and} \quad Q = K$$

Applying these conditions to the Nernst equation valid at 25°C,

$$\mathcal{E} = \mathcal{E}^\circ - \frac{0.0591}{n} \log(Q)$$

gives

$$0 = \mathcal{E}^\circ - \frac{0.0591}{n} \log(K)$$

or

$$\log(K) = \frac{n\mathcal{E}^\circ}{0.0591} \quad \text{at } 25^\circ\text{C}$$

Sample Exercise 17.8**Equilibrium Constants from Cell Potentials**

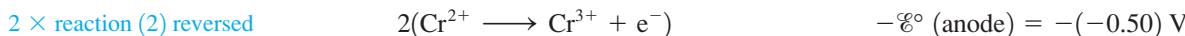
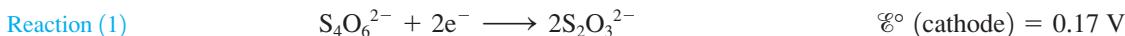
For the oxidation-reduction reaction



the appropriate half-reactions are

Balance the redox reaction, and calculate \mathcal{E}° and K (at 25°C).**Solution**

To obtain the balanced reaction, we must reverse reaction (2), multiply it by 2, and add it to reaction (1):

In this reaction, 2 moles of electrons are transferred for every unit of reaction, that is, for every 2 mol Cr^{2+} reacting with 1 mol $\text{S}_4\text{O}_6^{2-}$ to form 2 mol Cr^{3+} and 2 mol $\text{S}_2\text{O}_3^{2-}$. Thus $n = 2$. Then

$$\log(K) = \frac{n\mathcal{E}^\circ}{0.0591} = \frac{2(0.67)}{0.0591} = 22.6$$

The value of K is found by taking the antilog of 22.6:

$$K = 10^{22.6} = 4 \times 10^{22}$$

This very large equilibrium constant is not unusual for a redox reaction.

See Exercises 17.65, 17.66, 17.69, and 17.70.

The blue solution contains Cr^{2+} ions, and the green solution contains Cr^{3+} ions.

17.5 Batteries

A **battery** is a galvanic cell or, more commonly, a group of galvanic cells connected in series, where the potentials of the individual cells add to give the total battery potential. Batteries are a source of direct current and have become an essential source of portable power in our society. In this section we examine the most common types of batteries. Some new batteries currently being developed are described at the end of the chapter.

Lead Storage Battery

Since about 1915 when self-starters were first used in automobiles, the **lead storage battery** has been a major factor in making the automobile a practical means of transportation. This type of battery can function for several years under temperature extremes from -30°F to 120°F and under incessant punishment from rough roads.

CHEMICAL IMPACT

Printed Batteries

Soon you may reach for a compact disc in your local record store and, as you touch it, the package will start playing one of the songs on the disc. Or you may stop to look at a product because the package begins to glow as you pass it in the store. These effects could happen soon thanks to the invention of a flexible, superthin battery that can actually be printed onto the package. This battery was developed by Power Paper, Ltd., a company founded by Baruch Levanon and several colleagues.

The battery developed by Power Paper consists of five layers of zinc (anode) and manganese dioxide (cathode) and is only 0.5 millimeter thick. The battery can be printed onto paper with a regular printing press and appears to present no environmental hazards.

The new battery has been licensed by International Paper Company, which intends to use it to bring light, sound, and other special effects to packaging to entice potential customers. You might see talking, singing, or glowing packages on the shelves within a year or two.



A CD case with an ultrathin battery that can be “printed” on packages like ink.

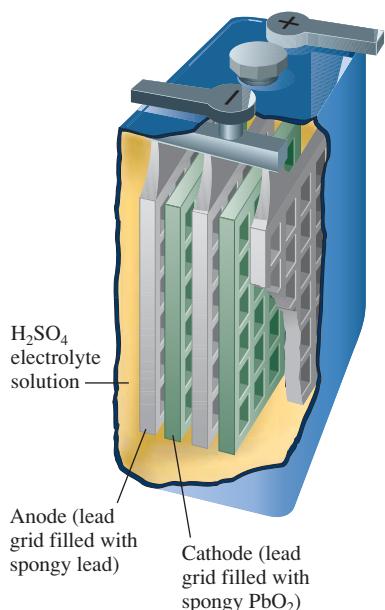
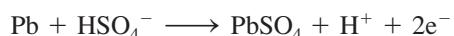


FIGURE 17.13

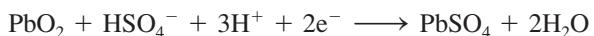
One of the six cells in a 12-V lead storage battery. The anode consists of a lead grid filled with spongy lead, and the cathode is a lead grid filled with lead dioxide. The cell also contains 38% (by mass) sulfuric acid.

In this battery, lead serves as the anode, and lead coated with lead dioxide serves as the cathode. Both electrodes dip into an electrolyte solution of sulfuric acid. The electrode reactions are

Anode reaction:



Cathode reaction:



Cell reaction: $\text{Pb}(s) + \text{PbO}_2(s) + 2\text{H}^+(aq) + 2\text{HSO}_4^-(aq) \longrightarrow 2\text{PbSO}_4(s) + 2\text{H}_2\text{O}(l)$

The typical automobile lead storage battery has six cells connected in series. Each cell contains multiple electrodes in the form of grids (Fig. 17.13) and produces approximately 2 V, to give a total battery potential of about 12 V. Note from the cell reaction that sulfuric acid is consumed as the battery discharges. This lowers the density of the electrolyte solution from its initial value of about 1.28 g/cm³ in the fully charged battery. As a result, the condition of the battery can be monitored by measuring the density of the sulfuric acid solution. The solid lead sulfate formed in the cell reaction during discharge adheres to the grid surfaces of the electrodes. The battery is recharged by forcing current through it in the opposite direction to reverse the cell reaction. A car’s battery is continuously charged by an alternator driven by the automobile engine.

An automobile with a dead battery can be “jump-started” by connecting its battery to the battery in a running automobile. This process can be dangerous, however, because the resulting flow of current causes electrolysis of water in the dead battery, producing hydrogen and oxygen gases (see Section 17.7 for details). Disconnecting the jumper cables after the disabled car starts causes an arc that can ignite the gaseous



CHEMICAL IMPACT

Thermophotovoltaics: Electricity from Heat

A photovoltaic cell transforms the energy of sunlight into an electric current. These devices are used to power calculators, electric signs in rural areas, experimental cars, and an increasing number of other devices. But what happens at night or on cloudy days? Usually photovoltaic power sources employ a battery as a reserve energy source when light levels are low.

Now there is an emerging technology, called *thermophotovoltaics* (TPV), that uses a heat source instead of the sun for energy. These devices can operate at night or on an overcast day without a battery. Although TPV devices could use many different sources of heat, the examples currently under development use a propane burner. To produce an electric current, the radiant heat from the burner is used to excite a “radiator,” a device that emits infrared (IR) radiation when heated. The emitted IR radiation then falls on a “converter,” which is a semiconductor that contains p–n junctions. The IR radiation excites electrons from valence bands to conduction bands in the semiconductor so that the electrons can flow as a current. A schematic of a TPV generator is illustrated in the diagram.

TPV technology has advanced recently because researchers have found that it is possible to use radiators such as silicon carbide, which can operate at relatively low temperatures (approximately 1000°C), with III–V semiconductor converters such as gallium antimonide (GSb) or gallium arsenide (GaAs). While development work continues on many fronts, the first commercial TPV product is being marketed by JX Crystals of Issaquah, Washington. The product—Midnight Sun—is a propane-powered TPV generator that can produce 30 watts of electricity and is intended for use on boats to charge the batteries that power navigation and other essential equipment. Although at \$3000 the TPV generator is more expensive than a conventional diesel-powered generator, Midnight Sun is silent and more reliable because it has no moving parts.

Although TPV technology is still in its infancy, it has many possible uses. The utilization of industrial waste heat—generated by glass and steel manufacturing and other industries—could establish a huge market for TPV. For example, two-thirds of the energy used in the manufacture of glass ends up as waste heat. If a significant quantity of this

mixture. If this happens, the battery may explode, ejecting corrosive sulfuric acid. This problem can be avoided by connecting the ground jumper cable to a part of the engine remote from the battery. Any arc produced when this cable is disconnected will then be harmless.

Traditional types of storage batteries require periodic “topping off” because the water in the electrolyte solution is depleted by the electrolysis that accompanies the charging process. Recent types of batteries have electrodes made of an alloy of calcium and lead that inhibits the electrolysis of water. These batteries can be sealed, since they require no addition of water.

It is rather amazing that in the 85 years in which lead storage batteries have been used, no better system has been found. Although a lead storage battery does provide excellent service, it has a useful lifetime of 3 to 5 years in an automobile. While it might seem that the battery could undergo an indefinite number of discharge/charge cycles, physical damage from road shock and chemical side-reactions eventually cause it to fail.

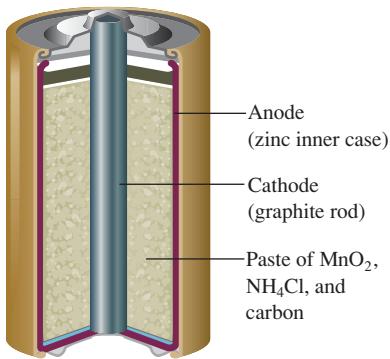
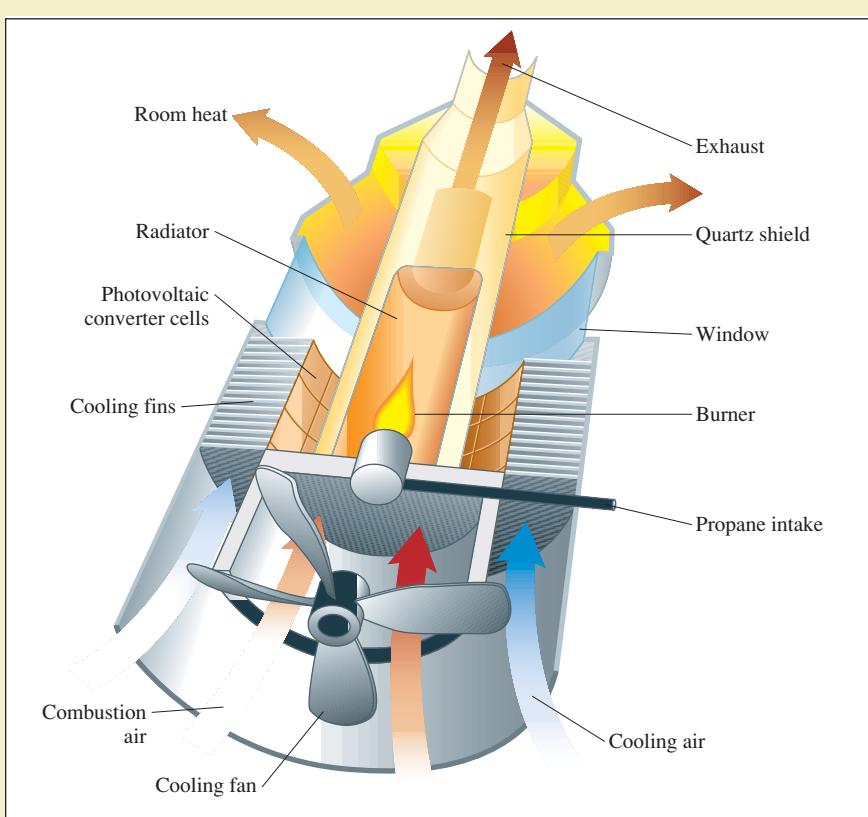


FIGURE 17.14

A common dry cell battery.

Other Batteries

The calculators, electronic games, digital watches, and portable CD players that are so familiar to us are all powered by small, efficient batteries. The common **dry cell battery** was invented more than 100 years ago by George Leclanché (1839–1882), a French chemist. In its *acid version*, the dry cell battery contains a zinc inner case that acts as the anode and a carbon rod in contact with a moist paste of solid MnO_2 , solid NH_4Cl , and carbon that acts as the cathode (Fig. 17.14). The half-reactions are complex but can be



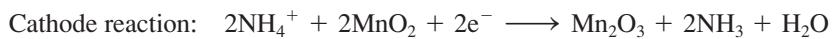
now wasted energy could be used to produce electricity, this would have tremendous fiscal implications.

Another promising application of TPV technology is for cars with hybrid energy sources. For example, an experimental electric car built at Western Washington University uses a 10-kW TPV generator to supplement the batteries that serve as the main power source.

Projections indicate that TPV devices could account for \$500 million in sales by 2005, mainly by substituting TPV generators for small diesel-powered generators used on boats and by the military in the field. It appears that this technology has a hot future.

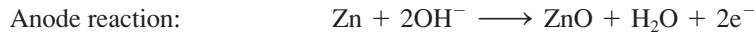
Diagram of a TPV generator.

approximated as follows:



This cell produces a potential of about 1.5 V.

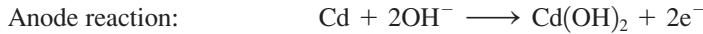
In the *alkaline version* of the dry cell battery, the solid NH_4Cl is replaced with KOH or NaOH. In this case the half-reactions can be approximated as follows:



The alkaline dry cell lasts longer mainly because the zinc anode corrodes less rapidly under basic conditions than under acidic conditions.

Other types of useful batteries include the *silver cell*, which has a Zn anode and a cathode that employs Ag_2O as the oxidizing agent in a basic environment. *Mercury cells*, often used in calculators, have a Zn anode and a cathode involving HgO as the oxidizing agent in a basic medium (see Fig. 17.15).

An especially important type of battery is the *nickel–cadmium battery*, in which the electrode reactions are



As in the lead storage battery, the products adhere to the electrodes. Therefore, a nickel–cadmium battery can be recharged an indefinite number of times.



Batteries for electronic watches are, by necessity, very tiny.



CHEMICAL IMPACT

Fuel Cells for Cars

Your next car may be powered by a fuel cell. Until recently only affordable to NASA, fuel cells are now ready to become practical power plants in cars. Many car companies are testing vehicles that should be commercially available by 2004 or 2005. All of these vehicles are powered by hydrogen–oxygen fuel cells (see Fig. 17.16).

One of the most common types of fuel cells for automobiles uses a proton-exchange membrane (PEM). When H₂ releases electrons at the anode, H⁺ ions form and then travel through the membrane to the cathode, where they combine with O₂ and electrons to form water. This cell generates about 0.7 V of power. To achieve the desired power level, several cells are stacked in series. Fuel cells of this type have appeared in several prototype vehicles, such as Nissan's Xterra FCV, Ford's Focus FCV, and DaimlerChrysler's Mercedes Benz NECAR 5 (see photo).

The main question yet to be answered deals with whether the fuel cells in these cars will be fueled by H₂ stored on board or by H₂ made from gasoline or methanol as it is needed. The latter systems include an onboard reformer that uses catalysts to produce H₂ from other fuels. The on-board storage of hydrogen could take place in a tank at high pressure (approximately 5000 psi) or it could utilize a metal-hydride-based solid. Energy Conversion Devices



A gathering of several cars powered by fuel cells at Los Angeles Memorial Coliseum.

(ECD) of Troy, Michigan, is developing a storage system based on a magnesium alloy that absorbs H₂ to form a magnesium hydride. The H₂ gas can be released from this solid by heating it to 300°C. According to ECD, the alloy can be fully charged with H₂ in about 5 minutes, achieving a hydrogen density of 103 g/L. This density compares to 71 g/L for liquid hydrogen and 31 g/L for gaseous hydrogen at 5000 psi. ECD claims its storage system furnishes enough H₂ to power a fuel-cell car for 300 miles of driving.

Clearly, fuel-cell-powered cars are on the near horizon.

Fuel Cells

A **fuel cell** is a galvanic cell for which the reactants are continuously supplied. To illustrate the principles of fuel cells, let's consider the exothermic redox reaction of methane with oxygen:

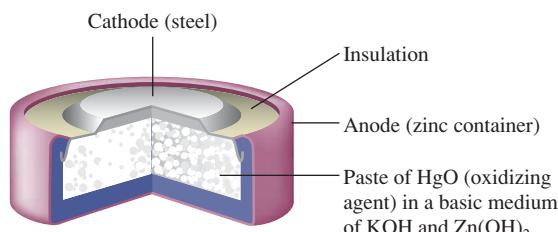
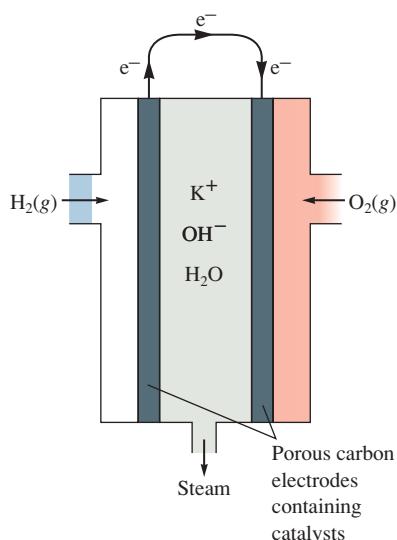


FIGURE 17.15

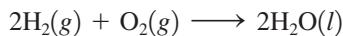
A mercury battery of the type used in calculators.

**FIGURE 17.16**

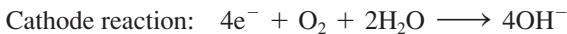
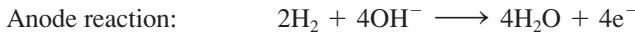
Schematic of the hydrogen–oxygen fuel cell.

Usually the energy from this reaction is released as heat to warm homes and to run machines. However, in a fuel cell designed to use this reaction, the energy is used to produce an electric current: The electrons flow from the reducing agent (CH_4) to the oxidizing agent (O_2) through a conductor.

The U.S. space program has supported extensive research to develop fuel cells. The space shuttle uses a fuel cell based on the reaction of hydrogen and oxygen to form water:



A schematic of a fuel cell that employs this reaction is shown in Fig. 17.16. The half-reactions are



A cell of this type weighing about 500 pounds has been designed for space vehicles, but this fuel cell is not practical enough for general use as a source of portable power. However, current research on portable electrochemical power is now proceeding at a rapid pace. In fact, cars powered by fuel cells are now being tested on the streets.

Fuel cells are also finding use as permanent power sources. For example, a power plant built in New York City contains stacks of hydrogen–oxygen fuel cells, which can be rapidly put on-line in response to fluctuating power demands. The hydrogen gas is obtained by decomposing the methane in natural gas. A plant of this type also has been constructed in Tokyo.

In addition, new fuel cells are under development that can use fuels such as methane and diesel directly without having to produce hydrogen first.

17.6 Corrosion

Corrosion can be viewed as the process of returning metals to their natural state—the ores from which they were originally obtained. Corrosion involves oxidation of the metal. Since corroded metal often loses its structural integrity and attractiveness, this spontaneous process has great economic impact. Approximately one-fifth of the iron and steel produced annually is used to replace rusted metal.

Metals corrode because they oxidize easily. Table 17.1 shows that, with the exception of gold, those metals commonly used for structural and decorative purposes all have standard reduction potentials less positive than that of oxygen gas. When any of these half-reactions is reversed (to show oxidation of the metal) and combined with the reduction half-reaction for oxygen, the result is a positive E° value. Thus the oxidation of most metals by oxygen is spontaneous (although we cannot tell from the potential how fast it will occur).

In view of the large difference in reduction potentials between oxygen and most metals, it is surprising that the problem of corrosion does not completely prevent the use of metals in air. However, most metals develop a thin oxide coating, which tends to protect their internal atoms against further oxidation. The metal that best demonstrates this phenomenon is aluminum. With a reduction potential of -1.7 V, aluminum should be easily oxidized by O_2 . According to the apparent thermodynamics of the reaction, an aluminum airplane could dissolve in a rainstorm. The fact that this very active metal can be used as a structural material is due to the formation of a thin, adherent layer of aluminum oxide (Al_2O_3), more properly represented as $\text{Al}_2(\text{OH})_6$, which greatly inhibits further corrosion. The potential of the “passive,” oxide-coated aluminum is -0.6 V, a value that causes it to behave much like a noble metal.

Iron also can form a protective oxide coating. This coating is not an infallible shield against corrosion, however; when steel is exposed to oxygen in moist air, the oxide that forms tends to scale off and expose new metal surfaces to corrosion.

Some metals, such as copper, gold, silver, and platinum, are relatively difficult to oxidize. These are often called *noble metals*.



CHEMICAL IMPACT

Paint That Stops Rust—Completely

Traditionally, paint has provided the most economical method for protecting steel against corrosion. However, as people who live in the Midwest know well, paint cannot prevent a car from rusting indefinitely. Eventually, flaws develop in the paint that allow the ravages of rusting to take place.

This situation may soon change. Chemists at Glidden Research Center in Ohio have developed a paint called Rustmaster Pro that worked so well to prevent rusting in its initial tests that the scientists did not believe their results. Steel coated with the new paint showed no signs of rusting after an astonishing 10,000 hours of exposure in a salt spray chamber at 38°C.

Rustmaster is a water-based polymer formulation that prevents corrosion in two different ways. First, the polymer layer that cures in air forms a barrier impenetrable to both oxygen and water vapor. Second, the chemicals in the coating react with the steel surface to produce an interlayer between the metal and the polymer coating. This interlayer is a complex mineral called *pyroaurite* that contains cations

of the form $[M_{1-x}Z_x(OH)_2]^{x+}$, where M is a 2+ ion (Mg^{2+} , Fe^{2+} , Zn^{2+} , Co^{2+} , or Ni^{2+}), Z is a 3+ ion (Al^{3+} , Fe^{3+} , Mn^{3+} , Co^{3+} , or Ni^{3+}), and x is a number between 0 and 1. The anions in pyroaurite are typically CO_3^{2-} , Cl^- , and/or SO_4^{2-} .

This pyroaurite interlayer is the real secret of the paint's effectiveness. Because the corrosion of steel has an electrochemical mechanism, motion of ions must be possible between the cathodic and anodic areas on the surface of the steel for rusting to occur. However, the pyroaurite interlayer grows into the neighboring polymer layer, thus preventing this crucial movement of ions. In effect, this layer prevents corrosion in the same way that removing the salt bridge prevents current from flowing in a galvanic cell.

In addition to having an extraordinary corrosion-fighting ability, Rustmaster yields an unusually small quantity of volatile solvents as it dries. A typical paint can produce from 1 to 5 kg of volatiles per gallon; Rustmaster produces only 0.05 kg. This paint may signal a new era in corrosion prevention.

The corrosion products of noble metals such as copper and silver are complex and affect the use of these metals as decorative materials. Under normal atmospheric conditions, copper forms an external layer of greenish copper carbonate called *patina*. *Silver tarnish* is silver sulfide (Ag_2S), which in thin layers gives the silver surface a richer appearance. Gold, with a positive standard reduction potential of 1.50 V, significantly larger than that for oxygen (1.23 V), shows no appreciable corrosion in air.

Corrosion of Iron

Since steel is the main structural material for bridges, buildings, and automobiles, controlling its corrosion is extremely important. To do this, we must understand the corrosion mechanism. Instead of being a direct oxidation process as we might expect, the corrosion of iron is an electrochemical reaction, as shown in Fig. 17.17.

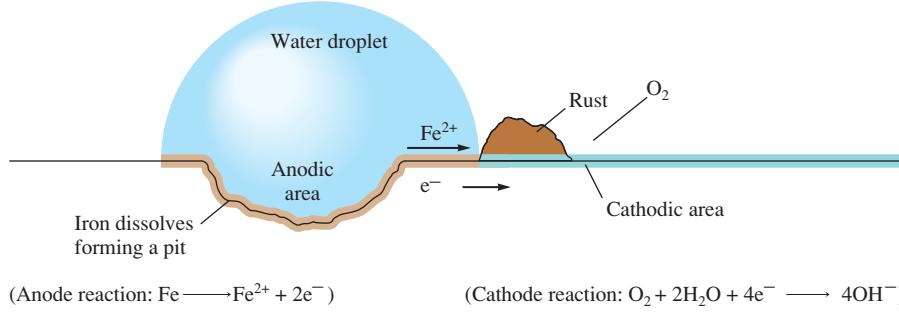


FIGURE 17.17

The electrochemical corrosion of iron.

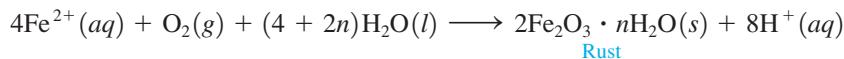
Steel has a nonuniform surface because the chemical composition is not completely homogeneous. Also, physical strains leave stress points in the metal. These nonuniformities cause areas where the iron is more easily oxidized (*anodic regions*) than it is at others (*cathodic regions*). In the anodic regions each iron atom gives up two electrons to form the Fe^{2+} ion:



The electrons that are released flow through the steel, as they do through the wire of a galvanic cell, to a cathodic region, where they react with oxygen:



The Fe^{2+} ions formed in the anodic regions travel to the cathodic regions through the moisture on the surface of the steel, just as ions travel through a salt bridge in a galvanic cell. In the cathodic regions Fe^{2+} ions react with oxygen to form rust, which is hydrated iron(III) oxide of variable composition:

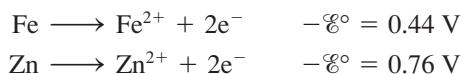


Because of the migration of ions and electrons, rust often forms at sites that are remote from those where the iron dissolved to form pits in the steel. The degree of hydration of the iron oxide affects the color of the rust, which may vary from black to yellow to the familiar reddish brown.

The electrochemical nature of the rusting of iron explains the importance of moisture in the corrosion process. Moisture must be present to act as a kind of salt bridge between anodic and cathodic regions. Steel does not rust in dry air, a fact that explains why cars last much longer in the arid Southwest than in the relatively humid Midwest. Salt also accelerates rusting, a fact all too easily recognized by car owners in the colder parts of the United States, where salt is used on roads to melt snow and ice. The severity of rusting is greatly increased because the dissolved salt on the moist steel surface increases the conductivity of the aqueous solution formed there and thus accelerates the electrochemical corrosion process. Chloride ions also form very stable complex ions with Fe^{3+} , and this factor tends to encourage the dissolving of the iron, again accelerating the corrosion.

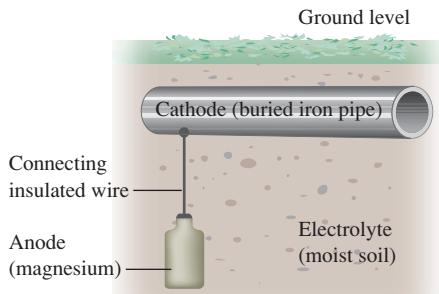
Prevention of Corrosion

Prevention of corrosion is an important way of conserving our natural resources of energy and metals. The primary means of protection is the application of a coating, most commonly paint or metal plating, to protect the metal from oxygen and moisture. Chromium and tin are often used to plate steel (see Section 17.8) because they oxidize to form a durable, effective oxide coating. Zinc, also used to coat steel in a process called **galvanizing**, forms a mixed oxide–carbonate coating. Since zinc is a more active metal than iron, as the potentials for the oxidation half-reactions show,



any oxidation that occurs dissolves zinc rather than iron. Recall that the reaction with the most positive standard potential has the greatest thermodynamic tendency to occur. Thus zinc acts as a “sacrificial” coating on steel.

Alloying is also used to prevent corrosion. *Stainless steel* contains chromium and nickel, both of which form oxide coatings that change steel’s reduction potential to one characteristic of the noble metals. In addition, a new technology is now being developed

**FIGURE 17.18**

Cathodic protection of an underground pipe.

to create surface alloys. That is, instead of forming a metal alloy such as stainless steel, which has the same composition throughout, a cheaper carbon steel is treated by ion bombardment to produce a thin layer of stainless steel or other desirable alloy on the surface. In this process, a “plasma” or “ion gas” of the alloying ions is formed at high temperatures and is then directed onto the surface of the metal.

Cathodic protection is a method most often employed to protect steel in buried fuel tanks and pipelines. An active metal, such as magnesium, is connected by a wire to the pipeline or tank to be protected (Fig. 17.18). Because the magnesium is a better reducing agent than iron, electrons are furnished by the magnesium rather than by the iron, keeping the iron from being oxidized. As oxidation occurs, the magnesium anode dissolves, and so it must be replaced periodically. Ships’ hulls are protected in a similar way by attaching bars of titanium metal to the steel hull (Fig. 17.18). In salt water the titanium acts as the anode and is oxidized instead of the steel hull (the cathode).

17.7 Electrolysis

An electrolytic cell uses electrical energy to produce a chemical change that would otherwise not occur spontaneously.

A galvanic cell produces current when an oxidation-reduction reaction proceeds spontaneously. A similar apparatus, an **electrolytic cell**, uses electrical energy to produce chemical change. The process of **electrolysis** involves *forcing a current through a cell to produce a chemical change for which the cell potential is negative*; that is, electrical work causes an otherwise nonspontaneous chemical reaction to occur. Electrolysis has great practical importance; for example, charging a battery, producing aluminum metal, and chrome plating an object are all done electrolytically.

To illustrate the difference between a galvanic cell and an electrolytic cell, consider the cell shown in Fig. 17.19(a) as it runs spontaneously to produce 1.10 V. In this *galvanic cell* the reaction at the anode is



whereas at the cathode the reaction is

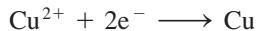
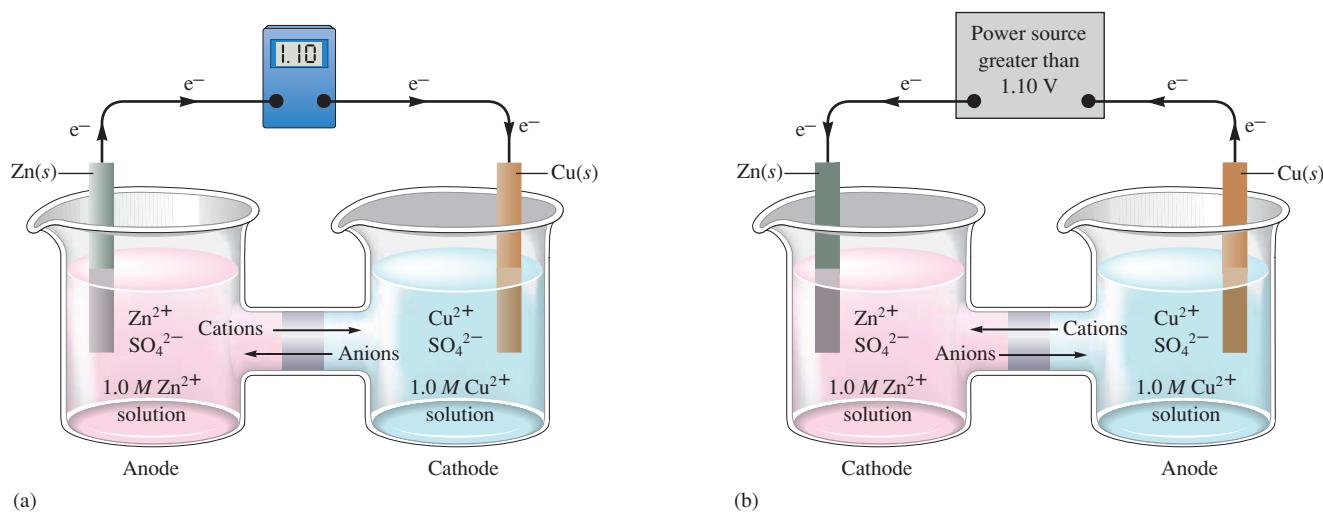


Figure 17.19(b) shows an external power source forcing electrons through the cell in the *opposite* direction to that in (a). This requires an external potential greater than 1.10 V, which must be applied in opposition to the natural cell potential. This device is an **electrolytic cell**. Notice that since electron flow is opposite in the two cases, the anode and cathode are reversed between (a) and (b). Also, ion flow through the salt bridge is opposite in the two cells.

Now we will consider the stoichiometry of electrolytic processes, that is, *how much chemical change occurs with the flow of a given current for a specified time*. Suppose we wish to determine the mass of copper that is plated out when a current of 10.0 amps

**FIGURE 17.19**

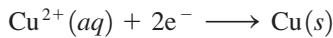
(a) A standard galvanic cell based on the spontaneous reaction



(b) A standard electrolytic cell. A power source forces the opposite reaction

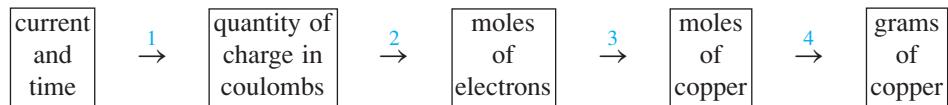


(an **ampere** [amp], abbreviated A, is *1 coulomb of charge per second*) is passed for 30.0 minutes through a solution containing Cu^{2+} . *Plating* means depositing the neutral metal on the electrode by reducing the metal ions in solution. In this case each Cu^{2+} ion requires two electrons to become an atom of copper metal:



This reduction process will occur at the cathode of the electrolytic cell.

To solve this stoichiometry problem, we need the following steps:



→ 1 Since an amp is a coulomb of charge per second, we multiply the current by the time in seconds to obtain the total coulombs of charge passed into the Cu^{2+} solution at the cathode:

$$\begin{aligned}\text{Coulombs of charge} &= \text{amps} \times \text{seconds} = \frac{\text{C}}{\text{s}} \times \text{s} \\ &= 10.0 \frac{\text{C}}{\text{s}} \times 30.0 \text{ min} \times 60.0 \frac{\text{s}}{\text{min}} \\ &= 1.80 \times 10^4 \text{ C}\end{aligned}$$

→ 2 Since 1 mole of electrons carries a charge of 1 faraday, or 96,485 coulombs, we can calculate the number of moles of electrons required to carry 1.80×10^4 coulombs of charge:

$$1.80 \times 10^4 \text{ C} \times \frac{1 \text{ mol e}^-}{96,485 \text{ C}} = 1.87 \times 10^{-1} \text{ mol e}^-$$

This means that 0.187 mole of electrons flowed into the Cu^{2+} solution.

→ 3 Each Cu^{2+} ion requires two electrons to become a copper atom. Thus each mole of electrons produces $\frac{1}{2}$ mole of copper metal:

$$1.87 \times 10^{-1} \text{ mol e}^- \times \frac{1 \text{ mol Cu}}{2 \text{ mol e}^-} = 9.35 \times 10^{-2} \text{ mol Cu}$$

→ 4 We now know the moles of copper metal plated onto the cathode, and we can calculate the mass of copper formed:

$$9.35 \times 10^{-2} \text{ mol Cu} \times \frac{63.546 \text{ g}}{\text{mol Cu}} = 5.94 \text{ g Cu}$$

Sample Exercise 17.9

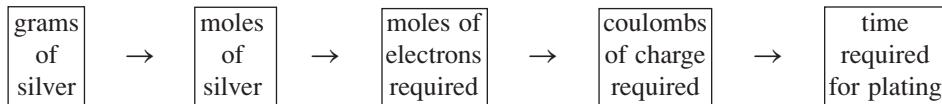
Electroplating

Sample Exercise 17.9 describes only the half-cell of interest. There also must be an anode at which oxidation is occurring.

How long must a current of 5.00 A be applied to a solution of Ag^+ to produce 10.5 g silver metal?

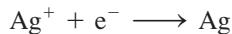
Solution

In this case, we must use the steps given earlier in reverse:



$$10.5 \text{ g Ag} \times \frac{1 \text{ mol Ag}}{107.868 \text{ g Ag}} = 9.73 \times 10^{-2} \text{ mol Ag}$$

Each Ag^+ ion requires one electron to become a silver atom:



Thus 9.73×10^{-2} mol of electrons is required, and we can calculate the quantity of charge carried by these electrons:

$$9.73 \times 10^{-2} \text{ mol e}^- \times \frac{96,485 \text{ C}}{\text{mol e}^-} = 9.39 \times 10^3 \text{ C}$$

The 5.00 A (5.00 C/s) of current must produce 9.39×10^3 C of charge. Thus

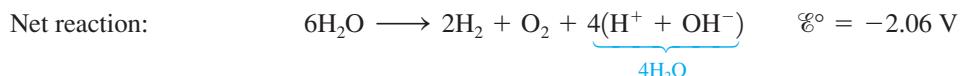
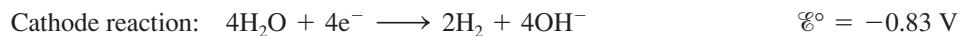
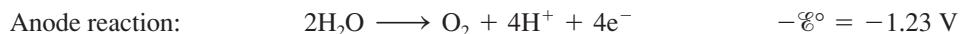
$$\left(5.00 \frac{\text{C}}{\text{s}}\right) \times (\text{time, in s}) = 9.39 \times 10^3 \text{ C}$$

$$\text{Time} = \frac{9.39 \times 10^3}{5.00} \text{ s} = 1.88 \times 10^3 \text{ s} = 31.3 \text{ min}$$

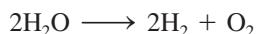
See Exercises 17.77 through 17.80.

Electrolysis of Water

We have seen that hydrogen and oxygen combine spontaneously to form water and that the accompanying decrease in free energy can be used to run a fuel cell to produce electricity. The reverse process, which is of course nonspontaneous, can be forced by electrolysis:



or





Visualization: Electrolysis of Water



FIGURE 17.20

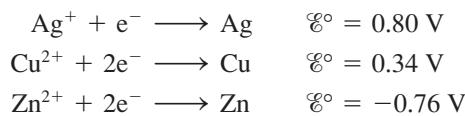
The electrolysis of water produces hydrogen gas at the cathode (on the right) and oxygen gas at the anode (on the left).

Note that these potentials assume an anode chamber with 1 M H⁺ and a cathode chamber with 1 M OH⁻. In pure water, where [H⁺] = [OH⁻] = 10⁻⁷ M, the potential for the overall process is -1.23 V.

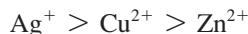
In practice, however, if platinum electrodes connected to a 6-V battery are dipped into pure water, no reaction is observed because pure water contains so few ions that only a negligible current can flow. However, addition of even a small amount of a soluble salt causes an immediate evolution of bubbles of hydrogen and oxygen, as illustrated in Fig. 17.20.

Electrolysis of Mixtures of Ions

Suppose a solution in an electrolytic cell contains the ions Cu²⁺, Ag⁺, and Zn²⁺. If the voltage is initially very low and is gradually turned up, in which order will the metals be plated out onto the cathode? This question can be answered by looking at the standard reduction potentials of these ions:



Remember that the more *positive* the E° value, the more the reaction has a tendency to proceed in the direction indicated. Of the three reactions listed, the reduction of Ag⁺ occurs most easily, and the order of oxidizing ability is



This means that silver will plate out first as the potential is increased, followed by copper, and finally zinc.

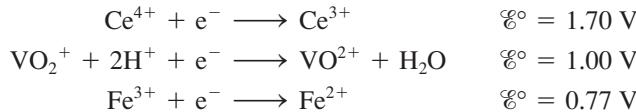
Sample Exercise 17.10

Relative Oxidizing Abilities

An acidic solution contains the ions Ce⁴⁺, VO₂⁺, and Fe³⁺. Using the E° values listed in Table 17.1, give the order of oxidizing ability of these species and predict which one will be reduced at the cathode of an electrolytic cell at the lowest voltage.

Solution

The half-reactions and E° values are



The order of oxidizing ability is therefore



The Ce⁴⁺ ion will be reduced at the lowest voltage in an electrolytic cell.

See Exercise 17.89.

The principle described in this section is very useful, but it must be applied with some caution. For example, in the electrolysis of an aqueous solution of sodium chloride, we should be able to use E° values to predict the products. Of the major species in the solution



CHEMICAL IMPACT

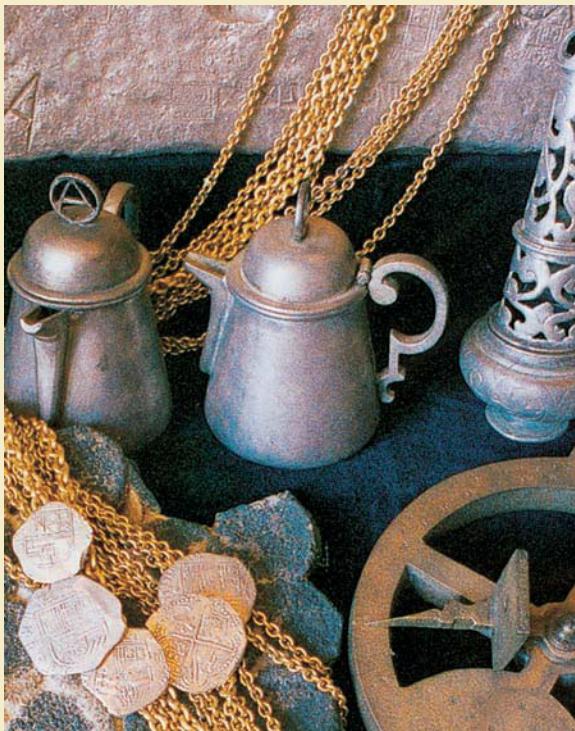
The Chemistry of Sunken Treasure

When the galleon *Atocha* was destroyed on a reef by a hurricane in 1622, it was bound for Spain carrying approximately 47 tons of copper, gold, and silver from the New World. The bulk of the treasure was silver bars and coins packed in wooden chests. When treasure hunter Mel Fisher salvaged the silver in 1985, corrosion and marine growth had transformed the shiny metal into something that looked like coral. Restoring the silver to its original condition required an understanding of the chemical changes that had occurred in 350 years of being submerged in the ocean. Much of this chemistry we have already considered at various places in this text.

As the wooden chests containing the silver decayed, the oxygen supply was depleted, favoring the growth of certain bacteria that use the sulfate ion rather than oxygen as an oxidizing agent to generate energy. As these bacteria consume sulfate ions, they release hydrogen sulfide gas that reacts with silver to form black silver sulfide:

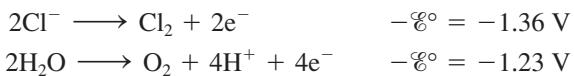


Thus, over the years, the surface of the silver became covered with a tightly adhering layer of corrosion, which fortunately protected the silver underneath and thus prevented total conversion of the silver to silver sulfide.



Silver coins and tankards salvaged from the wreck of the *Atocha*.

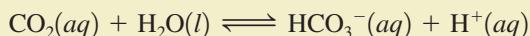
(Na^+ , Cl^- , and H_2O), only Cl^- and H_2O can be readily oxidized. The half-reactions (written as oxidation processes) are



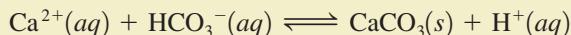
Since water has the more positive potential, we would expect to see O_2 produced at the anode because it is easier (thermodynamically) to oxidize H_2O than Cl^- . Actually, this does not happen. As the voltage is increased in the cell, the Cl^- ion is the first to be oxidized. A much higher potential than expected is required to oxidize water. The voltage required in excess of the expected value (called the *overvoltage*) is much greater for the production of O_2 than for Cl_2 , which explains why chlorine is produced first.

The causes of overvoltage are very complex. Basically, the phenomenon is caused by difficulties in transferring electrons from the species in the solution to the atoms on the electrode across the electrode–solution interface. Because of this situation, \mathcal{E}° values must be used cautiously in predicting the actual order of oxidation or reduction of species in an electrolytic cell.

Another change that took place as the wood decomposed was the formation of carbon dioxide. This shifted the equilibrium that is present in the ocean,

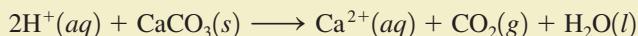


to the right, producing higher concentrations of HCO_3^- . In turn, the HCO_3^- reacted with Ca^{2+} ions present in the seawater to form calcium carbonate:

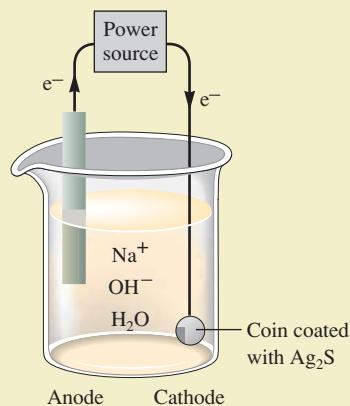


Calcium carbonate is the main component of limestone. Thus, over time, the corroded silver coins and bars became encased in limestone.

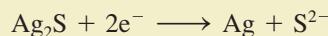
Both the limestone formation and the corrosion had to be dealt with. Since CaCO_3 contains the basic anion CO_3^{2-} , acid dissolves limestone:



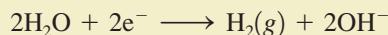
Soaking the mass of coins in a buffered acidic bath for several hours allowed the individual pieces to be separated, and the black Ag_2S on the surfaces was revealed. An abrasive could not be used to remove this corrosion; it would have destroyed the details of the engraving—a very valuable feature of the coins to a historian or a collector—and it would have washed away some of the silver. Instead, the corrosion reaction was reversed through electrolytic reduction. The coins were connected to the cathode of an electrolytic cell in a dilute sodium hydroxide solution as represented in the figure.



As electrons flow, the Ag^+ ions in the silver sulfide are reduced to silver metal:



As a by-product, bubbles of hydrogen gas from the reduction of water form on the surface of the coins:



The agitation caused by the bubbles loosens the flakes of metal sulfide and helps clean the coins.

These procedures have made it possible to restore the treasure to very nearly its condition when the *Atocha* sailed many years ago.

17.8 Commercial Electrolytic Processes

The chemistry of metals is characterized by their ability to donate electrons to form ions. Because metals are typically such good reducing agents, most are found in nature in *ores*, mixtures of ionic compounds often containing oxide, sulfide, and silicate anions. The noble metals, such as gold, silver, and platinum, are more difficult to oxidize and are often found as pure metals.

Production of Aluminum

Aluminum is one of the most abundant elements on earth, ranking third behind oxygen and silicon. Since aluminum is a very active metal, it is found in nature as its oxide in an ore called *bauxite* (named after Les Baux, France, where it was discovered in 1821). Production of aluminum metal from its ore proved to be more difficult than production of most other metals. In 1782 Lavoisier recognized aluminum to be a metal “whose affinity for oxygen is so strong that it cannot be overcome by any known reducing agent.” As a result, pure aluminum metal remained unknown. Finally, in 1854

**FIGURE 17.21**

Charles Martin Hall (1863–1914) was a student at Oberlin College in Ohio when he first became interested in aluminum. One of his professors commented that anyone who could manufacture aluminum cheaply would make a fortune, and Hall decided to give it a try. The 21-year-old Hall worked in a wooden shed near his house with an iron frying pan as a container, a blacksmith's forge as a heat source, and galvanic cells constructed from fruit jars. Using these crude galvanic cells, Hall found that he could produce aluminum by passing a current through a molten $\text{Al}_2\text{O}_3/\text{Na}_3\text{AlF}_6$ mixture. By a strange coincidence, Paul Heroult, a Frenchman who was born and died in the same years as Hall, made the same discovery at about the same time.

a process was found for producing metallic aluminum using sodium, but aluminum remained a very expensive rarity. In fact, it is said that Napoleon III served his most honored guests with aluminum forks and spoons, while the others had to settle for gold and silver utensils.

The breakthrough came in 1886 when two men, Charles M. Hall in the United States and Paul Heroult in France, almost simultaneously discovered a practical electrolytic process for producing aluminum (see Fig. 17.21). The key factor in the *Hall-Heroult process* is the use of molten cryolite (Na_3AlF_6) as the solvent for the aluminum oxide.

Electrolysis is possible only if ions can move to the electrodes. A common method for producing ion mobility is dissolving the substance to be electrolyzed in water. This is not possible in the case of aluminum because water is more easily reduced than Al^{3+} , as the following standard reduction potentials show:



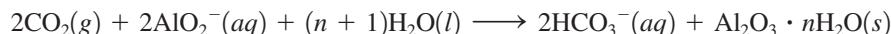
Thus aluminum metal cannot be plated out of an aqueous solution of Al^{3+} .

Ion mobility also can be produced by melting the salt. But the melting point of solid Al_2O_3 is much too high (2050°C) to allow practical electrolysis of the molten oxide. A mixture of Al_2O_3 and Na_3AlF_6 , however, has a melting point of 1000°C, and the resulting molten mixture can be used to obtain aluminum metal electrolytically. Because of this discovery by Hall and Heroult, the price of aluminum plunged (see Table 17.3), and its use became economically feasible.

Bauxite is not pure aluminum oxide (called *alumina*); it also contains the oxides of iron, silicon, and titanium, and various silicate materials. To obtain the pure hydrated alumina ($\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$), the crude bauxite is treated with aqueous sodium hydroxide. Being amphoteric, alumina dissolves in the basic solution:



The other metal oxides, which are basic, remain as solids. The solution containing the aluminate ion (AlO_2^-) is separated from the sludge of the other oxides and is acidified with carbon dioxide gas, causing the hydrated alumina to reprecipitate:



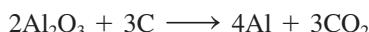
The purified alumina is then mixed with cryolite and melted, and the aluminum ion is reduced to aluminum metal in an electrolytic cell of the type shown in Fig. 17.22. Because the electrolyte solution contains a large number of aluminum-containing ions, the chemistry is not completely clear. However, the alumina probably reacts with the cryolite anion as follows:



The electrode reactions are thought to be



The overall cell reaction can be written as

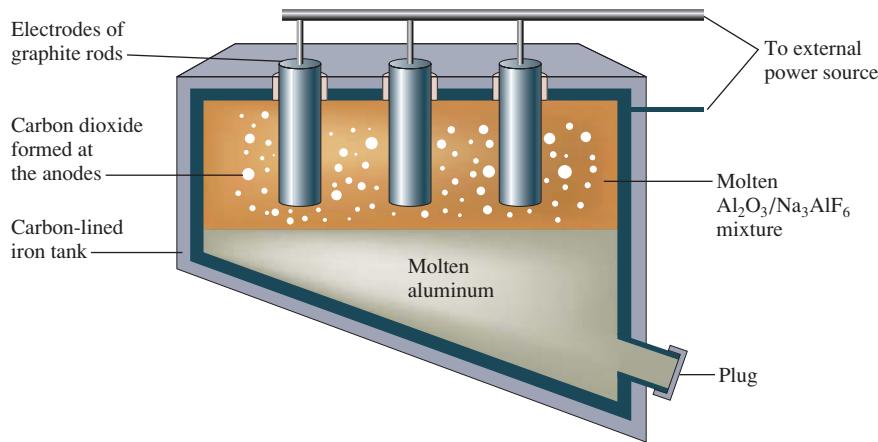


The aluminum produced in this electrolytic process is 99.5% pure. To be useful as a structural material, aluminum is alloyed with metals such as zinc (used for trailer and aircraft construction) and manganese (used for cooking utensils, storage tanks, and highway signs). The production of aluminum consumes about 5% of all the electricity used in the United States.

TABLE 17.3 The Price of Aluminum over the Past Century

Date	Price of Aluminum (\$/lb)*
1855	100,000
1885	100
1890	2
1895	0.50
1970	0.30
1980	0.80
1990	0.74

*Note the precipitous drop in price after the discovery of the Hall-Heroult process.

**FIGURE 17.22**

A schematic diagram of an electrolytic cell for producing aluminum by the Hall–Heroult process. Because molten aluminum is more dense than the mixture of molten cryolite and alumina, it settles to the bottom of the cell and is drawn off periodically. The graphite electrodes are gradually eaten away and must be replaced from time to time. The cell operates at a current flow of up to 250,000 A.

Electrorefining of Metals

Purification of metals is another important application of electrolysis. For example, impure copper from the chemical reduction of copper ore is cast into large slabs that serve as the anodes for electrolytic cells. Aqueous copper sulfate is the electrolyte, and thin sheets of ultrapure copper function as the cathodes (see Fig. 17.23).

The main reaction at the anode is



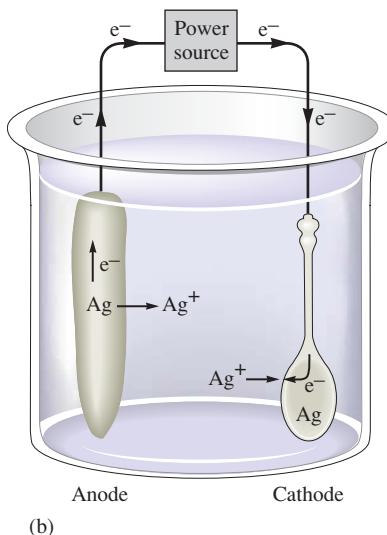
Other metals such as iron and zinc are also oxidized from the impure anode:

**FIGURE 17.23**

Ultrapure copper sheets that serve as the cathodes are lowered between slabs of impure copper that serve as the anodes into a tank containing an aqueous solution of copper sulfate (CuSO_4). It takes about four weeks for the anodes to dissolve and for the pure copper to be deposited on the cathodes.



(a)



(b)

FIGURE 17.24

(a) A silver-plated teapot. Silver plating is often used to beautify and protect cutlery and items of table service.
 (b) Schematic of the electroplating of a spoon. The item to be plated is the cathode, and the anode is a silver bar. Silver is plated out at the cathode: $Ag^+ + e^- \rightarrow Ag$. Note that a salt bridge is not needed here because Ag^+ ions are involved at both electrodes.

Noble metal impurities in the anode are not oxidized at the voltage used; they fall to the bottom of the cell to form a sludge, which is processed to remove the valuable silver, gold, and platinum.

The Cu^{2+} ions from the solution are deposited onto the cathode



producing copper that is 99.95% pure.

Metal Plating

Metals that readily corrode can often be protected by the application of a thin coating of a metal that resists corrosion. Examples are “tin” cans, which are actually steel cans with a thin coating of tin, and chrome-plated steel bumpers for automobiles.

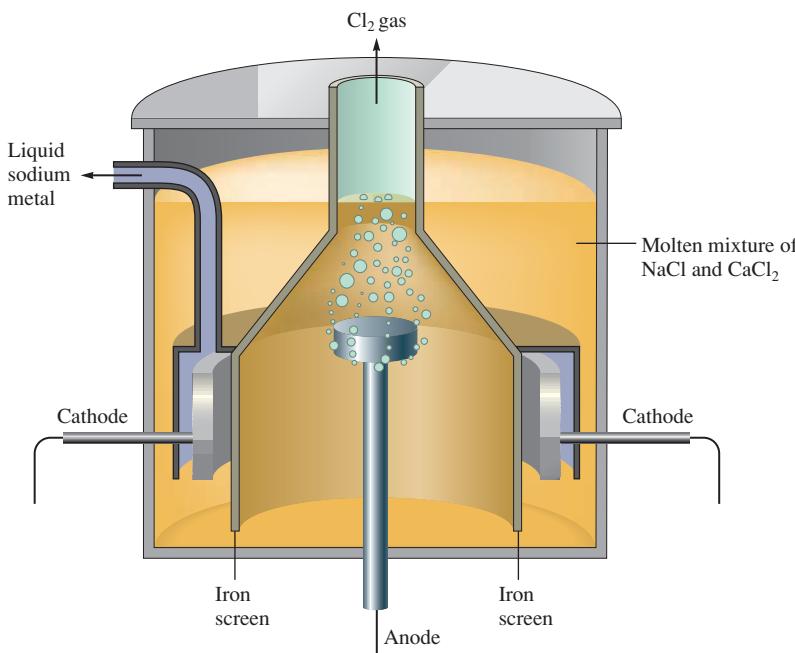
An object can be plated by making it the cathode in a tank containing ions of the plating metal. The silver plating of a spoon is shown schematically in Fig. 17.24(b). In an actual plating process, the solution also contains ligands that form complexes with the silver ion. By lowering the concentration of Ag^+ in this way, a smooth, even coating of silver is obtained.

Electrolysis of Sodium Chloride

Addition of a nonvolatile solute lowers the melting point of the solvent, molten $NaCl$ in this case.

Sodium metal is mainly produced by the electrolysis of molten sodium chloride. Because solid $NaCl$ has a rather high melting point ($800^\circ C$), it is usually mixed with solid $CaCl_2$ to lower the melting point to about ($600^\circ C$). The mixture is then electrolyzed in a **Downs cell**, as illustrated in Fig. 17.25, where the reactions are

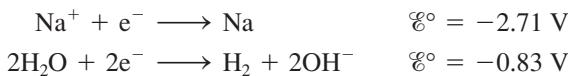


**FIGURE 17.25**

The Downs cell for the electrolysis of molten sodium chloride. The cell is designed so that the sodium and chlorine produced cannot come into contact with each other to re-form NaCl.

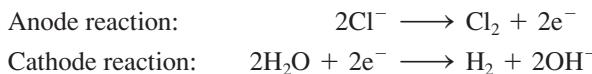
At the temperatures in the Downs cell, the sodium is liquid and is drained off, then cooled, and cast into blocks. Because it is so reactive, sodium must be stored in an inert solvent, such as mineral oil, to prevent its oxidation.

Electrolysis of aqueous sodium chloride (brine) is an important industrial process for the production of chlorine and sodium hydroxide. In fact, this process is the second largest consumer of electricity in the United States, after the production of aluminum. Sodium is not produced in this process under normal circumstances because H₂O is more easily reduced than Na⁺, as the standard reduction potentials show:



Hydrogen, not sodium, is produced at the cathode.

For the reasons we discussed in Section 17.7, chlorine gas is produced at the anode. Thus the electrolysis of brine produces hydrogen and chlorine:

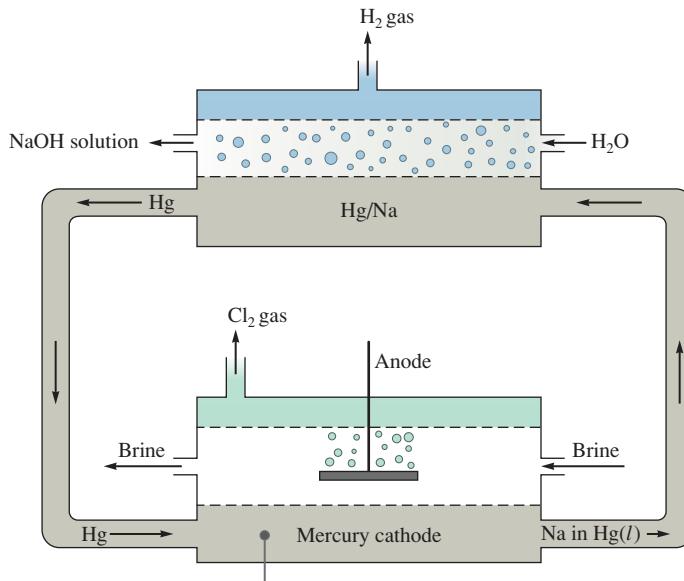


It leaves a solution containing dissolved NaOH and NaCl.

The contamination of the sodium hydroxide by NaCl can be virtually eliminated using a special **mercury cell** for electrolyzing brine (see Fig. 17.26). In this cell, mercury is the conductor at the cathode, and because hydrogen gas has an extremely high overvoltage with a mercury electrode, Na⁺ is reduced instead of H₂O. The resulting sodium metal dissolves in the mercury, forming a liquid alloy, which is then pumped to a chamber where the dissolved sodium reacts with water to produce hydrogen:



Relatively pure solid NaOH can be recovered from the aqueous solution, and the regenerated mercury is then pumped back to the electrolysis cell. This process, called the **chlor-alkali process**, was the main method for producing chlorine and sodium hydroxide in the United States for many years. However, because of the environmental problems associated with the mercury cell, it has been largely displaced in the

**FIGURE 17.26**

The mercury cell for production of chlorine and sodium hydroxide. The large overvoltage required to produce hydrogen at a mercury electrode means that Na^+ ions are reduced rather than water. The sodium formed dissolves in the liquid mercury and is pumped to a chamber where it reacts with water.

chlor–alkali industry by other technologies. In the United States, nearly 75% of the chlor–alkali production is now carried out in diaphragm cells. In a diaphragm cell the cathode and anode are separated by a diaphragm that allows passage of H_2O molecules, Na^+ ions, and, to a limited extent, Cl^- ions. The diaphragm does not allow OH^- ions to pass through it. Thus the H_2 and OH^- formed at the cathode are kept separate from the Cl_2 formed at the anode. The major disadvantage of this process is that the aqueous effluent pumped from the cathode compartment contains a mixture of sodium hydroxide and unreacted sodium chloride, which must be separated if pure sodium hydroxide is a desired product.

In the past 30 years, a new process has been developed in the chlor–alkali industry that employs a membrane to separate the anode and cathode compartments in brine electrolysis cells. The membrane is superior to a diaphragm because the membrane is impermeable to anions. Only cations can flow through the membrane. Because neither Cl^- nor OH^- ions can pass through the membrane separating the anode and cathode compartments, NaCl contamination of the NaOH formed at the cathode does not occur. Although membrane technology is now just becoming prominent in the United States, it is the dominant method for chlor–alkali production in Japan.

Key Terms

electrochemistry

Section 17.1

oxidation–reduction (redox) reaction

reducing agent

oxidizing agent

oxidation

reduction

half-reactions

salt bridge

porous disk

galvanic cell

anode

cathode

For Review

Electrochemistry

- The study of the interchange of chemical and electrical energy
- Employs oxidation–reduction reactions
- Galvanic cell: chemical energy is transformed into electrical energy by separating the oxidizing and reducing agents and forcing the electrons to travel through a wire
- Electrolytic cell: electrical energy is used to produce a chemical change

Galvanic cell

- Anode: the electrode where oxidation occurs
- Cathode: the electrode where reduction occurs

cell potential (electromotive force)
volt
voltmeter
potentiometer

Section 17.2

standard hydrogen electrode
standard reduction potentials

Section 17.3

faraday

Section 17.4

concentration cell
Nernst equation
glass electrode
ion-selective electrode

Section 17.5

battery
lead storage battery
dry cell battery
fuel cell

Section 17.6

corrosion
galvanizing
cathodic protection

Section 17.7

electrolytic cell
electrolysis
ampere

Section 17.8

Downs cell
mercury cell
chlor-alkali process

- The driving force behind the electron transfer is called the cell potential ($\mathcal{E}_{\text{cell}}$)
 - The potential is measured in units of volts (V), defined as a joule of work per coulomb of charge:

$$\mathcal{E}(\text{V}) = \frac{-\text{work (J)}}{\text{charge (C)}} = -\frac{w}{q}$$

- A system of half-reactions, called standard reduction potentials, can be used to calculate the potentials of various cells
 - The half-reaction $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ is arbitrarily assigned a potential of 0 V

Free energy and work

- The maximum work that a cell can perform is

$$-w_{\text{max}} = q\mathcal{E}_{\text{max}}$$

where \mathcal{E}_{max} represents the cell potential when no current is flowing

- The actual work obtained from a cell is always less than the maximum because energy is lost through frictional heating of the wire when current flows
- For a process carried out at constant temperature and pressure, the change in free energy equals the maximum useful work obtainable from that process:

$$\Delta G = w_{\text{max}} = -q\mathcal{E}_{\text{max}} = -nF\mathcal{E}$$

where F (faraday) equals 96,485 C and n is the number of moles of electrons transferred in the process

Concentration cell

- A galvanic cell in which both compartments have the same components but at different concentrations
- The electrons flow in the direction that tends to equalize the concentrations

Nernst equation

- Shows how the cell potential depends on the concentrations of the cell components:

$$\mathcal{E} = \mathcal{E}_0 - \frac{0.0591}{n} \log Q \quad \text{at } 25^\circ\text{C}$$

- When a galvanic cell is at equilibrium, $\mathcal{E} = 0$ and $Q = K$

Batteries

- A battery consists of a galvanic cell or group of cells connected in series that serve as a source of direct current
- Lead storage battery
 - Anode: lead
 - Cathode: lead coated with PbO_2
 - Electrolyte: $\text{H}_2\text{SO}_4(aq)$
- Dry cell battery
 - Contains a moist paste instead of a liquid electrolyte
 - Anode: usually Zn
 - Cathode: carbon rod in contact with an oxidizing agent (which varies depending on the application)

Fuel cells

- Galvanic cells in which the reactants are continuously supplied
- The H_2/O_2 fuel cell is based on the reaction between H_2 and O_2 to form water

Corrosion

- Involves the oxidation of metals to form mainly oxides and sulfides

- Some metals, such as aluminum and chromium, form a thin protective oxide coating that prevents further corrosion
- The corrosion of iron to form rust is an electrochemical process
 - The Fe^{2+} ions formed at anodic areas of the surface migrate through the moisture layer to cathodic regions, where they react with oxygen from the air
 - Iron can be protected from corrosion by coating it with paint or with a thin layer of metal such as chromium, tin, or zinc; by alloying; and by cathodic protection

Electrolysis

- Used to place a thin coating of metal onto steel
- Used to produce pure metals such as aluminum and copper

REVIEW QUESTIONS

- What is electrochemistry? What are redox reactions? Explain the difference between a galvanic and an electrolytic cell.
- Galvanic cells harness spontaneous oxidation-reduction reactions to produce work by producing a current. They do so by controlling the flow of electrons from the species oxidized to the species reduced. How is a galvanic cell designed? What is in the cathode compartment? The anode compartment? What purpose do electrodes serve? Which way do electrons always flow in the wire connecting the two electrodes in a galvanic cell? Why is it necessary to use a salt bridge or a porous disk in a galvanic cell? Which way do cations flow in the salt bridge? Which way do the anions flow? What is a cell potential and what is a volt?
- Table 17.1 lists common half-reactions along with the standard reduction potential associated with each half-reaction. These standard reduction potentials are all relative to some standard. What is the standard (zero point)? If \mathcal{E}° is positive for a half-reaction, what does it mean? If \mathcal{E}° is negative for a half-reaction, what does it mean? Which species in Table 17.1 is most easily reduced? Least easily reduced? The reverse of the half-reactions in Table 17.1 are the oxidation half-reactions. How are standard oxidation potentials determined? In Table 17.1, which species is the best reducing agent? The worst reducing agent?

To determine the standard cell potential for a redox reaction, the standard reduction potential is added to the standard oxidation potential. What must be true about this sum if the cell is to be spontaneous (produce a galvanic cell)? Standard reduction and oxidation potentials are intensive. What does this mean? Summarize how line notation is used to describe galvanic cells.

- Consider the equation $\Delta G^\circ = -nF\mathcal{E}^\circ$. What are the four terms in this equation? Why does a minus sign appear in the equation? What does the superscript $^\circ$ indicate?
- The Nernst equation allows determination of the cell potential for a galvanic cell at nonstandard conditions. Write out the Nernst equation. What are non-standard conditions? What do \mathcal{E} , \mathcal{E}° , n , and Q stand for in the Nernst equation? What does the Nernst equation reduce to when a redox reaction is at equilibrium? What are the signs of ΔG° and \mathcal{E}° when $K < 1$? When $K > 1$? When $K = 1$? Explain the following statement: \mathcal{E} determines spontaneity, while \mathcal{E}° determines the equilibrium position. Under what conditions can you use \mathcal{E}° to predict spontaneity?
- What are concentration cells? What is \mathcal{E}° in a concentration cell? What is the driving force for a concentration cell to produce a voltage? Is the higher or the lower ion concentration solution present at the anode? When the anode ion concentration is decreased and/or the cathode ion concentration is increased, both

give rise to larger cell potentials. Why? Concentration cells are commonly used to calculate the value of equilibrium constants for various reactions. For example, the silver concentration cell illustrated in Fig. 17.9 can be used to determine the K_{sp} value for $\text{AgCl}(s)$. To do so, NaCl is added to the anode compartment until no more precipitate forms. The $[\text{Cl}^-]$ in solution is then determined somehow. What happens to $\mathcal{E}_{\text{cell}}$ when NaCl is added to the anode compartment? To calculate the K_{sp} value, $[\text{Ag}^+]$ must be calculated. Given the value of $\mathcal{E}_{\text{cell}}$, how is $[\text{Ag}^+]$ determined at the anode?

7. Batteries are galvanic cells. What happens to $\mathcal{E}_{\text{cell}}$ as a battery discharges? Does a battery represent a system at equilibrium? Explain. What is $\mathcal{E}_{\text{cell}}$ when a battery reaches equilibrium? How are batteries and fuel cells alike? How are they different? The U.S. space program utilizes hydrogen–oxygen fuel cells to produce power for its spacecraft. What is a hydrogen–oxygen fuel cell?
8. Not all spontaneous redox reactions produce wonderful results. Corrosion is an example of a spontaneous redox process that has negative effects. What happens in the corrosion of a metal such as iron? What must be present for the corrosion of iron to take place? How can moisture and salt increase the severity of corrosion? Explain how the following protect metals from corrosion:
 - a. paint
 - b. durable oxide coatings
 - c. galvanizing
 - d. sacrificial metal
 - e. alloying
 - f. cathodic protection
9. What characterizes an electrolytic cell? What is an ampere? When the current applied to an electrolytic cell is multiplied by the time in seconds, what quantity is determined? How is this quantity converted to moles of electrons required? How are moles of electrons required converted to moles of metal plated out? What does plating mean? How do you predict the cathode and the anode half-reactions in an electrolytic cell? Why is the electrolysis of molten salts much easier to predict in terms of what occurs at the anode and cathode than the electrolysis of aqueous dissolved salts? What is overvoltage?
10. Electrolysis has many important industrial applications. What are some of these applications? The electrolysis of molten NaCl is the major process by which sodium metal is produced. However, the electrolysis of aqueous NaCl does not produce sodium metal under normal circumstances. Why? What is purification of a metal by electrolysis?

Active Learning Questions

These questions are designed to be used by groups of students in class. The questions allow students to explore their understanding of concepts through discussion and peer teaching. The real value of these questions is the learning that occurs while students talk to each other about chemical concepts.

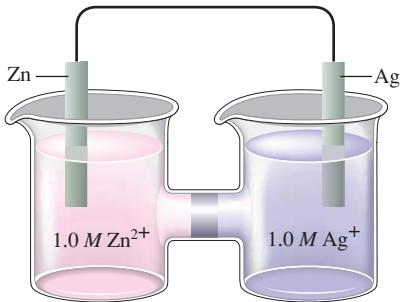
1. Sketch a galvanic cell, and explain how it works. Look at Figs. 17.1 and 17.2. Explain what is occurring in each container and why the cell in Fig. 17.2 “works” but the one in Fig. 17.1 does not.
2. In making a specific galvanic cell, explain how one decides on the electrodes and the solutions to use in the cell.

3. You want to “plate out” nickel metal from a nickel nitrate solution onto a piece of metal inserted into the solution. Should you use copper or zinc? Explain.
4. A copper penny can be dissolved in nitric acid but not in hydrochloric acid. Using reduction potentials from the book, show why this is so. What are the products of the reaction? Newer pennies contain a mixture of zinc and copper. What happens to the zinc in the penny when the coin is placed in nitric acid? Hydrochloric acid? Support your explanations with data from the book, and include balanced equations for all reactions.
5. Sketch a cell that forms iron metal from iron(II) while changing chromium metal to chromium(III). Calculate the voltage, show

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the electron flow, label the anode and cathode, and balance the overall cell equation.

6. Which of the following is the best reducing agent: F₂, H₂, Na, Na⁺, F⁻? Explain. Order as many of these species as possible from the best to the worst oxidizing agent. Why can't you order all of them? From Table 17.1 choose the species that is the best oxidizing agent. Choose the best reducing agent. Explain.
7. You are told that metal A is a better reducing agent than metal B. What, if anything, can be said about A⁺ and B⁺? Explain.
8. Explain the following relationships: ΔG and w, cell potential and w, cell potential and ΔG, cell potential and Q. Using these relationships, explain how you could make a cell in which both electrodes are the same metal and both solutions contain the same compound, but at different concentrations. Why does such a cell run spontaneously?
9. Explain why cell potentials are not multiplied by the coefficients in the balanced redox equation. (Use the relationship between ΔG and cell potential to do this.)
10. What is the difference between \mathcal{E} and \mathcal{E}° ? When is \mathcal{E} equal to zero? When is \mathcal{E}° equal to zero? (Consider "regular" galvanic cells as well as concentration cells.)
11. Consider the following galvanic cell:



What happens to \mathcal{E} as the concentration of Zn²⁺ is increased? As the concentration of Ag⁺ is increased? What happens to \mathcal{E}° in these cases?

12. Look up the reduction potential for Fe³⁺ to Fe²⁺. Look up the reduction potential for Fe²⁺ to Fe. Finally, look up the reduction potential for Fe³⁺ to Fe. You should notice that adding the reduction potentials for the first two does not give the potential for the third. Why not? Show how you can use the first two potentials to calculate the third potential.

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide*.

Review of Oxidation–Reduction Reactions

If you have trouble with these exercises, you should review Sections 4.9 and 4.10.

13. Define *oxidation* and *reduction* in terms of both change in oxidation number and electron loss or gain.
14. Assign oxidation numbers to all the atoms in each of the following.

- a. HNO₃
- b. CuCl₂
- c. O₂
- d. H₂O₂
- e. C₆H₁₂O₆
- f. Ag
- g. PbSO₄
- h. PbO₂
- i. Na₂C₂O₄
- j. CO₂
- k. (NH₄)₂Ce(SO₄)₃
- l. Cr₂O₃

15. Specify which of the following equations represent oxidation–reduction reactions, and indicate the oxidizing agent, the reducing agent, the species being oxidized, and the species being reduced.
 - a. CH₄(g) + H₂O(g) → CO(g) + 3H₂(g)
 - b. 2AgNO₃(aq) + Cu(s) → Cu(NO₃)₂(aq) + 2Ag(s)
 - c. Zn(s) + 2HCl(aq) → ZnCl₂(aq) + H₂(g)
 - d. 2H⁺(aq) + 2CrO₄²⁻(aq) → Cr₂O₇²⁻(aq) + H₂O(l)
16. Balance each of the following equations by the half-reaction method for the pH conditions specified.
 - a. Cr(s) + NO₃⁻(aq) → Cr³⁺(aq) + NO(g) (acidic)
 - b. Al(s) + MnO₄⁻(aq) → Al³⁺(aq) + Mn²⁺(aq) (acidic)
 - c. CH₃OH(aq) + Ce⁴⁺(aq) → CO₂(aq) + Ce³⁺(aq) (acidic)
 - d. PO₃³⁻(aq) + MnO₄⁻(aq) → PO₄³⁻(aq) + MnO₂(s) (basic)
 - e. Mg(s) + OCl⁻(aq) → Mg(OH)₂(s) + Cl⁻(aq) (basic)
 - f. H₂CO(aq) + Ag(NH₃)₂⁺(aq) → HCO₃⁻(aq) + Ag(s) + NH₃(aq) (basic)

Questions

17. When magnesium metal is added to a beaker of HCl(aq), a gas is produced. Knowing that magnesium is oxidized and that hydrogen is reduced, write the balanced equation for the reaction. How many electrons are transferred in the balanced equation? What quantity of useful work can be obtained when Mg is added directly to the beaker of HCl? How can you harness this reaction to do useful work?
18. How can one construct a galvanic cell from two substances, each having a negative standard reduction potential?
19. The free energy change for a reaction, ΔG, is an extensive property. What is an extensive property? Surprisingly, one can calculate ΔG from the cell potential, \mathcal{E} , for the reaction. This is surprising because \mathcal{E} is an intensive property. How can the extensive property ΔG be calculated from the intensive property \mathcal{E} ?
20. What is wrong with the following statement: The best concentration cell will consist of the substance having the most positive standard reduction potential. What drives a concentration cell to produce a large voltage?
21. When jump-starting a car with a dead battery, the ground jumper should be attached to a remote part of the engine block. Why?
22. In theory, most metals should easily corrode in air. Why? A group of metals called the noble metals are relatively difficult to corrode in air. Some noble metals include: gold, platinum, and silver. Reference Table 17.1 to come up with a possible reason why the noble metals are relatively difficult to corrode.
23. Consider the electrolysis of a molten salt of some metal. What information must you know to calculate the mass of metal plated out in the electrolytic cell?
24. Although aluminum is one of the most abundant elements on earth, production of pure Al proved very difficult until the late 1800s. At this time, the Hall–Heroult process made it relatively easy to produce pure Al. Why was pure Al so difficult to produce and what was the key discovery behind the Hall–Heroult process?

Exercises

In this section similar exercises are paired.

Galvanic Cells, Cell Potentials, Standard Reduction Potentials, and Free Energy

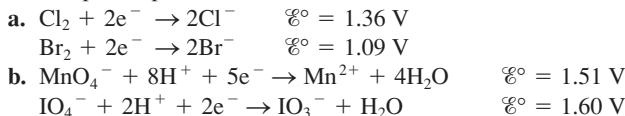
- 25.** Sketch the galvanic cells based on the following overall reactions. Show the direction of electron flow and identify the cathode and anode. Give the overall balanced reaction. Assume that all concentrations are 1.0 M and that all partial pressures are 1.0 atm.
- $\text{Cr}^{3+}(aq) + \text{Cl}_2(g) \rightleftharpoons \text{Cr}_2\text{O}_7^{2-}(aq) + \text{Cl}^-(aq)$
 - $\text{Cu}^{2+}(aq) + \text{Mg}(s) \rightleftharpoons \text{Mg}^{2+}(aq) + \text{Cu}(s)$

- 26.** Sketch the galvanic cells based on the following overall reactions. Show the direction of electron flow, the direction of ion migration through the salt bridge, and identify the cathode and anode. Give the overall balanced reaction. Assume that all concentrations are 1.0 M and that all partial pressures are 1.0 atm.
- $\text{IO}_3^-(aq) + \text{Fe}^{2+}(aq) \rightleftharpoons \text{Fe}^{3+}(aq) + \text{I}_2(aq)$
 - $\text{Zn}(s) + \text{Ag}^+(aq) \rightleftharpoons \text{Zn}^{2+}(aq) + \text{Ag}(s)$

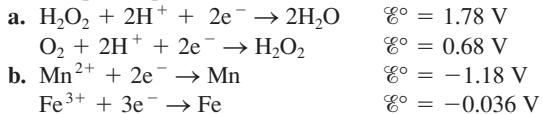
- 27.** Calculate \mathcal{E}° values for the galvanic cells in Exercise 25.

- 28.** Calculate \mathcal{E}° values for the galvanic cells in Exercise 26.

- 29.** Sketch the galvanic cells based on the following half-reactions. Show the direction of electron flow, show the direction of ion migration through the salt bridge, and identify the cathode and anode. Give the overall balanced reaction, and determine \mathcal{E}° for the galvanic cells. Assume that all concentrations are 1.0 M and that all partial pressures are 1.0 atm.



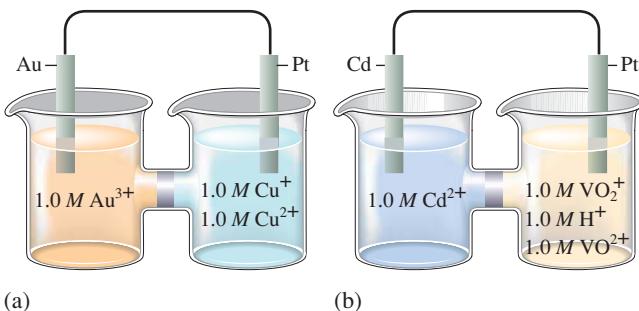
- 30.** Sketch the galvanic cells based on the following half-reactions. Show the direction of electron flow, show the direction of ion migration through the salt bridge, and identify the cathode and anode. Give the overall balanced reaction, and determine \mathcal{E}° for the galvanic cells. Assume that all concentrations are 1.0 M and that all partial pressures are 1.0 atm.



- 31.** Give the standard line notation for each cell in Exercises 25 and 29.

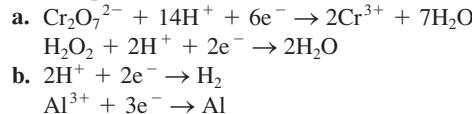
- 32.** Give the standard line notation for each cell in Exercises 26 and 30.

- 33.** Consider the following galvanic cells:

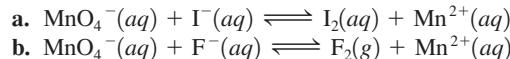


For each galvanic cell, give the balanced cell reaction and determine \mathcal{E}° . Standard reduction potentials are found in Table 17.1.

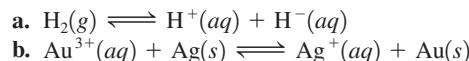
- 34.** Give the balanced cell reaction and determine \mathcal{E}° for the galvanic cells based on the following half-reactions. Standard reduction potentials are found in Table 17.1.



- 35.** Calculate \mathcal{E}° values for the following cells. Which reactions are spontaneous as written (under standard conditions)? Balance the reactions. Standard reduction potentials are found in Table 17.1.



- 36.** Calculate \mathcal{E}° values for the following cells. Which reactions are spontaneous as written (under standard conditions)? Balance the reactions that are not already balanced. Standard reduction potentials are found in Table 17.1.

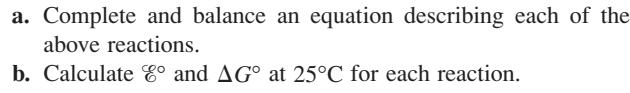


- 37.** Chlorine dioxide (ClO_2), which is produced by the reaction



has been tested as a disinfectant for municipal water treatment. Using data from Table 17.1, calculate \mathcal{E}° and ΔG° at 25°C for the production of ClO_2 .

- 38.** The amount of manganese in steel is determined by changing it to permanganate ion. The steel is first dissolved in nitric acid, producing Mn^{2+} ions. These ions are then oxidized to the deeply colored MnO_4^- ions by periodate ion (IO_4^-) in acid solution.



- 39.** Calculate the maximum amount of work that can be obtained from the galvanic cells at standard conditions in Exercise 33.

- 40.** Calculate the maximum amount of work that can be obtained from the galvanic cells at standard conditions in Exercise 34.

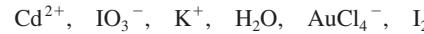
- 41.** Calculate \mathcal{E}° for the reaction



using values of ΔG_f° in Appendix 4.

- 42.** The equation $\Delta G^\circ = -nF\mathcal{E}^\circ$ also can be applied to half-reactions. Use standard reduction potentials to estimate ΔG_f° for $\text{Fe}^{2+}(aq)$ and $\text{Fe}^{3+}(aq)$. (ΔG_f° for $e^- = 0$.)

- 43.** Using data from Table 17.1, place the following in order of increasing strength as oxidizing agents (all under standard conditions).



- 44.** Using data from Table 17.1, place the following in order of increasing strength as reducing agents (all under standard conditions).



45. Answer the following questions using data from Table 17.1 (all under standard conditions).

- Is $H^+(aq)$ capable of oxidizing $Cu(s)$ to $Cu^{2+}(aq)$?
- Is $Fe^{3+}(aq)$ capable of oxidizing $I^-(aq)$?
- Is $H_2(g)$ capable of reducing $Ag^+(aq)$?
- Is $Fe^{2+}(aq)$ capable of reducing $Cr^{3+}(aq)$ to $Cr^{2+}(aq)$?

46. Consider only the species (at standard conditions)



in answering the following questions. Give reasons for your answers. (Use data from Table 17.1.)

- Which is the strongest oxidizing agent?
- Which is the strongest reducing agent?
- Which species can be oxidized by $SO_4^{2-}(aq)$ in acid?
- Which species can be reduced by $Al(s)$?

47. Use the table of standard reduction potentials (Table 17.1) to pick a reagent that is capable of each of the following oxidations (under standard conditions in acidic solution).

- Oxidize Br^- to Br_2 but not oxidize Cl^- to Cl_2
- Oxidize Mn to Mn^{2+} but not oxidize Ni to Ni^{2+}

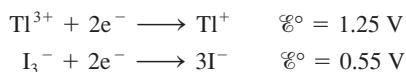
48. Use the table of standard reduction potentials (Table 17.1) to pick a reagent that is capable of each of the following reductions (under standard conditions in acidic solution).

- Reduce Cu^{2+} to Cu but not reduce Cu^{2+} to Cu^+ .
- Reduce Br_2 to Br^- but not reduce I_2 to I^- .

49. Hydrazine is somewhat toxic. Use the half-reactions shown below to explain why household bleach (a highly alkaline solution of sodium hypochlorite) should not be mixed with household ammonia or glass cleaners that contain ammonia.



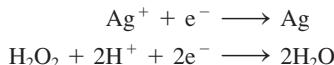
50. The compound with the formula TlI_3 is a black solid. Given the following standard reduction potentials,



would you formulate this compound as thallium(III) iodide or thallium(I) triiodide?

The Nernst Equation

51. A galvanic cell is based on the following half-reactions at 25°C:



Predict whether E_{cell} is larger or smaller than E_{cell}° for the following cases.

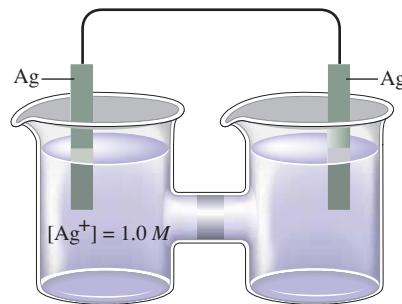
- $[Ag^+] = 1.0\text{ M}$, $[H_2O_2] = 2.0\text{ M}$, $[H^+] = 2.0\text{ M}$
- $[Ag^+] = 2.0\text{ M}$, $[H_2O_2] = 1.0\text{ M}$, $[H^+] = 1.0 \times 10^{-7}\text{ M}$

52. Consider the concentration cell in Fig. 17.10. If the Fe^{2+} concentration in the right compartment is changed from 0.1 M to $1 \times 10^{-7}\text{ M}$ Fe^{2+} , predict the direction of electron flow, and designate the anode and cathode compartments.

53. Consider the concentration cell shown below. Calculate the cell potential at 25°C when the concentration of Ag^+ in the compartment on the right is the following.

- 1.0 M
- 2.0 M
- 0.10 M
- $4.0 \times 10^{-5}\text{ M}$

e. Calculate the potential when both solutions are 0.10 M in Ag^+ . For each case, also identify the cathode, the anode, and the direction in which electrons flow.

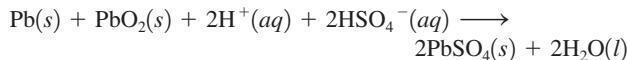


54. Consider a concentration cell similar to the one shown in Exercise 53, except that both electrodes are made of Ni and in the left-hand compartment $[Ni^{2+}] = 1.0\text{ M}$. Calculate the cell potential at 25°C when the concentration of Ni^{2+} in the compartment on the right has each of the following values.

- 1.0 M
- 2.0 M
- 0.10 M
- $4.0 \times 10^{-5}\text{ M}$

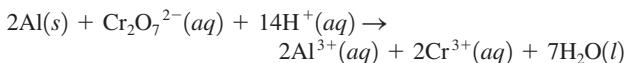
e. Calculate the potential when both solutions are 2.5 M in Ni^{2+} . For each case, also identify the cathode, anode, and the direction in which electrons flow.

55. The overall reaction in the lead storage battery is

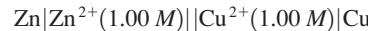


Calculate E at 25°C for this battery when $[H_2SO_4] = 4.5\text{ M}$, that is, $[H^+] = [HSO_4^-] = 4.5\text{ M}$. At 25°C, $E^\circ = 2.04\text{ V}$ for the lead storage battery.

56. Calculate the pH of the cathode compartment for the following reaction given $E_{cell} = 3.01\text{ V}$ when $[Cr^{3+}] = 0.15\text{ M}$, $[Al^{3+}] = 0.30\text{ M}$, and $[Cr_2O_7^{2-}] = 0.55\text{ M}$.

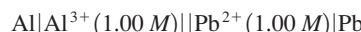


57. Consider the cell described below:



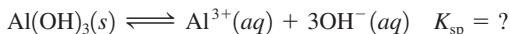
Calculate the cell potential after the reaction has operated long enough for the $[Zn^{2+}]$ to have changed by 0.20 mol/L. (Assume $T = 25^\circ\text{C}$.)

58. Consider the cell described below:

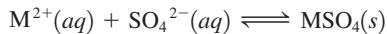


Calculate the cell potential after the reaction has operated long enough for the $[Al^{3+}]$ to have changed by 0.60 mol/L. (Assume $T = 25^\circ C$.)

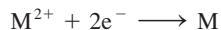
- 59.** An electrochemical cell consists of a standard hydrogen electrode and a copper metal electrode.
- What is the potential of the cell at $25^\circ C$ if the copper electrode is placed in a solution in which $[Cu^{2+}] = 2.5 \times 10^{-4} M$?
 - The copper electrode is placed in a solution of unknown $[Cu^{2+}]$. The measured potential at $25^\circ C$ is 0.195 V. What is $[Cu^{2+}]$? (Assume Cu^{2+} is reduced.)
- 60.** An electrochemical cell consists of a nickel metal electrode immersed in a solution with $[Ni^{2+}] = 1.0 M$ separated by a porous disk from an aluminum metal electrode.
- What is the potential of this cell at $25^\circ C$ if the aluminum electrode is placed in a solution in which $[Al^{3+}] = 7.2 \times 10^{-3} M$?
 - When the aluminum electrode is placed in a certain solution in which $[Al^{3+}]$ is unknown, the measured cell potential at $25^\circ C$ is 1.62 V. Calculate $[Al^{3+}]$ in the unknown solution. (Assume Al is oxidized.)
- 61.** An electrochemical cell consists of a standard hydrogen electrode and a copper metal electrode. If the copper electrode is placed in a solution of $0.10 M$ NaOH that is saturated with $Cu(OH)_2$, what is the cell potential at $25^\circ C$? (For $Cu(OH)_2$, $K_{sp} = 1.6 \times 10^{-19}$.)
- 62.** An electrochemical cell consists of a nickel metal electrode immersed in a solution with $[Ni^{2+}] = 1.0 M$ separated by a porous disk from an aluminum metal electrode immersed in a solution with $[Al^{3+}] = 1.0 M$. Sodium hydroxide is added to the aluminum compartment, causing $Al(OH)_3(s)$ to precipitate. After precipitation of $Al(OH)_3$ has ceased, the concentration of OH^- is $1.0 \times 10^{-4} M$ and the measured cell potential is 1.82 V. Calculate the K_{sp} value for $Al(OH)_3$.



- 63.** Consider a concentration cell that has both electrodes made of some metal M. Solution A in one compartment of the cell contains $1.0 M$ M^{2+} . Solution B in the other cell compartment has a volume of 1.00 L. At the beginning of the experiment 0.0100 mol of $M(NO_3)_2$ and 0.0100 mol of Na_2SO_4 are dissolved in solution B (ignore volume changes), where the reaction



occurs. For this reaction equilibrium is rapidly established, whereupon the cell potential is found to be $+0.44 V$ at $25^\circ C$. Assume that the process



has a standard reduction potential of $-0.31 V$ and that no other redox process occurs in the cell. Calculate the value of K_{sp} for $MSO_4(s)$ at $25^\circ C$.

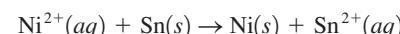
- 64.** You have a concentration cell in which the cathode has a silver electrode with $0.10 M$ Ag^+ . The anode also has a silver electrode with $Ag^+(aq)$, $0.050 M$ $S_2O_3^{2-}$, and $1.0 \times 10^{-3} M$ $Ag(S_2O_3)_2^{3-}$. You read the voltage to be $0.76 V$.

- Calculate the concentration of Ag^+ at the cathode.
- Determine the value of the equilibrium constant for the formation of $Ag(S_2O_3)_2^{3-}$.



- 65.** Calculate ΔG° and K at $25^\circ C$ for the reactions in Exercises 25 and 29.
- 66.** Calculate ΔG° and K at $25^\circ C$ for the reactions in Exercises 26 and 30.
- 67.** An excess of finely divided iron is stirred up with a solution that contains Cu^{2+} ion, and the system is allowed to come to equilibrium. The solid materials are then filtered off, and electrodes of solid copper and solid iron are inserted into the remaining solution. What is the value of the ratio $[Fe^{2+}]/[Cu^{2+}]$ at $25^\circ C$?

- 68.** Consider the following reaction:



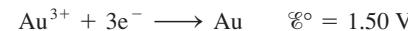
Determine the minimum ratio of $[Sn^{2+}]/[Ni^{2+}]$ necessary to make this reaction spontaneous as written.

- 69.** Under standard conditions, what reaction occurs, if any, when each of the following operations is performed?
- Crystals of I_2 are added to a solution of $NaCl$.
 - Cl_2 gas is bubbled into a solution of NaI .
 - A silver wire is placed in a solution of $CuCl_2$.
 - An acidic solution of $FeSO_4$ is exposed to air.
- For the reactions that occur, write a balanced equation and calculate \mathcal{E}° , ΔG° , and K at $25^\circ C$.
- 70.** A disproportionation reaction involves a substance that acts as both an oxidizing and a reducing agent, producing higher and lower oxidation states of the same element in the products. Which of the following disproportionation reactions are spontaneous under standard conditions? Calculate ΔG° and K at $25^\circ C$ for those reactions that are spontaneous under standard conditions.
- $2Cu^{+}(aq) \rightarrow Cu^{2+}(aq) + Cu(s)$
 - $3Fe^{2+}(aq) \rightarrow 2Fe^{3+}(aq) + Fe(s)$
 - $HClO_2(aq) \rightarrow ClO_3^-(aq) + HClO(aq)$ (unbalanced)

Use the half-reactions:

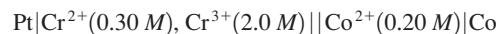


- 71.** Consider the galvanic cell based on the following half-reactions:



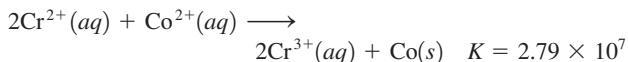
- Determine the overall cell reaction and calculate \mathcal{E}_{cell}° .
- Calculate ΔG° and K for the cell reaction at $25^\circ C$.
- Calculate \mathcal{E}_{cell}° at $25^\circ C$ when $[Au^{3+}] = 1.0 \times 10^{-2} M$ and $[Tl^+] = 1.0 \times 10^{-4} M$.

- 72.** Consider the following galvanic cell at $25^\circ C$:



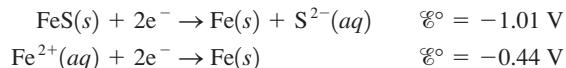
834 Chapter Seventeen Electrochemistry

The overall reaction and equilibrium constant value are

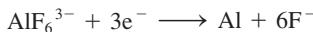


Calculate the cell potential, \mathcal{E} , for this galvanic cell and ΔG for the cell reaction at these conditions.

- 73.** Calculate K_{sp} for iron(II) sulfide given the following data:



- 74.** For the following half-reaction, $\mathcal{E}^\circ = -2.07 \text{ V}$:

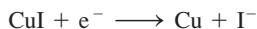


Using data from Table 17.1, calculate the equilibrium constant at 25°C for the reaction



- 75.** Calculate the value of the equilibrium constant for the reaction of zinc metal in a solution of silver nitrate at 25°C.

- 76.** The solubility product for CuI(s) is 1.1×10^{-12} . Calculate the value of \mathcal{E}° for the half-reaction



Electrolysis

- 77.** How long will it take to plate out each of the following with a current of 100.0 A?

- a. 1.0 kg Al from aqueous Al^{3+}
- b. 1.0 g Ni from aqueous Ni^{2+}
- c. 5.0 mol Ag from aqueous Ag^+

- 78.** The electrolysis of BiO^+ produces pure bismuth. How long would it take to produce 10.0 g of Bi by the electrolysis of a BiO^+ solution using a current of 25.0 A?

- 79.** What mass of each of the following substances can be produced in 1.0 h with a current of 15 A?

- a. Co from aqueous Co^{2+}
- b. Hf from aqueous Hf^{4+}
- c. I_2 from aqueous KI
- d. Cr from molten CrO_3

- 80.** Aluminum is produced commercially by the electrolysis of Al_2O_3 in the presence of a molten salt. If a plant has a continuous capacity of 1.00 million amp, what mass of aluminum can be produced in 2.00 h?

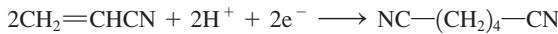
- 81.** An unknown metal M is electrolyzed. It took 74.1 s for a current of 2.00 amp to plate out 0.107 g of the metal from a solution containing $\text{M}(\text{NO}_3)_3$. Identify the metal.

- 82.** Electrolysis of an alkaline earth metal chloride using a current of 5.00 A for 748 s deposits 0.471 g of metal at the cathode. What is the identity of the alkaline earth metal chloride?

- 83.** What volume of F_2 gas, at 25°C and 1.00 atm, is produced when molten KF is electrolyzed by a current of 10.0 A for 2.00 h? What mass of potassium metal is produced? At which electrode does each reaction occur?

- 84.** What volumes of $\text{H}_2(g)$ and $\text{O}_2(g)$ at STP are produced from the electrolysis of water by a current of 2.50 A in 15.0 min?

- 85.** One of the few industrial-scale processes that produce organic compounds electrochemically is used by the Monsanto Company to produce 1,4-dicyanobutane. The reduction reaction is



The $\text{NC}-(\text{CH}_2)_4-\text{CN}$ is then chemically reduced using hydrogen gas to $\text{H}_2\text{N}-(\text{CH}_2)_6-\text{NH}_2$, which is used in the production of nylon. What current must be used to produce 150. kg of $\text{NC}-(\text{CH}_2)_4-\text{CN}$ per hour?

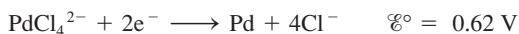
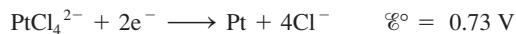
- 86.** A single Hall–Heroult cell (as shown in Fig. 17.22) produces about 1 ton of aluminum in 24 hours. What current must be used to accomplish this?

- 87.** It took 2.30 min using a current of 2.00 A to plate out all the silver from 0.250 L of a solution containing Ag^+ . What was the original concentration of Ag^+ in the solution?

- 88.** A solution containing Pt^{4+} is electrolyzed with a current of 4.00 A. How long will it take to plate out 99% of the platinum in 0.50 L of a 0.010 M solution of Pt^{4+} ?

- 89.** A solution at 25°C contains 1.0 M Cd^{2+} , 1.0 M Ag^+ , 1.0 M Au^{3+} , and 1.0 M Ni^{2+} in the cathode compartment of an electrolytic cell. Predict the order in which the metals will plate out as the voltage is gradually increased.

- 90.** Consider the following half-reactions:



A hydrochloric acid solution contains platinum, palladium, and iridium as chloro-complex ions. The solution is a constant 1.0 M in chloride ion and 0.020 M in each complex ion. Is it feasible to separate the three metals from this solution by electrolysis? (Assume that 99% of a metal must be plated out before another metal begins to plate out.)

- 91.** What reactions take place at the cathode and the anode when each of the following is electrolyzed?

- a. molten NiBr_2
- b. molten AlF_3
- c. molten MnI_2

- 92.** What reactions take place at the cathode and the anode when each of the following is electrolyzed? (Assume standard conditions.)

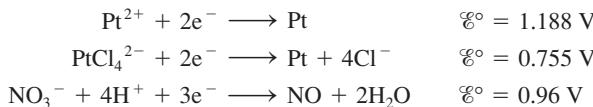
- a. 1.0 M NiBr_2 solution
- b. 1.0 M AlF_3 solution
- c. 1.0 M MnI_2 solution

Additional Exercises

- 93.** The saturated calomel electrode, abbreviated SCE, is often used as a reference electrode in making electrochemical measurements. The SCE is composed of mercury in contact with a saturated solution of calomel (Hg_2Cl_2). The electrolyte solution is saturated KCl. \mathcal{E}_{SCE} is +0.242 V relative to the standard hydrogen electrode. Calculate the potential for each of the following galvanic cells containing a saturated calomel electrode and the given half-cell components at standard conditions. In each case, indicate whether the SCE is the cathode or the anode. Standard reduction potentials are found in Table 17.1.

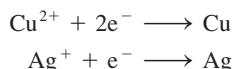
- $\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}$
- $\text{Fe}^{3+} + \text{e}^- \longrightarrow \text{Fe}^{2+}$
- $\text{AgCl} + \text{e}^- \longrightarrow \text{Ag} + \text{Cl}^-$
- $\text{Al}^{3+} + 3\text{e}^- \longrightarrow \text{Al}$
- $\text{Ni}^{2+} + 2\text{e}^- \longrightarrow \text{Ni}$

94. Consider the following half-reactions:



Explain why platinum metal will dissolve in aqua regia (a mixture of hydrochloric and nitric acids) but not in either concentrated nitric or concentrated hydrochloric acid individually.

95. Consider the standard galvanic cell based on the following half-reactions



The electrodes in this cell are $\text{Ag}(s)$ and $\text{Cu}(s)$. Does the cell potential increase, decrease, or remain the same when the following changes occur to the standard cell?

- $\text{CuSO}_4(s)$ is added to the copper half-cell compartment (assume no volume change).
- $\text{NH}_3(aq)$ is added to the copper half-cell compartment. Hint: Cu^{2+} reacts with NH_3 to form $\text{Cu}(\text{NH}_3)_4^{2+}(aq)$.
- $\text{NaCl}(s)$ is added to the silver half-cell compartment. Hint: Ag^+ reacts with Cl^- to form $\text{AgCl}(s)$.
- Water is added to both half-cell compartments until the volume of solution is doubled.
- The silver electrode is replaced with a platinum electrode.

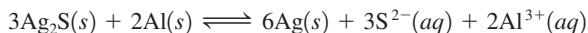


96. A standard galvanic cell is constructed so that the overall cell reaction is

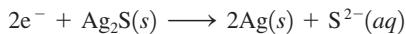


where M is an unknown metal. If $\Delta G^\circ = -411 \text{ kJ}$ for the overall cell reaction, identify the metal used to construct the standard cell.

97. The black silver sulfide discoloration of silverware can be removed by heating the silver article in a sodium carbonate solution in an aluminum pan. The reaction is



- Using data in Appendix 4, calculate ΔG° , K, and \mathcal{E}° for the above reaction at 25°C . (For $\text{Al}^{3+}(aq)$, $\Delta G_f^\circ = -480 \text{ kJ/mol}$.)
- Calculate the value of the standard reduction potential for the following half-reaction:



98. In 1973 the wreckage of the Civil War ironclad USS *Monitor* was discovered near Cape Hatteras, North Carolina. (The *Monitor* and the CSS *Virginia* [formerly the USS *Merrimack*] fought the first battle between iron-armored ships.) In 1987 investigations were begun to see if the ship could be salvaged. It was reported in *Time* (June 22, 1987) that scientists were considering adding sacrificial anodes of zinc to the rapidly

corroding metal hull of the *Monitor*. Describe how attaching zinc to the hull would protect the *Monitor* from further corrosion.

- When aluminum foil is placed in hydrochloric acid, nothing happens for the first 30 seconds or so. This is followed by vigorous bubbling and the eventual disappearance of the foil. Explain these observations.
 - Which of the following statements concerning corrosion is/are true? For the false statements, correct them.
 - Corrosion is an example of an electrolytic process.
 - Corrosion of steel involves the reduction of iron coupled with the oxidation of oxygen.
 - Steel rusts more easily in the dry (arid) Southwest states than in the humid Midwest states.
 - Salting roads in the winter has the added benefit of hindering the corrosion of steel.
 - The key to cathodic protection is to connect via a wire a metal more easily oxidized than iron to the steel surface to be protected.
 - A patent attorney has asked for your advice concerning the merits of a patent application that describes a single aqueous galvanic cell capable of producing a 12-V potential. Comment.
 - The overall reaction and equilibrium constant value for a hydrogen–oxygen fuel cell at 298 K is
- $$2\text{H}_2(g) + \text{O}_2(g) \longrightarrow 2\text{H}_2\text{O}(l) \quad K = 1.28 \times 10^{83}$$
- Calculate \mathcal{E}° and ΔG° at 298 K for the fuel cell reaction.
 - Predict the signs of ΔH° and ΔS° for the fuel cell reaction.
 - As temperature increases, does the maximum amount of work obtained from the fuel cell reaction increase, decrease, or remain the same? Explain.
- What is the maximum work that can be obtained from a hydrogen–oxygen fuel cell at standard conditions that produces 1.00 kg of water at 25°C ? Why do we say that this is the maximum work that can be obtained? What are the advantages and disadvantages in using fuel cells rather than the corresponding combustion reactions to produce electricity?
 - The overall reaction and standard cell potential at 25°C for the rechargeable nickel–cadmium alkaline battery is
- $$\text{Cd}(s) + \text{NiO}_2(s) + 2\text{H}_2\text{O}(l) \longrightarrow \text{Ni}(\text{OH})_2(s) + \text{Cd}(\text{OH})_2(s) \quad \mathcal{E}^\circ = 1.10 \text{ V}$$
- For every mole of Cd consumed in the cell, what is the maximum useful work that can be obtained at standard conditions?
- An experimental fuel cell has been designed that uses carbon monoxide as fuel. The overall reaction is
- $$2\text{CO}(g) + \text{O}_2(g) \longrightarrow 2\text{CO}_2(g)$$
- The two half-cell reactions are
- $$\begin{array}{l} \text{CO} + \text{O}^{2-} \longrightarrow \text{CO}_2 + 2\text{e}^- \\ \text{O}_2 + 4\text{e}^- \longrightarrow 2\text{O}^{2-} \end{array}$$
- The two half-reactions are carried out in separate compartments connected with a solid mixture of CeO_2 and Gd_2O_3 . Oxide ions can move through this solid at high temperatures (about 800°C). ΔG for the overall reaction at 800°C under certain concentration conditions is -380 kJ . Calculate the cell potential for this fuel cell at the same temperature and concentration conditions.

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- 106.** A fuel cell designed to react grain alcohol with oxygen has the following net reaction:



The maximum work 1 mol of alcohol can yield by this process is 1320 kJ. What is the theoretical maximum voltage this cell can achieve?

- 107.** Gold is produced electrochemically from an aqueous solution of $\text{Au}(\text{CN})_2^-$ containing an excess of CN^- . Gold metal and oxygen gas are produced at the electrodes. What amount (moles) of O_2 will be produced during the production of 1.00 mol of gold?
- 108.** In the electrolysis of a sodium chloride solution, what volume of $\text{H}_2(g)$ is produced in the same time it takes to produce 257 L of $\text{Cl}_2(g)$, with both volumes measured at 50.°C and 2.50 atm?
- 109.** An aqueous solution of an unknown salt of ruthenium is electrolyzed by a current of 2.50 A passing for 50.0 min. If 2.618 g Ru is produced at the cathode, what is the charge on the ruthenium ions in solution?
- 110.** It takes 15 kWh (kilowatt-hours) of electrical energy to produce 1.0 kg of aluminum metal from aluminum oxide by the Hall–Heroult process. Compare this to the amount of energy necessary to melt 1.0 kg of aluminum metal. Why is it economically feasible to recycle aluminum cans? (The enthalpy of fusion for aluminum metal is 10.7 kJ/mol [1 watt = 1 J/s].)

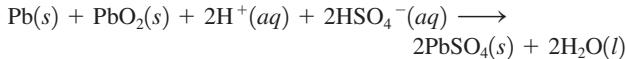
Challenge Problems

- 111.** Combine the equations

$$\Delta G^\circ = -nF\mathcal{E}^\circ \quad \text{and} \quad \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

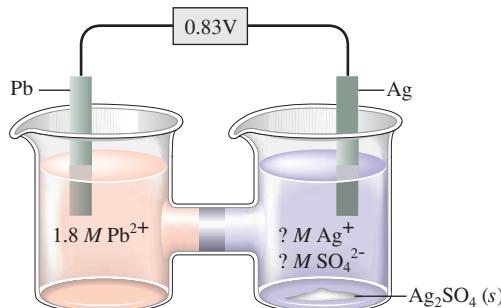
to derive an expression for \mathcal{E}° as a function of temperature. Describe how one can graphically determine ΔH° and ΔS° from measurements of \mathcal{E}° at different temperatures, assuming that ΔH° and ΔS° do not depend on temperature. What property would you look for in designing a reference half-cell that would produce a potential relatively stable with respect to temperature?

- 112.** The overall reaction in the lead storage battery is



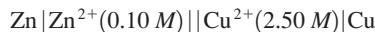
- a. For the cell reaction $\Delta H^\circ = -315.9$ kJ and $\Delta S^\circ = 263.5$ J/K. Calculate \mathcal{E}° at $-20.^\circ\text{C}$. Assume ΔH° and ΔS° do not depend on temperature.
 b. Calculate \mathcal{E} at $-20.^\circ\text{C}$ when $[\text{HSO}_4^-] = [\text{H}^+] = 4.5$ M.
 c. Consider your answer to Exercise 55. Why does it seem that batteries fail more often on cold days than on warm days?

- 113.** Consider the following galvanic cell:



Calculate the K_{sp} value for $\text{Ag}_2\text{SO}_4(s)$. Note that to obtain silver ions in the right compartment (the cathode compartment), excess solid Ag_2SO_4 was added and some of the salt dissolved.

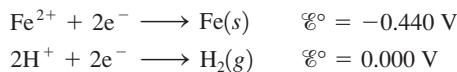
- 114.** A zinc–copper battery is constructed as follows at 25°C :



The mass of each electrode is 200. g.

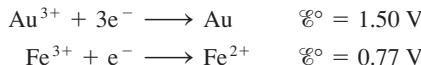
- a. Calculate the cell potential when this battery is first connected.
 b. Calculate the cell potential after 10.0 A of current has flowed for 10.0 h. (Assume each half-cell contains 1.00 L of solution.)
 c. Calculate the mass of each electrode after 10.0 h.
 d. How long can this battery deliver a current of 10.0 A before it goes dead?

- 115.** A galvanic cell is based on the following half-reactions:

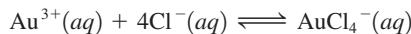


where the iron compartment contains an iron electrode and $[\text{Fe}^{2+}] = 1.00 \times 10^{-3}\text{ M}$ and the hydrogen compartment contains a platinum electrode, $P_{\text{H}_2} = 1.00$ atm, and a weak acid, HA, at an initial concentration of 1.00 M. If the observed cell potential is 0.333 V at 25°C , calculate the K_a value for the weak acid HA.

- 116.** Consider a cell based on the following half-reactions:



- a. Draw this cell under standard conditions, labeling the anode, the cathode, the direction of electron flow, and the concentrations, as appropriate.
 b. When enough $\text{NaCl}(s)$ is added to the compartment containing gold to make the $[\text{Cl}^-] = 0.10\text{ M}$, the cell potential is observed to be 0.31 V. Assume that Au^{3+} is reduced and assume that the reaction in the compartment containing gold is



Calculate the value of K for this reaction at 25°C .

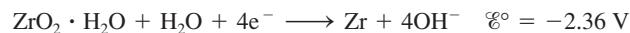
- 117.** The measurement of pH using a glass electrode obeys the Nernst equation. The typical response of a pH meter at 25.00°C is given by the equation

$$\mathcal{E}_{\text{meas}} = \mathcal{E}_{\text{ref}} + 0.05916\text{ pH}$$

where \mathcal{E}_{ref} contains the potential of the reference electrode and all other potentials that arise in the cell that are not related to the hydrogen ion concentration. Assume that $\mathcal{E}_{\text{ref}} = 0.250\text{ V}$ and that $\mathcal{E}_{\text{meas}} = 0.480\text{ V}$.

- a. What is the uncertainty in the values of pH and $[\text{H}^+]$ if the uncertainty in the measured potential is ± 1 mV (± 0.001 V)?
 b. To what precision must the potential be measured for the uncertainty in pH to be ± 0.02 pH unit?

- 118.** Zirconium is one of the few metals that retains its structural integrity upon exposure to radiation. For this reason, the fuel rods in most nuclear reactors are made of zirconium. Answer the following questions about the redox properties of zirconium based on the half-reaction

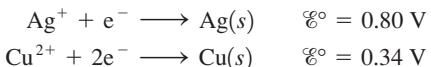


- Is zirconium metal capable of reducing water to form hydrogen gas at standard conditions?
- Write a balanced equation for the reduction of water by zirconium metal.
- Calculate \mathcal{E}° , ΔG° , and K for the reduction of water by zirconium metal.
- The reduction of water by zirconium occurred during the accident at Three Mile Island, Pennsylvania, in 1979. The hydrogen produced was successfully vented and no chemical explosion occurred. If 1.00×10^3 kg of Zr reacts, what mass of H₂ is produced? What volume of H₂ at 1.0 atm and 1000.°C is produced?
- At Chernobyl, USSR, in 1986, hydrogen was produced by the reaction of superheated steam with the graphite reactor core:



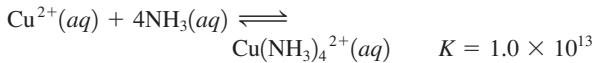
A chemical explosion involving the hydrogen gas did occur at Chernobyl. In light of this fact, do you think it was a correct decision to vent the hydrogen and other radioactive gases into the atmosphere at Three Mile Island? Explain.

- 119.** A galvanic cell is based on the following half-reactions:



In this cell, the silver compartment contains a silver electrode and excess AgCl(s) ($K_{\text{sp}} = 1.6 \times 10^{-10}$), and the copper compartment contains a copper electrode and $[\text{Cu}^{2+}] = 2.0 \text{ M}$.

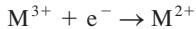
- Calculate the potential for this cell at 25°C.
- Assuming 1.0 L of 2.0 M Cu²⁺ in the copper compartment, calculate the moles of NH₃ that would have to be added to give a cell potential of 0.52 V at 25°C (assume no volume change on addition of NH₃).



- 120.** Given the following two standard reduction potentials,



solve for the standard reduction potential of the half-reaction



(Hint: You must use the extensive property ΔG° to determine the standard reduction potential.)

- You make a galvanic cell with a piece of nickel, 1.0 M Ni²⁺(aq), a piece of silver, and 1.0 M Ag⁺(aq). Calculate the concentrations of Ag⁺(aq) and Ni²⁺(aq) once the cell is “dead.”
- A chemist wishes to determine the concentration of CrO₄²⁻ electrochemically. A cell is constructed consisting of a saturated calomel electrode (SCE; see Exercise 93) and a silver wire coated with Ag₂CrO₄. The \mathcal{E}° value for the following half-reaction is +0.446 V relative to the standard hydrogen electrode:



- Calculate $\mathcal{E}_{\text{cell}}$ and ΔG at 25°C for the cell reaction when [CrO₄²⁻] = 1.00 mol/L.
- Write the Nernst equation for the cell. Assume that the SCE concentrations are constant.

- If the coated silver wire is placed in a solution (at 25°C) in which [CrO₄²⁻] = $1.00 \times 10^{-5} \text{ M}$, what is the expected cell potential?
- The measured cell potential at 25°C is 0.504 V when the coated wire is dipped into a solution of unknown [CrO₄²⁻]. What is [CrO₄²⁻] for this solution?
- Using data from this problem and from Table 17.1, calculate the solubility product (K_{sp}) for Ag₂CrO₄.

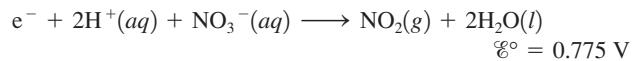
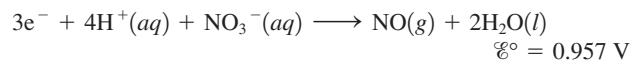
- 123.** You have a concentration cell with Cu electrodes and [Cu²⁺] = 1.00 M (right side) and $1.0 \times 10^{-4} \text{ M}$ (left side).

- Calculate the potential for this cell at 25°C.
- The Cu²⁺ ion reacts with NH₃ to form Cu(NH₃)₄²⁺ where the stepwise formation constants are $K_1 = 1.0 \times 10^3$, $K_2 = 1.0 \times 10^4$, $K_3 = 1.0 \times 10^3$, and $K_4 = 1.0 \times 10^3$. Calculate the new cell potential after enough NH₃ is added to the left cell compartment such that at equilibrium [NH₃] = 2.0 M.

- 124.** When copper reacts with nitric acid, a mixture of NO(g) and NO₂(g) is evolved. The volume ratio of the two product gases depends on the concentration of the nitric acid according to the equilibrium



Consider the following standard reduction potentials at 25°C:

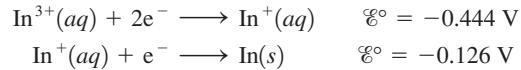


- Calculate the equilibrium constant for the above reaction.
- What concentration of nitric acid will produce a NO and NO₂ mixture with only 0.20% NO₂ (by moles) at 25°C and 1.00 atm? Assume that no other gases are present and that the change in acid concentration can be neglected.

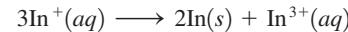
Integrative Problems

These problems require the integration of multiple concepts to find the solutions.

- 125.** The following standard reduction potentials have been determined for the aqueous chemistry of indium:



- What is the equilibrium constant for the disproportionation reaction, where a species is both oxidized and reduced, shown below?

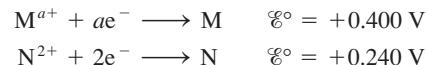


- What is ΔG_f° for In⁺(aq) if $\Delta G_f^\circ = -97.9 \text{ kJ/mol}$ for In³⁺(aq)?

- 126.** An electrochemical cell is set up using the following balanced reaction:



Given the standard reduction potentials are:



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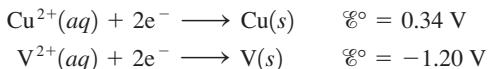
The cell contains 0.10 M N^{2+} and produces a voltage of 0.180 V . If the concentration of M^{a+} is such that the value of the reaction quotient Q is 9.32×10^{-3} , calculate $[\text{M}^{a+}]$. Calculate w_{\max} for this electrochemical cell.

- 127.** Three electrochemical cells were connected in series so that the same quantity of electrical current passes through all three cells. In the first cell, 1.15 g of chromium metal was deposited from a chromium(III) nitrate solution. In the second cell, 3.15 g of osmium was deposited from a solution made of Os^{n+} and nitrate ions. What is the name of the salt? In the third cell, the electrical charge passed through a solution containing X^{2+} ions caused deposition of 2.11 g of metallic X. What is the electron configuration of X?

Marathon Problems

These problems are designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

- 128.** A galvanic cell is based on the following half-reactions:



In this cell, the copper compartment contains a copper electrode and $[\text{Cu}^{2+}] = 1.00\text{ M}$, and the vanadium compartment contains

a vanadium electrode and V^{2+} at an unknown concentration. The compartment containing the vanadium (1.00 L of solution) was titrated with $0.0800\text{ M H}_2\text{EDTA}^{2-}$, resulting in the reaction



The potential of the cell was monitored to determine the stoichiometric point for the process, which occurred at a volume of 500.0 mL of $\text{H}_2\text{EDTA}^{2-}$ solution added. At the stoichiometric point, $\mathcal{E}_{\text{cell}}$ was observed to be 1.98 V . The solution was buffered at a pH of 10.00 .

- Calculate $\mathcal{E}_{\text{cell}}$ before the titration was carried out.
- Calculate the value of the equilibrium constant, K , for the titration reaction.
- Calculate $\mathcal{E}_{\text{cell}}$ at the halfway point in the titration.

- 129.** The table below lists the cell potentials for the 10 possible galvanic cells assembled from the metals A, B, C, D, and E, and their respective 1.00 M 2+ ions in solution. Using the data in the table, establish a standard reduction potential table similar to Table 17.1 in the text. Assign a reduction potential of 0.00 V to the half-reaction that falls in the middle of the series. You should get two different tables. Explain why, and discuss what you could do to determine which table is correct.

A(s) in $\text{A}^{2+}(aq)$	B(s) in $\text{B}^{2+}(aq)$	C(s) in $\text{C}^{2+}(aq)$	D(s) in $\text{D}^{2+}(aq)$
E(s) in $\text{E}^{2+}(aq)$	0.28 V	0.81 V	0.13 V
D(s) in $\text{D}^{2+}(aq)$	0.72 V	0.19 V	—
C(s) in $\text{C}^{2+}(aq)$	0.41 V	0.94 V	—
B(s) in $\text{B}^{2+}(aq)$	0.53 V	—	—



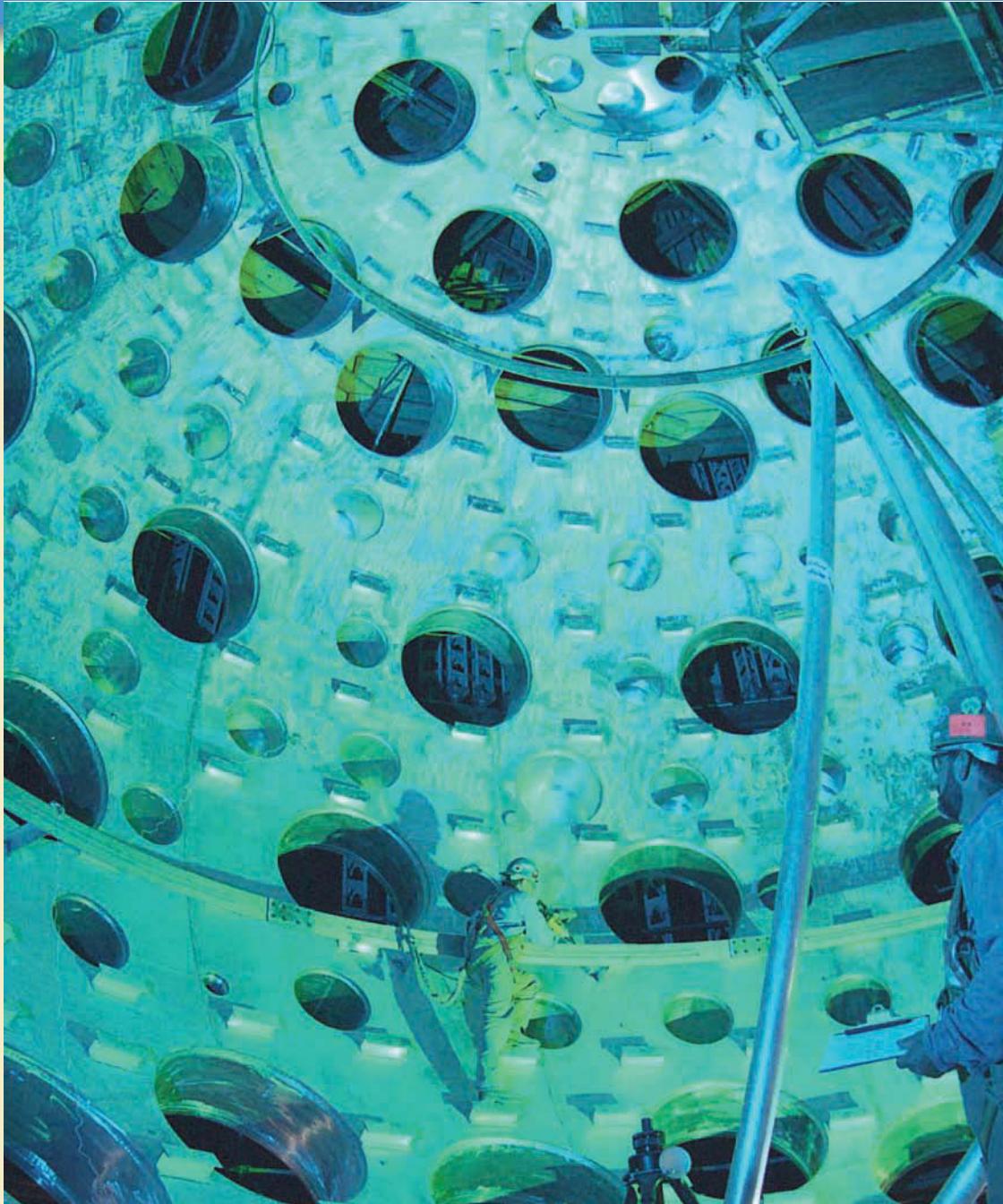
Get help understanding core concepts and visualizing molecular-level interactions, and practice problem solving, by visiting the Online Study Center at college.hmco.com/PIC/zumdahl7e.

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18 The Nucleus: A Chemist's View

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- 18.1 Nuclear Stability and Radioactive Decay**
 - Types of Radioactive Decay
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 - Nuclear Fission
 - Nuclear Reactors
 - Breeder Reactors
 - Fusion
- 18.7 Effects of Radiation**



Workers inside a giant chamber at the National Ignition Facility in California. This chamber will be used to induce nuclear fusion by aiming 192 lasers at a pellet of fuel.

Since the chemistry of an atom is determined by the number and arrangement of its electrons, the properties of the nucleus are not of primary importance to chemists. In the simplest view, the nucleus provides the positive charge to bind the electrons in atoms and molecules. However, a quick reading of any daily newspaper will show you that the nucleus and its properties have an important impact on our society. This chapter considers those aspects of the nucleus about which everyone should have some knowledge.

Several aspects of the nucleus are immediately impressive: its very small size, its very large density, and the magnitude of the energy that holds it together. The radius of a typical nucleus appears to be about 10^{-13} cm. This can be compared to the radius of a typical atom, which is on the order of 10^{-8} cm. A visualization will help you appreciate the small size of the nucleus: If the nucleus of the hydrogen atom were the size of a Ping-Pong ball, the electron in the 1s orbital would be, on average, 0.5 kilometer (0.3 mile) away. The density of the nucleus is equally impressive—approximately 1.6×10^{14} g/cm³. A sphere of nuclear material the size of a Ping-Pong ball would have a mass of *2.5 billion tons!* In addition, the energies involved in nuclear processes are typically millions of times larger than those associated with normal chemical reactions. This fact makes nuclear processes very attractive for feeding the voracious energy appetite of our civilization.

Atomos, the Greek root of the word *atom*, means “indivisible.” It was originally believed that the atom was the ultimate indivisible particle of which all matter was composed. However, as we discussed in Chapter 2, Lord Rutherford showed in 1911 that the atom is not homogeneous, but rather has a dense, positively charged center surrounded by electrons. Subsequently, scientists have learned that the nucleus of the atom can be subdivided into particles called **neutrons** and **protons**. In fact, in the past two decades it has become apparent that even the protons and neutrons are composed of smaller particles called *quarks*.

For most purposes, the nucleus can be regarded as a collection of **nucleons** (neutrons and protons), and the internal structures of these particles can be ignored. As we discussed in Chapter 2, the number of protons in a particular nucleus is called the **atomic number** (*Z*), and the sum of the neutrons and protons is the **mass number** (*A*). Atoms that have identical atomic numbers but different mass number values are called **isotopes**. However, we usually do not use the singular form *isotope* to refer to a particular member of a group of isotopes. Rather, we use the term *nuclide*. A **nuclide** is a unique atom, represented by the symbol



where X represents the symbol for a particular element. For example, the following nuclides constitute the isotopes of carbon: carbon-12 (${}^{12}_6 C$), carbon-13 (${}^{13}_6 C$), and carbon-14 (${}^{14}_6 C$).

The atomic number *Z* is the number of protons in a nucleus; the mass number *A* is the sum of protons and neutrons in a nucleus.

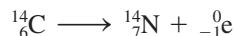
The term *isotopes* refers to a group of nuclides with the same atomic number. Each individual atom is properly called a *nuclide*, not an isotope.

18.1 Nuclear Stability and Radioactive Decay

Nuclear stability is the central topic of this chapter and forms the basis for all the important applications related to nuclear processes. Nuclear stability can be considered from both a kinetic and a thermodynamic point of view. **Thermodynamic stability**, as we will use the term here, refers to the potential energy of a particular nucleus as compared with the sum of the potential energies of its component protons and neutrons. We will use the term **kinetic stability** to describe the probability that a nucleus will undergo decomposition

to form a different nucleus—a process called **radioactive decay**. We will consider radioactivity in this section.

Many nuclei are radioactive; that is, they decompose, forming another nucleus and producing one or more particles. An example is carbon-14, which decays as follows:



where ${}_{-1}^0\text{e}$ represents an electron, which is called a **beta particle**, or **β particle**, in nuclear terminology. This equation is typical of those representing radioactive decay in that both A and Z must be conserved. That is, the Z values must give the same sum on both sides of the equation ($6 = 7 - 1$), as must the A values ($14 = 14 + 0$).

Of the approximately 2000 known nuclides, only 279 are stable with respect to radioactive decay. Tin has the largest number of stable isotopes—10.

It is instructive to examine how the numbers of neutrons and protons in a nucleus are related to its stability with respect to radioactive decay. Figure 18.1 shows a plot of the positions of the stable nuclei as a function of the number of protons (Z) and the number of neutrons ($A - Z$). The stable nuclides are said to reside in the **zone of stability**.

The following are some important observations concerning radioactive decay:

- All nuclides with 84 or more protons are unstable with respect to radioactive decay.
- Light nuclides are stable when Z equals $A - Z$, that is, when the neutron/proton ratio is 1. However, for heavier elements the neutron/proton ratio required for stability is greater than 1 and increases with Z .

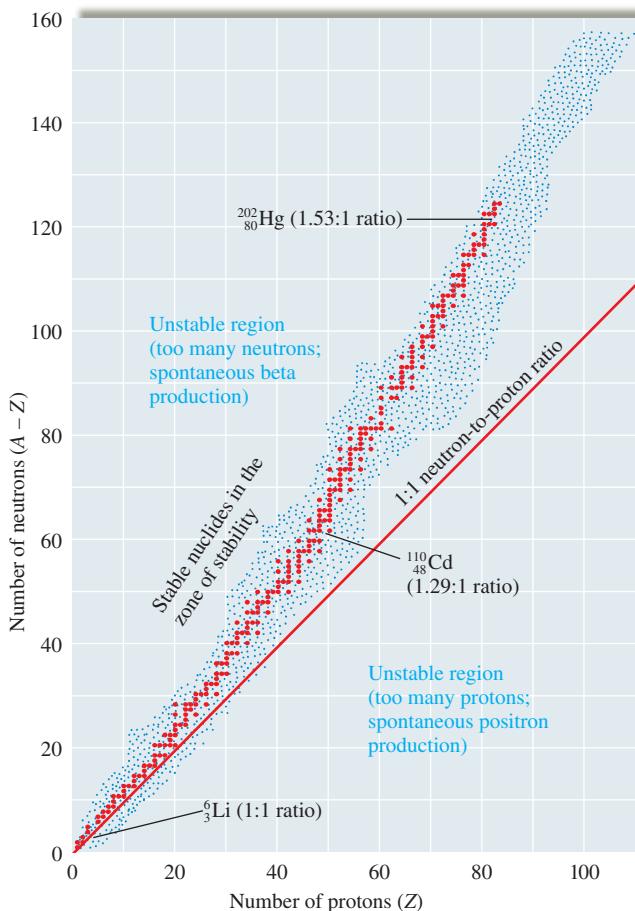


FIGURE 18.1

The zone of stability. The red dots indicate the nuclides that do not undergo radioactive decay. Note that as the number of protons in a nuclide increases, the neutron/proton ratio required for stability also increases.

TABLE 18.1 Number of Stable Nuclides Related to Numbers of Protons and Neutrons

Number of Protons	Number of Neutrons	Number of Stable Nuclides	Examples
Even	Even	168	$^{12}_{6}\text{C}$, $^{16}_{8}\text{O}$
Even	Odd	57	$^{13}_{6}\text{C}$, $^{47}_{22}\text{Ti}$
Odd	Even	50	$^{19}_{9}\text{F}$, $^{23}_{11}\text{Na}$
Odd	Odd	4	$^{2}_{1}\text{H}$, $^{6}_{3}\text{Li}$

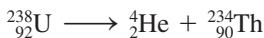
Note: Even numbers of protons and neutrons seem to favor stability.

- Certain combinations of protons and neutrons seem to confer special stability. For example, nuclides with even numbers of protons and neutrons are more often stable than those with odd numbers, as shown by the data in Table 18.1.
- There are also certain specific numbers of protons or neutrons that produce especially stable nuclides. These *magic numbers* are 2, 8, 20, 28, 50, 82, and 126. This behavior parallels that for atoms in which certain numbers of electrons (2, 10, 18, 36, 54, and 86) produce special chemical stability (the noble gases).

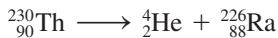
Types of Radioactive Decay

Radioactive nuclei can undergo decomposition in various ways. These decay processes fall into two categories: those that involve a change in the mass number of the decaying nucleus and those that do not. We will consider the former type of process first.

An **alpha particle**, or **α particle**, is a helium nucleus ($^{4}_{2}\text{He}$). **Alpha-particle production** is a very common mode of decay for heavy radioactive nuclides. For example, $^{238}_{92}\text{U}$, the predominant (99.3%) isotope of natural uranium, decays by α -particle production:

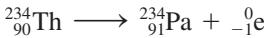


Another α -particle producer is $^{230}_{90}\text{Th}$:

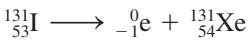


Another decay process in which the mass number of the decaying nucleus changes is **spontaneous fission**, the splitting of a heavy nuclide into two lighter nuclides with similar mass numbers. Although this process occurs at an extremely slow rate for most nuclides, it is important in some cases, such as for $^{254}_{98}\text{Cf}$, where spontaneous fission is the predominant mode of decay.

The most common decay process in which the mass number of the decaying nucleus remains constant is **β -particle production**. For example, the thorium-234 nuclide produces a β particle and is converted to protactinium-234:



Iodine-131 is also a β -particle producer:



The β particle is assigned the mass number 0, since its mass is tiny compared with that of a proton or neutron. Because the value of Z is -1 for the β particle, the atomic number for the new nuclide is greater by 1 than for the original nuclide. Thus *the net effect of β -particle production is to change a neutron to a proton*. We therefore expect nuclides

α -particle production involves a change in A for the decaying nucleus; β -particle production has no effect on A .

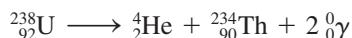


Visualization: Nuclear Particles

that lie above the zone of stability (those nuclides whose neutron/proton ratios are too high) to be β -particle producers.

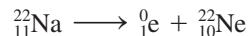
It should be pointed out that although the β particle is an electron, the emitting nucleus does not contain electrons. As we shall see later in this chapter, a given quantity of energy (which is best regarded as a form of matter) can become a particle (another form of matter) under certain circumstances. The unstable nuclide creates an electron as it releases energy in the decay process. The electron thus results from the decay process rather than being present before the decay occurs. Think of this as somewhat like talking: Words are not stored inside us but are formed as we speak. Later in this chapter we will discuss in more detail this very interesting phenomenon where matter in the form of particles and matter in the form of energy can interchange.

A **gamma ray**, or **γ ray**, refers to a high-energy photon. Frequently, γ -ray production accompanies nuclear decays and particle reactions, such as in the α -particle decay of $^{238}_{92}\text{U}$:



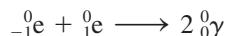
where two γ rays of different energies are produced in addition to the α particle. The emission of γ rays is one way a nucleus with excess energy (in an excited nuclear state) can relax to its ground state.

Positron production occurs for nuclides that are below the zone of stability (those nuclides whose neutron/proton ratios are too small). The positron is a particle with the same mass as the electron but opposite charge. An example of a nuclide that decays by positron production is sodium-22:



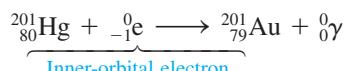
Note that *the net effect is to change a proton to a neutron*, causing the product nuclide to have a higher neutron/proton ratio than the original nuclide.

Besides being oppositely charged, the positron shows an even more fundamental difference from the electron: It is the *antiparticle* of the electron. When a positron collides with an electron, the particulate matter is changed to electromagnetic radiation in the form of high-energy photons:



This process, which is characteristic of matter–antimatter collisions, is called *annihilation* and is another example of the interchange of the forms of matter.

Electron capture is a process in which one of the inner-orbital electrons is captured by the nucleus, as illustrated by the process



This reaction would have been of great interest to the alchemists, but unfortunately it does not occur at a rate that would make it a practical means for changing mercury to gold. Gamma rays are always produced along with electron capture to release excess energy. The various types of radioactive decay are summarized in Table 18.2.

Sample Exercise 18.1

Nuclear Equations I

Write balanced equations for each of the following processes.

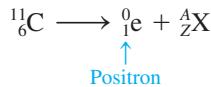
- ${}^{11}_6\text{C}$ produces a positron.
- ${}^{241}_{83}\text{Bi}$ produces a β particle.
- ${}^{237}_{93}\text{Np}$ produces an α particle.

TABLE 18.2 Various Types of Radioactive Processes Showing the Changes That Take Place in the Nuclides

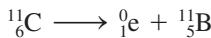
Process	Change in A	Change in Z	Change in Neutron/Proton Ratio	Example
β -particle (electron) production	0	+1	Decrease	$^{227}_{89}\text{Ac} \longrightarrow ^{227}_{90}\text{Th} + {}^0_{-1}\text{e}$
Positron production	0	-1	Increase	$^{13}_{7}\text{N} \longrightarrow ^{13}_{6}\text{C} + {}^0_{+1}\text{e}$
Electron capture	0	-1	Increase	$^{73}_{33}\text{As} + {}^0_{-1}\text{e} \longrightarrow ^{73}_{32}\text{Ge}$
α -particle production	-4	-2	Increase	$^{210}_{84}\text{Po} \longrightarrow ^{206}_{82}\text{Pb} + {}^4_2\text{He}$
γ -ray production	0	0	—	Excited nucleus \longrightarrow ground-state nucleus + ${}^0_0\gamma$
Spontaneous fission	—	—	—	$^{254}_{98}\text{Cf} \longrightarrow$ lighter nuclides + neutrons

Solution

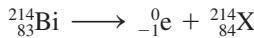
- a. We must find the product nuclide represented by ${}_Z^A\text{X}$ in the following equation:



We can find the identity of ${}_Z^A\text{X}$ by recognizing that the total of the Z and A values must be the same on both sides of the equation. Thus for X, Z must be $6 - 1 = 5$ and A must be $11 - 0 = 11$. Therefore, ${}_Z^A\text{X}$ is $^{11}_5\text{B}$. (The fact that Z is 5 tells us that the nuclide is boron.) Thus the balanced equation is

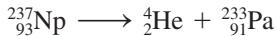


- b. Knowing that a β particle is represented by ${}^0_{-1}\text{e}$ and that Z and A are conserved, we can write



so ${}_Z^A\text{X}$ must be $^{214}_{84}\text{Po}$.

- c. Since an α particle is represented by ${}^4_2\text{He}$, the balanced equation must be



See Exercises 18.11 and 18.12.

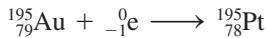
Sample Exercise 18.2**Nuclear Equations II**

In each of the following nuclear reactions, supply the missing particle.

- a. $^{195}_{79}\text{Au} + ? \rightarrow ^{195}_{78}\text{Pt}$
 b. $^{38}_{19}\text{K} \rightarrow ^{38}_{18}\text{Ar} + ?$

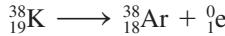
Solution

- a. Since A does not change and Z decreases by 1, the missing particle must be an electron:



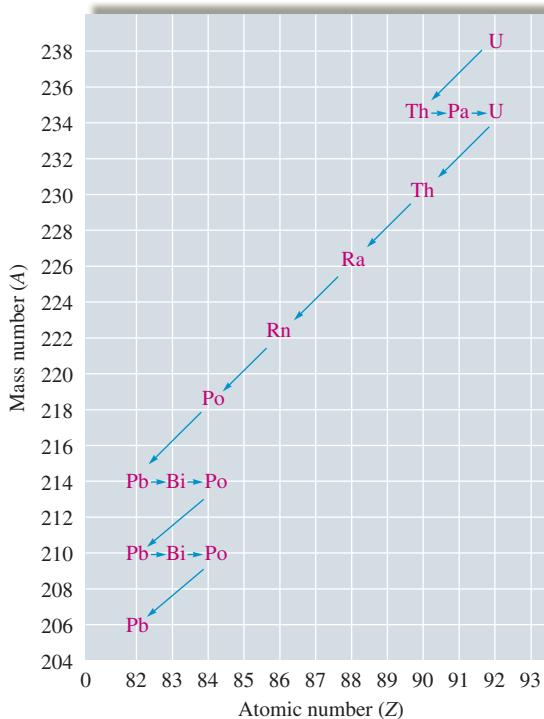
This is an example of electron capture.

- b. To conserve Z and A, the missing particle must be a positron:



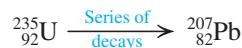
Thus potassium-38 decays by positron production.

See Exercises 18.13 and 18.14.

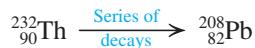
**FIGURE 18.2**

The decay series from $^{238}_{92}\text{U}$ to $^{206}_{82}\text{Pb}$. Each nuclide in the series except $^{206}_{82}\text{Pb}$ is unstable, and the successive transformations (shown by the arrows) continue until $^{206}_{82}\text{Pb}$ is finally formed. Note that horizontal arrows indicate processes where A is unchanged, while diagonal arrows signify that both A and Z change.

Often a radioactive nucleus cannot reach a stable state through a single decay process. In such a case, a **decay series** occurs until a stable nuclide is formed. A well-known example is the decay series that starts with $^{238}_{92}\text{U}$ and ends with $^{206}_{82}\text{Pb}$, as shown in Fig. 18.2. Similar series exist for $^{235}_{92}\text{U}$:



and for $^{232}_{90}\text{Th}$:



18.2 The Kinetics of Radioactive Decay

Rates of reaction are discussed in Chapter 12.

In a sample containing radioactive nuclides of a given type, each nuclide has a certain probability of undergoing decay. Suppose that a sample of 1000 atoms of a certain nuclide produces 10 decay events per hour. This means that over the span of an hour, 1 out of every 100 nuclides will decay. Given that this probability of decay is characteristic for this type of nuclide, we could predict that a 2000-atom sample would give 20 decay events per hour. Thus, for radioactive nuclides, the **rate of decay**, which is the negative of the change in the number of nuclides per unit time

$$\left(-\frac{\Delta N}{\Delta t} \right)$$

is directly proportional to the number of nuclides N in a given sample:

$$\text{Rate} = -\frac{\Delta N}{\Delta t} \propto N$$

The negative sign is included because the number of nuclides is decreasing. We now insert a proportionality constant k to give

$$\text{Rate} = -\frac{\Delta N}{\Delta t} = kN$$

This is the rate law for a first-order process, as we saw in Chapter 12. As shown in Section 12.4, the integrated first-order rate law is

$$\ln\left(\frac{N}{N_0}\right) = -kt$$

where N_0 represents the original number of nuclides (at $t = 0$) and N represents the number *remaining* at time t .



Visualization: Half-Life of Nuclear Decay

Half-Life

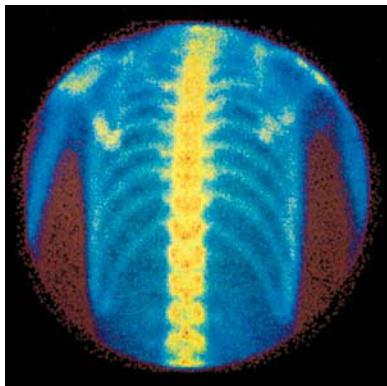
The **half-life** ($t_{1/2}$) of a radioactive sample is defined as the time required for the number of nuclides to reach half the original value ($N_0/2$). We can use this definition in connection with the integrated first-order rate law (as we did in Section 12.4) to produce the following expression for $t_{1/2}$:

$$t_{1/2} = \frac{\ln(2)}{k} = \frac{0.693}{k}$$

Thus, if the half-life of a radioactive nuclide is known, the rate constant can be easily calculated, and vice versa.

Sample Exercise 18.3

Kinetics of Nuclear Decay I



The image of a bone scan of a normal chest (posterior view). Radioactive technetium-99m is injected into the patient and is then concentrated in bones, allowing a physician to look for abnormalities such as might be caused by cancer.

The harmful effects of radiation will be discussed in Section 18.7.

Technetium-99m is used to form pictures of internal organs in the body and is often used to assess heart damage. The m for this nuclide indicates an excited nuclear state that decays to the ground state by gamma emission. The rate constant for decay of $^{99m}_{43}\text{Tc}$ is known to be $1.16 \times 10^{-1}/\text{h}$. What is the half-life of this nuclide?

Solution

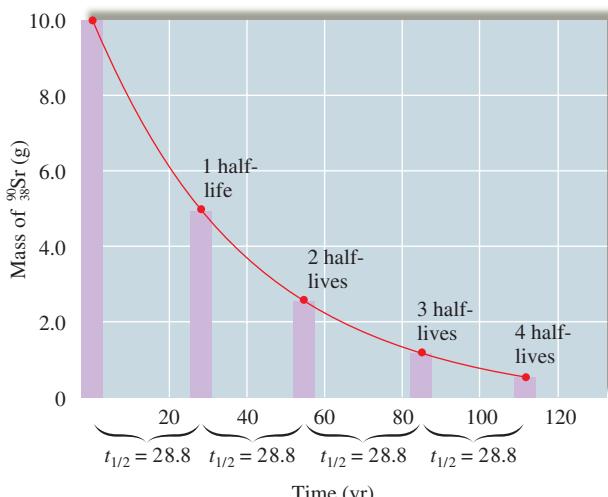
The half-life can be calculated from the expression

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.16 \times 10^{-1}/\text{h}} = 5.98 \text{ h}$$

Thus it will take 5.98 h for a given sample of technetium-99m to decrease to half the original number of nuclides.

See Exercise 18.21.

As we saw in Section 12.4, the half-life for a first-order process is constant. This is shown for the β -particle decay of strontium-90 in Fig. 18.3; it takes 28.8 years for each halving of the amount of ^{90}Sr . Contamination of the environment with ^{90}Sr poses serious health hazards because of the similar chemistry of strontium and calcium (both are in Group 2A). Strontium-90 in grass and hay is incorporated into cow's milk along with calcium and is then passed on to humans, where it lodges in the bones. Because of its relatively long half-life, it persists for years in humans, causing radiation damage that may lead to cancer.

**FIGURE 18.3**

The decay of a 10.0-g sample of strontium-90 over time. Note that the half-life is a constant 28.8 years.

Sample Exercise 18.4**Kinetics of Nuclear Decay II**

The half-life of molybdenum-99 is 67.0 h. How much of a 1.000-mg sample of ^{99}Mo is left after 335 h?

Solution

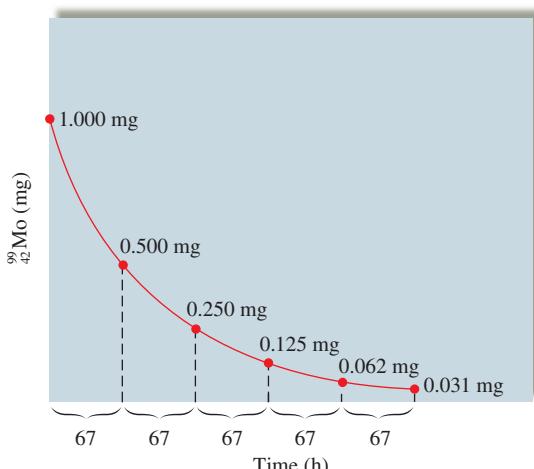
The easiest way to solve this problem is to recognize that 335 h represents five half-lives for ^{99}Mo :

$$335 = 5 \times 67.0$$

We can sketch the change that occurs, as is shown in Fig. 18.4. Thus, after 335 h, 0.031 mg ^{99}Mo remains.

See Exercise 18.23.

The half-lives of radioactive nuclides vary over a tremendous range. For example, $^{144}_{60}\text{Nd}$ has a half-life of 5×10^{15} years, while $^{214}_{84}\text{Po}$ has a half-life of 2×10^{-4} second. To give you some perspective on this, the half-lives of the nuclides in the $^{238}_{92}\text{U}$ decay series are given in Table 18.3.

**FIGURE 18.4**

The change in the amount of ^{99}Mo with time ($t_{1/2} = 67$ h).

TABLE 18.3 The Half-Lives of Nuclides in the $^{238}_{92}\text{U}$ Decay Series

Nuclide	Particle Produced	Half-Life
Uranium-238 ($^{238}_{92}\text{U}$) ↓	α	4.51×10^9 years
Thorium-234 ($^{234}_{90}\text{Th}$) ↓	β	24.1 days
Protactinium-234 ($^{234}_{91}\text{Pa}$) ↓	β	6.75 hours
Uranium-234 ($^{234}_{92}\text{U}$) ↓	α	2.48×10^5 years
Thorium-230 ($^{230}_{90}\text{Th}$) ↓	α	8.0×10^4 years
Radium-226 ($^{226}_{88}\text{Ra}$) ↓	α	1.62×10^3 years
Radon-222 ($^{222}_{86}\text{Rn}$) ↓	α	3.82 days
Polonium-218 ($^{218}_{84}\text{Po}$) ↓	α	3.1 minutes
Lead-214 ($^{214}_{82}\text{Pb}$) ↓	β	26.8 minutes
Bismuth-214 ($^{214}_{83}\text{Bi}$) ↓	β	19.7 minutes
Polonium-214 ($^{214}_{84}\text{Po}$) ↓	α	1.6×10^{-4} second
Lead-210 ($^{210}_{82}\text{Pb}$) ↓	β	20.4 years
Bismuth-210 ($^{210}_{83}\text{Bi}$) ↓	β	5.0 days
Polonium-210 ($^{210}_{84}\text{Po}$) ↓	α	138.4 days
Lead-206 ($^{206}_{82}\text{Pb}$)	—	Stable

18.3 Nuclear Transformations

In 1919 Lord Rutherford observed the first **nuclear transformation**, *the change of one element into another*. He found that by bombarding $^{14}_7\text{N}$ with α particles, the nuclide $^{17}_8\text{O}$ could be produced:



Fourteen years later, Irene Curie and her husband Frederick Joliot observed a similar transformation from aluminum to phosphorus:



where ${}_0^1\text{n}$ represents a neutron.

Over the years, many other nuclear transformations have been achieved, mostly using **particle accelerators**, which, as the name reveals, are devices used to give particles very high velocities. Because of the electrostatic repulsion between the target nucleus and a positive ion, accelerators are needed when positive ions are used as bombarding particles. The particle, accelerated to a very high velocity, can overcome the repulsion and penetrate the target nucleus, thus effecting the transformation. A schematic diagram of one type of particle accelerator, the **cyclotron**, is shown in Fig. 18.5. The ion is introduced at the center of the cyclotron and is accelerated in an expanding spiral path by use of alternating electric fields in the presence of a magnetic field. The **linear accelerator**

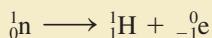


CHEMICAL IMPACT

Stellar Nucleosynthesis

How did all the matter around us originate? The scientific answer to this question is a theory called *stellar nucleosynthesis*—literally, the formation of nuclei in stars.

Many scientists believe that our universe originated as a cloud of neutrons that became unstable and produced an immense explosion, giving this model its name—*the big bang theory*. The model postulates that, following the initial explosion, neutrons decomposed into protons and electrons,



which eventually recombined to form clouds of hydrogen. Over the eons, gravitational forces caused many of these hydrogen clouds to contract and heat up sufficiently to reach temperatures where proton fusion was possible, which released large quantities of energy. When the tendency to

expand due to the heat from fusion and the tendency to contract due to the forces of gravity are balanced, a stable young star such as our sun can be formed.

Eventually, when the supply of hydrogen is exhausted, the core of the star will again contract with further heating until temperatures are reached where fusion of helium nuclei can occur, leading to the formation of ${}^{12}_6\text{C}$ and ${}^{16}_8\text{O}$ nuclei. In turn, when the supply of helium nuclei runs out, further contraction and heating will occur, until fusion of heavier nuclei takes place. This process occurs repeatedly, forming heavier and heavier nuclei until iron nuclei are formed. Because the iron nucleus is the most stable of all, energy is required to fuse iron nuclei. This endothermic fusion process cannot furnish energy to sustain the star, and therefore it cools to a small, dense *white dwarf*.

illustrated in Fig. 18.6 employs changing electric fields to achieve high velocities on a linear pathway.

In addition to positive ions, neutrons are often employed as bombarding particles to effect nuclear transformations. Because neutrons are uncharged and thus not repelled electrostatically by a target nucleus, they are readily absorbed by many nuclei, leading to new nuclides. The most common source of neutrons for this purpose is a fission reactor (see Section 18.6).

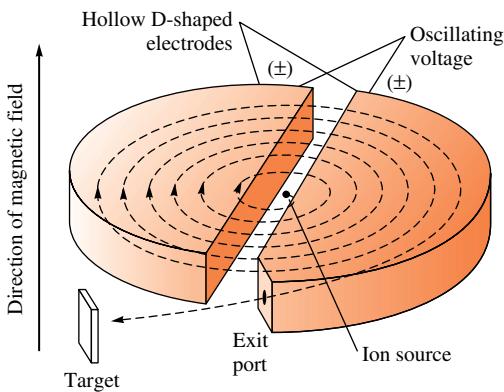


FIGURE 18.5

A schematic diagram of a cyclotron. The ion is introduced in the center and is pulled back and forth between the hollow D-shaped electrodes by constant reversals of the electric field. Magnets above and below these electrodes produce a spiral path that expands as the particle velocity increases. When the particle has sufficient speed, it exits the accelerator and is directed at the target nucleus.

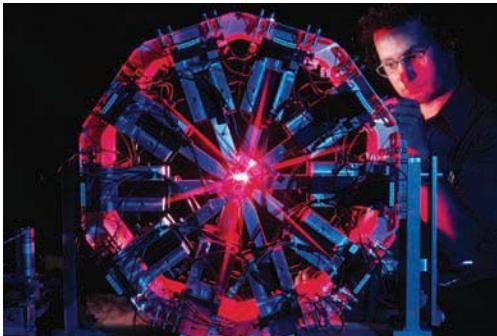
The evolution just described is characteristic of small and medium-sized stars. Much larger stars, however, become unstable at some time during their evolution and undergo a *supernova explosion*. In this explosion, some medium-mass nuclei are fused to form heavy elements. Also, some light nuclei capture neutrons. These neutron-rich nuclei then produce β particles, increasing their atomic number with each event. This eventually leads to heavy nuclei. In fact, almost all nuclei heavier than iron are thought to originate from supernova explosions. The debris of a supernova explosion thus contains a large variety of elements and might eventually form a solar system such as our own.

Although other theories for the origin of matter have been suggested, there is much evidence to support the big bang theory, and it continues to be widely accepted.

For more information see V. E. Viola, "Formation of the chemical elements and the evolution of our universe," *J. Chem. Ed.* **67** (1990): 723.

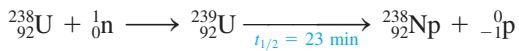


Image of a portion of the Cygnus Loop supernova remnant, taken by the Hubble space telescope.



A physicist works with a small cyclotron at the University of California at Berkeley.

By using neutron and positive-ion bombardment, scientists have been able to extend the periodic table. Prior to 1940, the heaviest known element was uranium ($Z = 92$), but in 1940, neptunium ($Z = 93$) was produced by neutron bombardment of $^{238}_{92}\text{U}$. The process initially gives $^{239}_{92}\text{U}$, which decays to $^{239}_{93}\text{Np}$ by β -particle production:



In the years since 1940, the elements with atomic numbers 93 through 112, called the **transuranium elements**,* have been synthesized. Many of these elements have very short half-lives, as shown in Table 18.4. As a result, only a few atoms of some have ever been formed. This, of course, makes the chemical characterization of these elements extremely difficult.

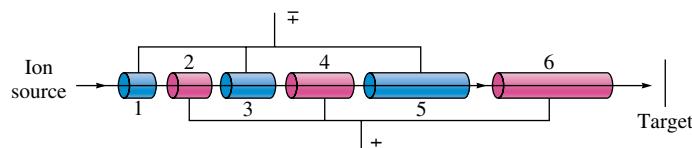


FIGURE 18.6

Schematic diagram of a linear accelerator, which uses a changing electric field to accelerate a positive ion along a linear path. As the ion leaves the source, the odd-numbered tubes are negatively charged, and the even-numbered tubes are positively charged. The positive ion is thus attracted into tube 1. As the ion leaves tube 1, the tube polarities are reversed. Now tube 1 is positive, repelling the positive ion, and tube 2 is negative, attracting the positive ion. This process continues, eventually producing high particle velocity.

*For more information see G. B. Kauffman, "Beyond uranium," *Chem. Eng. News* (Nov. 19, 1990): 18.

TABLE 18.4 Syntheses of Some of the Transuranium Elements

Element	Neutron Bombardment	Half-Life
Neptunium (Z = 93)	$^{238}_{92}\text{U} + {}^1_0\text{n} \longrightarrow {}^{239}_{93}\text{Np} + {}^{-1}_0\text{e}$	2.35 days (${}^{239}_{93}\text{Np}$)
Plutonium (Z = 94)	${}^{239}_{93}\text{Np} \longrightarrow {}^{239}_{94}\text{Pu} + {}^{-1}_0\text{e}$	24,400 years (${}^{239}_{94}\text{Pu}$)
Americium (Z = 95)	${}^{239}_{94}\text{Pu} + 2 {}^1_0\text{n} \longrightarrow {}^{241}_{94}\text{Pu} \longrightarrow {}^{241}_{95}\text{Am} + {}^{-1}_0\text{e}$	458 years (${}^{241}_{95}\text{Am}$)
Element	Positive-Ion Bombardment	Half-Life
Curium (Z = 96)	${}^{239}_{94}\text{Pu} + {}^4_2\text{He} \longrightarrow {}^{242}_{96}\text{Cm} + {}^1_0\text{n}$	163 days (${}^{242}_{96}\text{Cm}$)
Californium (Z = 98)	${}^{242}_{96}\text{Cm} + {}^4_2\text{He} \longrightarrow {}^{245}_{98}\text{Cf} + {}^1_0\text{n}$ or ${}^{238}_{92}\text{U} + {}^{12}_6\text{C} \longrightarrow {}^{246}_{98}\text{Cf} + 4 {}^1_0\text{n}$	44 minutes (${}^{245}_{98}\text{Cf}$)
Rutherfordium (Z = 104)	${}^{249}_{98}\text{Cf} + {}^{12}_6\text{C} \longrightarrow {}^{257}_{104}\text{Rf} + 4 {}^1_0\text{n}$	
Dubnium (Z = 105)	${}^{249}_{98}\text{Cf} + {}^{15}_7\text{N} \longrightarrow {}^{260}_{105}\text{Db} + 4 {}^1_0\text{n}$	
Seaborgium (Z = 106)	${}^{249}_{98}\text{Cf} + {}^{18}_8\text{O} \longrightarrow {}^{263}_{106}\text{Sg} + 4 {}^1_0\text{n}$	

18.4 Detection and Uses of Radioactivity

Although various instruments measure radioactivity levels, the most familiar of them is the **Geiger–Müller counter**, or **Geiger counter** (see Fig. 18.7). This instrument takes advantage of the fact that the high-energy particles from radioactive decay processes produce ions when they travel through matter. The probe of the Geiger counter is filled with argon gas, which can be ionized by a rapidly moving particle. This reaction is demonstrated by the equation:



Normally, a sample of argon gas will not conduct a current when an electrical potential is applied. However, the formation of ions and electrons produced by the passage of the high-energy particle allows a momentary current to flow. Electronic devices detect this current flow, and the number of these events can be counted. Thus the decay rate of the radioactive sample can be determined.

Another instrument often used to detect levels of radioactivity is a **scintillation counter**, which takes advantage of the fact that certain substances, such as zinc sulfide,

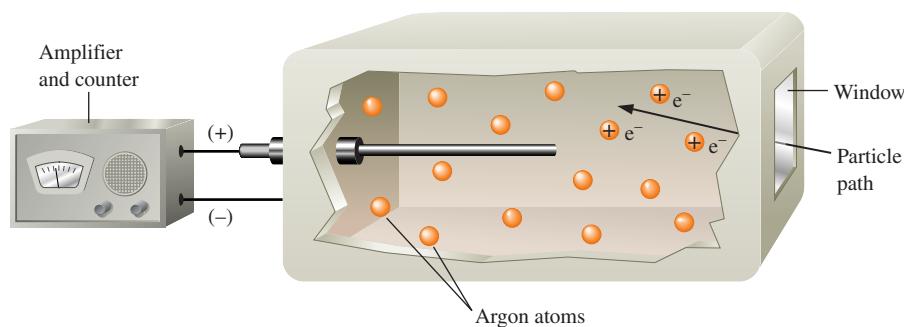
Geiger counters are often called *survey meters* in the industry.



Visualization: Geiger Counter

FIGURE 18.7

A schematic representation of a Geiger–Müller counter. The high-energy radioactive particle enters the window and ionizes argon atoms along its path. The resulting ions and electrons produce a momentary current pulse, which is amplified and counted.





Brigham Young researcher Scott Woodward taking a bone sample for carbon-14 dating at an archeological site in Egypt.

Radioactive nuclides are often called *radionuclides*. Carbon dating is based on the radionuclide ^{14}C .

The $^{14}\text{C}/^{12}\text{C}$ ratio is the basis for carbon-14 dating.



A dendrochronologist cutting a section from a dead tree in South Africa.

Sample Exercise 18.5

^{14}C Dating

The remnants of an ancient fire in a cave in Africa showed a ^{14}C decay rate of 3.1 counts per minute per gram of carbon. Assuming that the decay rate of ^{14}C in freshly cut wood (corrected for changes in the ^{14}C content of the atmosphere) is 13.6 counts per minute per gram of carbon, calculate the age of the remnants. The half-life of ^{14}C is 5730 years.

Solution

The key to solving this problem is to realize that the decay rates given are directly proportional to the number of ^{14}C nuclides present. Radioactive decay follows first-order kinetics:

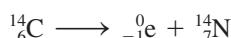
$$\text{Rate} = kN$$

give off light when they are struck by high-energy radiation. A photocell senses the flashes of light that occur as the radiation strikes and thus measures the number of decay events per unit of time.

Dating by Radioactivity

Archeologists, geologists, and others involved in reconstructing the ancient history of the earth rely heavily on radioactivity to provide accurate dates for artifacts and rocks. A method that has been very important for dating ancient articles made from wood or cloth is **radiocarbon dating**, or **carbon-14 dating**, a technique originated in the 1940s by Willard Libby, an American chemist who received a Nobel Prize for his efforts in this field.

Radiocarbon dating is based on the radioactivity of the nuclide ^{14}C , which decays via β -particle production:



Carbon-14 is continuously produced in the atmosphere when high-energy neutrons from space collide with nitrogen-14:



Thus carbon-14 is continuously produced by this process, and it continuously decomposes through β -particle production. Over the years, the rates for these two processes have become equal, and like a participant in a chemical reaction at equilibrium, the amount of ^{14}C that is present in the atmosphere remains approximately constant.

Carbon-14 can be used to date wood and cloth artifacts because the ^{14}C , along with the other carbon isotopes in the atmosphere, reacts with oxygen to form carbon dioxide. A living plant consumes carbon dioxide in the photosynthesis process and incorporates the carbon, including ^{14}C , into its molecules. As long as the plant lives, the $^{14}\text{C}/^{12}\text{C}$ ratio in its molecules remains the same as in the atmosphere because of the continuous uptake of carbon. However, as soon as a tree is cut to make a wooden bowl or a flax plant is harvested to make linen, the $^{14}\text{C}/^{12}\text{C}$ ratio begins to decrease because of the radioactive decay of ^{14}C (the ^{12}C nuclide is stable). Since the half-life of ^{14}C is 5730 years, a wooden bowl found in an archeological dig showing a $^{14}\text{C}/^{12}\text{C}$ ratio that is half that found in currently living trees is approximately 5730 years old. This reasoning assumes that the current $^{14}\text{C}/^{12}\text{C}$ ratio is the same as that found in ancient times.

Dendrochronologists, scientists who date trees from annual growth rings, have used data collected from long-lived species of trees, such as bristlecone pines and sequoias, to show that the ^{14}C content of the atmosphere has changed significantly over the ages. These data have been used to derive correction factors that allow very accurate dates to be determined from the observed $^{14}\text{C}/^{12}\text{C}$ ratio in an artifact, especially for artifacts 10,000 years old or younger. Recent measurements of uranium/thorium ratios in ancient coral indicate that dates in the 20,000- to 30,000-year range may have errors as large as 3000 years. As a result, efforts are now being made to recalibrate the ^{14}C dates over this period.

Thus

$$\frac{3.1 \text{ counts/min} \cdot g}{13.6 \text{ counts/min} \cdot g} = \frac{\text{rate at time } t}{\text{rate at time } 0} = \frac{kN}{kN_0}$$

↴ Number of nuclides
 present at time t
 ↴ Number of nuclides
 present at time 0

$$= \frac{N}{N_0} = 0.23$$

We can now use the integrated first-order rate law:

$$\ln\left(\frac{N}{N_0}\right) = -kt$$

$$\text{where } k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730 \text{ years}}$$

to solve for t , the time elapsed since the campfire:

$$\ln\left(\frac{N}{N_0}\right) = \ln(0.23) = -\left(\frac{0.693}{5730 \text{ years}}\right)t$$

Solving this equation gives $t = 12,000$ years; the campfire in the cave occurred about 12,000 years ago.

See Exercises 18.31 and 18.32.

One drawback of radiocarbon dating is that a fairly large piece of the object (from a half to several grams) must be burned to form carbon dioxide, which is then analyzed for radioactivity. Another method for counting $^{14}_6\text{C}$ nuclides avoids destruction of a significant portion of a valuable artifact. This technique, requiring only about 10^{-3} g, uses a mass spectrometer (see Chapter 3), in which the carbon atoms are ionized and accelerated through a magnetic field that deflects their path. Because of their different masses, the various ions are deflected by different amounts and can be counted separately. This allows a very accurate determination of the $^{14}_6\text{C}/^{12}_6\text{C}$ ratio in the sample.

In their attempts to establish the geologic history of the earth, geologists have made extensive use of radioactivity. For example, since $^{238}_{92}\text{U}$ decays to the stable $^{206}_{82}\text{Pb}$ nuclide, the ratio of $^{206}_{82}\text{Pb}$ to $^{238}_{92}\text{U}$ in a rock can, under favorable circumstances, be used to estimate the age of the rock. The radioactive nuclide $^{176}_{71}\text{Lu}$, which decays to $^{176}_{72}\text{Hf}$, has a half-life of 37 billion years (only 186 nuclides out of 10 trillion decay each year!). Thus this nuclide can be used to date very old rocks. With this technique, scientists have estimated that the earth's crust formed 4.3 billion years ago.

Sample Exercise 18.6

Dating by Radioactivity

Because the half-life of $^{238}_{92}\text{U}$ is very long compared with those of the other members of the decay series (see Table 18.3) to reach $^{206}_{82}\text{Pb}$, the number of nuclides present in intermediate stages of decay is negligible. That is, once a $^{238}_{92}\text{U}$ nuclide starts to decay, it reaches $^{206}_{82}\text{Pb}$ relatively fast.

A rock containing $^{238}_{92}\text{U}$ and $^{206}_{82}\text{Pb}$ was examined to determine its approximate age. Analysis showed the ratio of $^{206}_{82}\text{Pb}$ atoms to $^{238}_{92}\text{U}$ atoms to be 0.115. Assuming that no lead was originally present, that all the $^{206}_{82}\text{Pb}$ formed over the years has remained in the rock, and that the number of nuclides in intermediate stages of decay between $^{238}_{92}\text{U}$ and $^{206}_{82}\text{Pb}$ is negligible, calculate the age of the rock. The half-life of $^{238}_{92}\text{U}$ is 4.5×10^9 years.

Solution

This problem can be solved using the integrated first-order rate law:

$$\ln\left(\frac{N}{N_0}\right) = -kt = -\left(\frac{0.693}{4.5 \times 10^9 \text{ years}}\right)t$$

where N/N_0 represents the ratio of ^{238}U atoms now found in the rock to the number present when the rock was formed. We are assuming that each ^{206}Pb nuclide present must have come from decay of a ^{238}U atom:



Thus

Number of $^{238}_{\text{92}}\text{U}$ atoms originally present	=	number of $^{206}_{\text{82}}\text{Pb}$ atoms now present	+	number of $^{238}_{\text{92}}\text{U}$ atoms now present
--	---	--	---	---

$$\frac{\text{Atoms of } ^{206}_{\text{82}}\text{Pb now present}}{\text{Atoms of } ^{238}_{\text{92}}\text{U now present}} = 0.115 = \frac{0.115}{1.000} = \frac{115}{1000}$$

Think carefully about what this means. For every 1115 ^{238}U atoms originally present in the rock, 115 have been changed to ^{206}Pb and 1000 remain as ^{238}U . Thus

$$\begin{aligned} \frac{N}{N_0} &= \frac{\overset{\text{Now present}}{^{238}_{\text{92}}\text{U}}}{\underbrace{\overset{\text{238}_{\text{92}}\text{U originally present}}{^{206}_{\text{82}}\text{Pb} + ^{238}_{\text{92}}\text{U}}} = \frac{1000}{1115} = 0.8969 \\ \ln\left(\frac{N}{N_0}\right) &= \ln(0.8969) = -\left(\frac{0.693}{4.5 \times 10^9 \text{ years}}\right)t \\ t &= 7.1 \times 10^8 \text{ years} \end{aligned}$$

This is the approximate age of the rock. It was formed sometime in the Cambrian period.

See Exercises 18.33 and 18.34.

Medical Applications of Radioactivity

Although the rapid advances of the medical sciences in recent decades are due to many causes, one of the most important has been the discovery and use of **radiotracers**, radioactive nuclides that can be introduced into organisms in food or drugs and whose pathways can be *traced* by monitoring their radioactivity. For example, the incorporation of nuclides such as ^{14}C and ^{32}P into nutrients has produced important information about metabolic pathways.

Iodine-131 has proved very useful in the diagnosis and treatment of illnesses of the thyroid gland. Patients drink a solution containing small amounts of Na^{131}I , and the uptake of the iodine by the thyroid gland is monitored with a scanner (see Fig. 18.8).



A pellet containing radioactive ^{131}I .

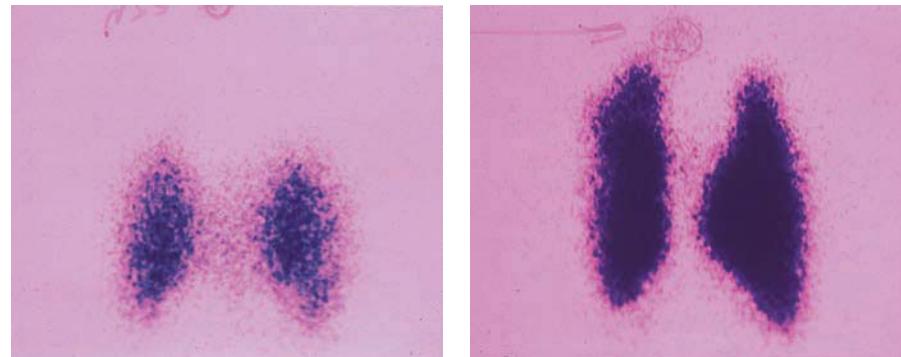


FIGURE 18.8

After consumption of Na^{131}I , the patient's thyroid is scanned for radioactivity levels to determine the efficiency of iodine absorption. (left) A normal thyroid. (right) An enlarged thyroid.

TABLE 18.5 Some Radioactive Nuclides, with Half-Lives and Medical Applications as Radiotracers

Nuclide	Half-Life	Area of the Body Studied
^{131}I	8.1 days	Thyroid
^{59}Fe	45.1 days	Red blood cells
^{99}Mo	67 hours	Metabolism
^{32}P	14.3 days	Eyes, liver, tumors
^{51}Cr	27.8 days	Red blood cells
^{87}Sr	2.8 hours	Bones
$^{99\text{m}}\text{Tc}$	6.0 hours	Heart, bones, liver, and lungs
^{133}Xe	5.3 days	Lungs
^{24}Na	14.8 hours	Circulatory system

Thallium-201 can be used to assess the damage to the heart muscle in a person who has suffered a heart attack, because thallium is concentrated in healthy muscle tissue. Technetium-99m is also taken up by normal heart tissue and is used for damage assessment in a similar way.

Radiotracers provide sensitive and noninvasive methods for learning about biologic systems, for detection of disease, for monitoring the action and effectiveness of drugs, and for early detection of pregnancy, and their usefulness should continue to grow. Some useful radiotracers are listed in Table 18.5.

18.5 Thermodynamic Stability of the Nucleus

We can determine the thermodynamic stability of a nucleus by calculating the change in potential energy that would occur if that nucleus were formed from its constituent protons and neutrons. For example, let's consider the hypothetical process of forming a $^{16}_8\text{O}$ nucleus from eight neutrons and eight protons:



The energy change associated with this process can be calculated by comparing the sum of the masses of eight protons and eight neutrons with that of the oxygen nucleus:

$$\begin{aligned} \text{Mass of } (8 \underset{0}{\text{n}} + 8 \underset{1}{\text{H}}) &= 8(1.67493 \times 10^{-24} \text{ g}) + 8(1.67262 \times 10^{-24} \text{ g}) \\ &\quad \uparrow \qquad \qquad \qquad \uparrow \\ &\quad \text{Mass of } \underset{0}{\text{n}} \qquad \qquad \qquad \text{Mass of } \underset{1}{\text{H}} \\ &= 2.67804 \times 10^{-23} \text{ g} \\ \text{Mass of } \underset{8}{\text{O}} \text{ nucleus} &= 2.65535 \times 10^{-23} \text{ g} \end{aligned}$$

The difference in mass for one nucleus is

$$\text{Mass of } \underset{8}{\text{O}} - \text{mass of } (8 \underset{0}{\text{n}} + 8 \underset{1}{\text{H}}) = -2.269 \times 10^{-25} \text{ g}$$

The difference in mass for formation of 1 mole of ^{16}O nuclei is therefore

$$(-2.269 \times 10^{-25} \text{ g/nucleus})(6.022 \times 10^{23} \text{ nuclei/mol}) = -0.1366 \text{ g/mol}$$

Thus 0.1366 g of mass would be lost if 1 mole of oxygen-16 were formed from protons and neutrons. What is the reason for this difference in mass, and how can this information be used to calculate the energy change that accompanies this process?

The answers to these questions can be found in the work of Albert Einstein. As we discussed in Section 7.2, Einstein's theory of relativity showed that energy should be considered a form of matter. His famous equation

$$E = mc^2$$

The energy changes associated with normal chemical reactions are small enough that the corresponding mass changes are not detectable.

where c is the speed of light, gives the relationship between a quantity of energy and its mass. When a system gains or loses energy, it also gains or loses a quantity of mass, given by E/c^2 . Thus the mass of a nucleus is less than that of its component nucleons because the process is so exothermic.

Einstein's equation in the form

$$\text{Energy change} = \Delta E = \Delta mc^2$$

where Δm is the change in mass, or the **mass defect**, can be used to calculate ΔE for the hypothetical formation of a nucleus from its component nucleons.

Sample Exercise 18.7

Nuclear Binding Energy I

Calculate the change in energy if 1 mol $^{16}_8\text{O}$ nuclei was formed from neutrons and protons.

Solution

We have already calculated that 0.1366 g of mass would be lost in the hypothetical process of assembling 1 mol $^{16}_8\text{O}$ nuclei from the component nucleons. We can calculate the change in energy for this process from

$$\Delta E = \Delta mc^2$$

where

$$c = 3.00 \times 10^8 \text{ m/s} \quad \text{and} \quad \Delta m = -0.1366 \text{ g/mol} = -1.366 \times 10^{-4} \text{ kg/mol}$$

Thus

$$\Delta E = (-1.366 \times 10^{-4} \text{ kg/mol})(3.00 \times 10^8 \text{ m/s})^2 = -1.23 \times 10^{13} \text{ J/mol}$$

The negative sign for the ΔE value indicates that the process is exothermic. Energy, and thus mass, is lost from the system.

See Exercises 18.35 through 18.37.

The energy changes observed for nuclear processes are extremely large compared with those observed for chemical and physical changes. Thus nuclear processes constitute a potentially valuable energy resource.

The thermodynamic stability of a particular nucleus is normally represented as energy released per nucleon. To illustrate how this quantity is obtained, we will continue to consider $^{16}_8\text{O}$. First, we calculate ΔE per nucleus by dividing the molar value from Sample Exercise 18.7 by Avogadro's number:

$$\Delta E \text{ per } ^{16}_8\text{O} \text{ nucleus} = \frac{-1.23 \times 10^{13} \text{ J/mol}}{6.022 \times 10^{23} \text{ nuclei/mol}} = -2.04 \times 10^{-11} \text{ J/nucleus}$$

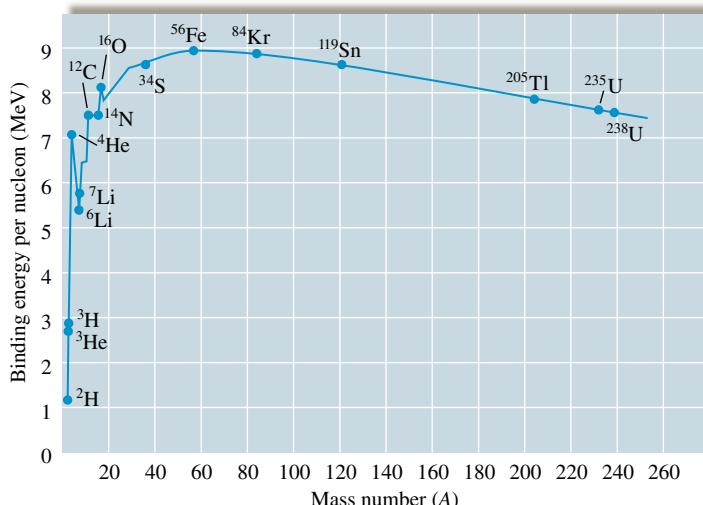
In terms of a more convenient energy unit, a million electronvolts (MeV), where

$$1 \text{ MeV} = 1.60 \times 10^{-13} \text{ J}$$

$$\begin{aligned} \Delta E \text{ per } ^{16}_8\text{O} \text{ nucleus} &= (-2.04 \times 10^{-11} \text{ J/nucleus}) \left(\frac{1 \text{ MeV}}{1.60 \times 10^{-13} \text{ J}} \right) \\ &= -1.28 \times 10^2 \text{ MeV/nucleus} \end{aligned}$$

Next, we can calculate the value of ΔE per nucleon by dividing by A , the sum of neutrons and protons:

$$\begin{aligned} \Delta E \text{ per nucleon for } ^{16}_8\text{O} &= \frac{-1.28 \times 10^2 \text{ MeV/nucleus}}{16 \text{ nucleons/nucleus}} \\ &= -7.98 \text{ MeV/nucleon} \end{aligned}$$

**FIGURE 18.9**

The binding energy per nucleon as a function of mass number. The most stable nuclei are at the top of the curve. The most stable nucleus is ${}^{56}\text{Fe}$.

This means that 7.98 MeV of energy per nucleon would be *released* if ${}^{16}\text{O}$ were formed from neutrons and protons. The energy required to *decompose* this nucleus into its components has the same numeric value but a positive sign (since energy is required). This is called the **binding energy** per nucleon for ${}^{16}\text{O}$.

The values of the binding energy per nucleon for the various nuclides are shown in Fig. 18.9. Note that the most stable nuclei (those requiring the largest energy per nucleon to decompose the nucleus) occur at the top of the curve. The most stable nucleus known is ${}^{56}\text{Fe}$, which has a binding energy per nucleon of 8.79 MeV.

Sample Exercise 18.8

Nuclear Binding Energy II

Calculate the binding energy per nucleon for the ${}^4\text{He}$ nucleus (atomic masses: ${}^4\text{He} = 4.0026$ amu; ${}^1\text{H} = 1.0078$ amu).

Solution

First, we must calculate the mass defect (Δm) for ${}^4\text{He}$. Since atomic masses (which include the electrons) are given, we must decide how to account for the electron mass:

$$4.0026 = \text{mass of } {}^4\text{He atom} = \text{mass of } {}^4\text{He nucleus} + 2m_e$$

↑
Electron mass
↓

$$1.0078 = \text{mass of } {}^1\text{H atom} = \text{mass of } {}^1\text{H nucleus} + m_e$$

Thus, since a ${}^4\text{He}$ nucleus is “synthesized” from two protons and two neutrons, we see that

$$\begin{aligned}\Delta m &= \underbrace{(4.0026 - 2m_e)}_{\text{Mass of } {}^4\text{He nucleus}} - [\underbrace{2(1.0078 - m_e)}_{\text{Mass of } {}^1\text{H nucleus (proton)}} + \underbrace{2(1.0087)}_{\text{Mass of neutron}}] \\ &= 4.0026 - 2m_e - 2(1.0078) + 2m_e - 2(1.0087) \\ &= 4.0026 - 2(1.0078) - 2(1.0087) \\ &= -0.0304 \text{ amu}\end{aligned}$$

Note that in this case the electron mass cancels out in taking the difference. This will always happen in this type of calculation if the atomic masses are used both for the nuclide of interest and for ${}^1\text{H}$. Thus 0.0304 amu of mass is *lost* per ${}^4\text{He}$ nucleus formed.

Since atomic masses include the masses of the electrons, to obtain the mass of a given atomic nucleus from its atomic mass, we must subtract the mass of the electrons.

The corresponding energy change can be calculated from

$$\Delta E = \Delta mc^2$$

where

$$\begin{aligned}\Delta m &= -0.0304 \frac{\text{amu}}{\text{nucleus}} = \left(-0.0304 \frac{\text{amu}}{\text{nucleus}} \right) \left(1.66 \times 10^{-27} \frac{\text{kg}}{\text{amu}} \right) \\ &= -5.04 \times 10^{-29} \frac{\text{kg}}{\text{nucleus}}\end{aligned}$$

and

$$c = 3.00 \times 10^8 \text{ m/s}$$

$$\begin{aligned}\text{Thus } \Delta E &= \left(-5.04 \times 10^{-29} \frac{\text{kg}}{\text{nucleus}} \right) \left(3.00 \times 10^8 \frac{\text{m}}{\text{s}} \right)^2 \\ &= -4.54 \times 10^{-12} \text{ J/nucleus}\end{aligned}$$

This means that $4.54 \times 10^{-12} \text{ J}$ of energy is *released* per nucleus formed and that $4.54 \times 10^{-12} \text{ J}$ would be required to decompose the nucleus into the constituent neutrons and protons. Thus the binding energy (BE) per nucleon is

$$\begin{aligned}\text{BE per nucleon} &= \frac{4.54 \times 10^{-12} \text{ J/nucleus}}{4 \text{ nucleons/nucleus}} \\ &= 1.14 \times 10^{-12} \text{ J/nucleon} \\ &= \left(1.14 \times 10^{-12} \frac{\text{J}}{\text{nucleon}} \right) \left(\frac{1 \text{ MeV}}{1.60 \times 10^{-13} \text{ J}} \right) \\ &= 7.13 \text{ MeV/nucleon}\end{aligned}$$

See Exercises 18.38 through 18.40.

18.6 Nuclear Fission and Nuclear Fusion

The graph shown in Fig. 18.9 has very important implications for the use of nuclear processes as sources of energy. Recall that energy is released, that is, ΔE is negative, when a process goes from a less stable to a more stable state. The higher a nuclide is on the curve, the more stable it is. This means that two types of nuclear processes will be exothermic (see Fig. 18.10):

- Combining two light nuclei to form a heavier, more stable nucleus. This process is called **fusion**.
- Splitting a heavy nucleus into two nuclei with smaller mass numbers. This process is called **fission**.

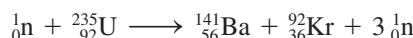
Because of the large binding energies involved in holding the nucleus together, both these processes involve energy changes more than a million times larger than those associated with chemical reactions.

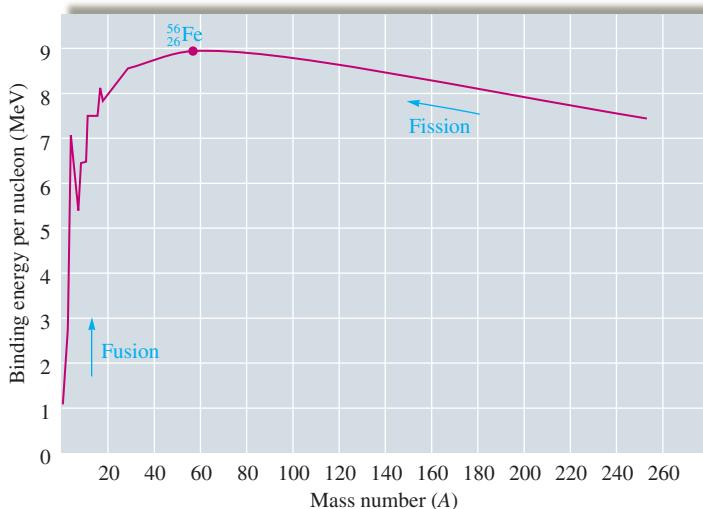


Visualization: Nuclear Fission

Nuclear Fission

Nuclear fission was discovered in the late 1930s when $^{235}_{92}\text{U}$ nuclides bombarded with neutrons were observed to split into two lighter elements:

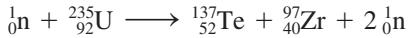


**FIGURE 18.10**

Both fission and fusion produce more stable nuclides and are thus exothermic.

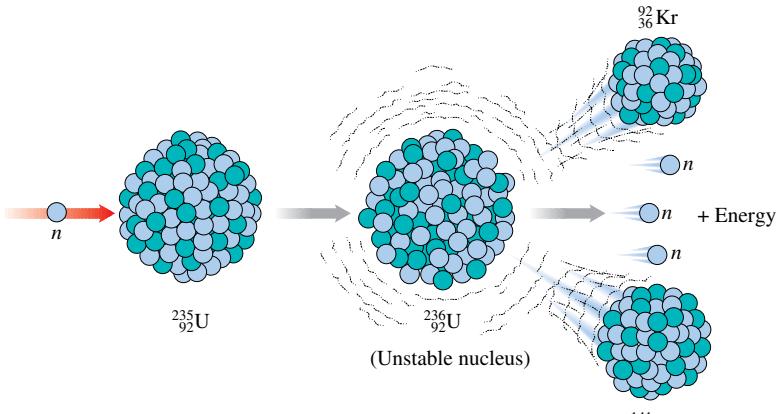
This process, shown schematically in Fig. 18.11, releases 3.5×10^{-11} J of energy per event, which translates to 2.1×10^{13} J per mole of ^{235}U . Compare this figure with that for the combustion of methane, which releases only 8.0×10^5 J of energy per mole. The fission of ^{235}U produces about 26 million times more energy than the combustion of methane.

The process shown in Fig. 18.11 is only one of the many fission reactions that ^{235}U can undergo. Another is

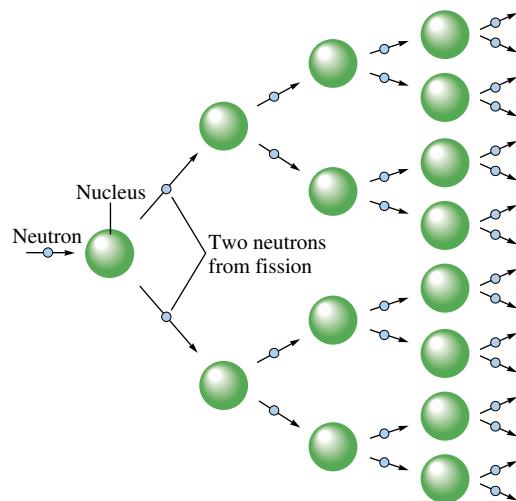


In fact, over 200 different isotopes of 35 different elements have been observed among the fission products of ^{235}U .

In addition to the product nuclides, neutrons are produced in the fission reactions of ^{235}U . This makes it possible to have a self-sustaining fission process—a **chain reaction** (see Fig. 18.12). For the fission process to be self-sustaining, at least one neutron from each fission event must go on to split another nucleus. If, on average, *less than one* neutron causes another fission event, the process dies out and the reaction is said to be **subcritical**. If *exactly one* neutron from each fission event causes another fission event, the process sustains itself at the same level and is said to be **critical**. If *more than one* neutron from each fission event causes another fission event, the process rapidly escalates and the heat buildup causes a violent explosion. This situation is described as **supercritical**.

**FIGURE 18.11**

On capturing a neutron, the ^{235}U nucleus undergoes fission to produce two lighter nuclides, free neutrons (typically three), and a large amount of energy.

**FIGURE 18.12**

Representation of a fission process in which each event produces two neutrons, which can go on to split other nuclei, leading to a self-sustaining chain reaction.

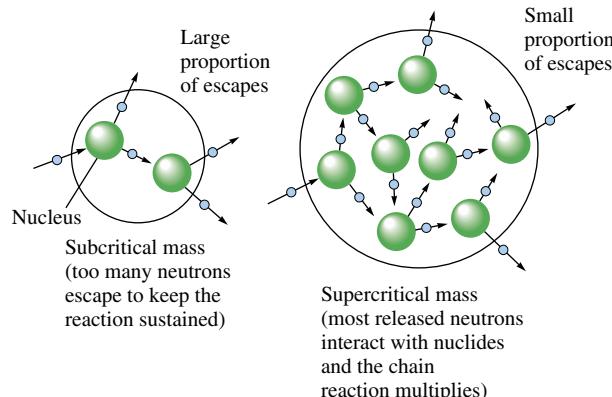
To achieve the critical state, a certain mass of fissionable material, called the **critical mass**, is needed. If the sample is too small, too many neutrons escape before they have a chance to cause a fission event, and the process stops. This is illustrated in Fig. 18.13.

During World War II, an intense research effort called the Manhattan Project was carried out by the United States to build a bomb based on the principles of nuclear fission. This program produced the fission bombs that were used with devastating effects on the cities of Hiroshima and Nagasaki in 1945. Basically, a fission bomb operates by suddenly combining subcritical masses of fissionable material to form a supercritical mass, thereby producing an explosion of incredible intensity.

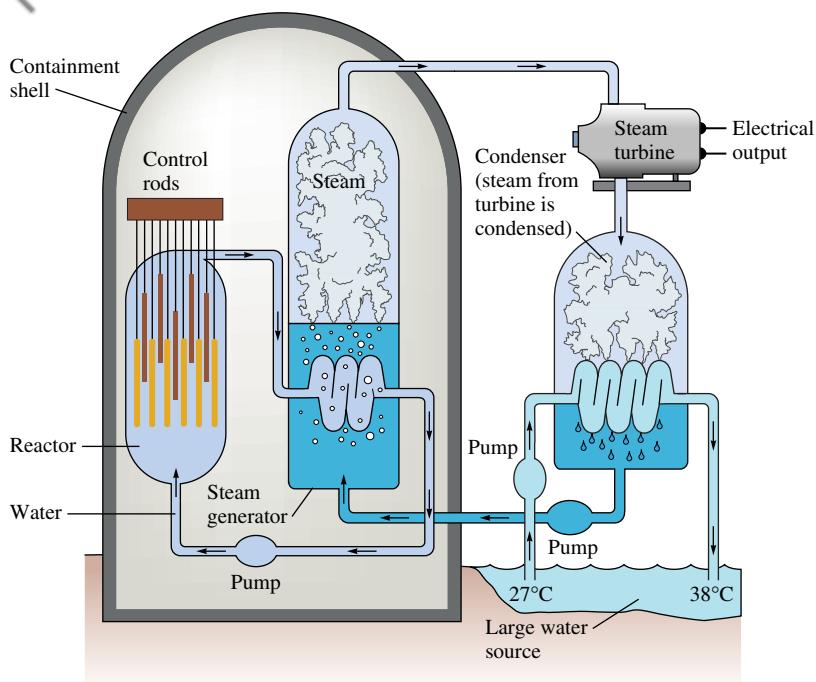
Nuclear Reactors

Because of the tremendous energies involved, it seemed desirable to develop the fission process as an energy source to produce electricity. To accomplish this, reactors were designed in which controlled fission can occur. The resulting energy is used to heat water to produce steam to run turbine generators, in much the same way that a coal-burning power plant generates energy. A schematic diagram of a nuclear power plant is shown in Fig. 18.14.

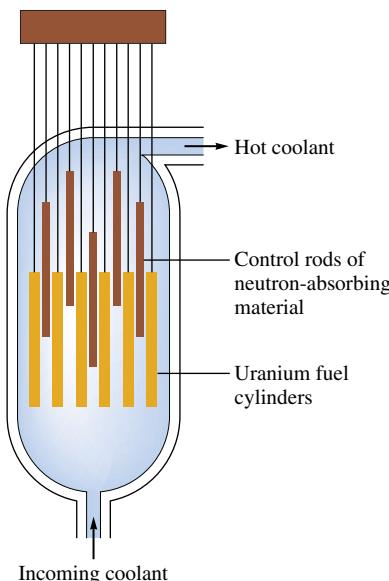
In the **reactor core**, shown in Fig. 18.15, uranium that has been enriched to approximately 3% $^{235}_{92}\text{U}$ (natural uranium contains only 0.7% $^{235}_{92}\text{U}$) is housed in cylinders. A **moderator** surrounds the cylinders to slow down the neutrons so that the uranium fuel can capture them more efficiently. **Control rods**, composed of substances that absorb

**FIGURE 18.13**

If the mass of fissionable material is too small, most of the neutrons escape before causing another fission event, and the process dies out.

**FIGURE 18.14**

A schematic diagram of a nuclear power plant.

**FIGURE 18.15**

A schematic of a reactor core. The position of the control rods determines the level of energy production by regulating the amount of fission taking place.

neutrons, are used to regulate the power level of the reactor. The reactor is designed so that should a malfunction occur, the control rods are automatically inserted into the core to stop the reaction. A liquid (usually water) is circulated through the core to extract the heat generated by the energy of fission; the energy can then be passed on via a heat exchanger to water in the turbine system.

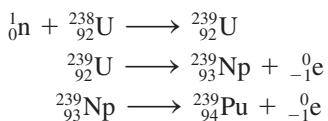
Although the concentration of $^{235}_{92}\text{U}$ in the fuel elements is not great enough to allow a supercritical mass to develop in the core, a failure of the cooling system can lead to temperatures high enough to melt the core. As a result, the building housing the core must be designed to contain the core even if meltdown occurs. A great deal of controversy now exists about the efficiency of the safety systems in nuclear power plants. Accidents such as the one at the Three Mile Island facility in Pennsylvania in 1979 and in Chernobyl,* Ukraine, in 1986 have led to questions about the wisdom of continuing to build fission-based power plants.



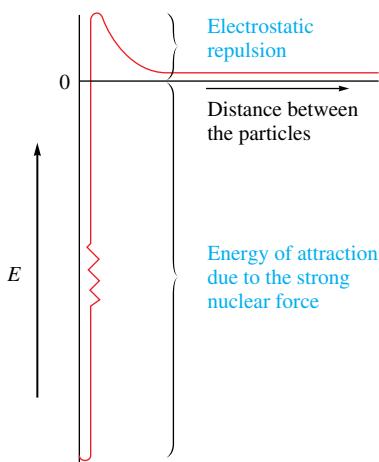
Uranium oxide (refined uranium).

Breeder Reactors

One potential problem facing the nuclear power industry is the supply of $^{235}_{92}\text{U}$. Some scientists have suggested that we have nearly depleted those uranium deposits rich enough in $^{235}_{92}\text{U}$ to make production of fissionable fuel economically feasible. Because of this possibility, **breeder reactors** have been developed, in which fissionable fuel is actually produced while the reactor runs. In the breeder reactors now being studied, the major component of natural uranium, nonfissionable $^{238}_{92}\text{U}$, is changed to fissionable $^{239}_{94}\text{Pu}$. The reaction involves absorption of a neutron, followed by production of two β particles:



*See C. A. Atwood, "Chernobyl—What happened?" *J. Chem. Ed.* 65 (1988): 1037.

**FIGURE 18.16**

A plot of energy versus the separation distance for two ${}^2\text{H}$ nuclei. The nuclei must have sufficient velocities to get over the electrostatic repulsion “hill” and get close enough for the nuclear binding forces to become effective, thus “fusing” the particles into a new nucleus and releasing large quantities of energy. The binding force is at least 100 times the electrostatic repulsion.



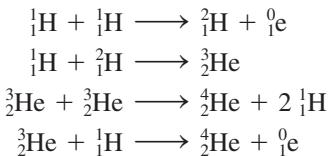
Visualization: Nuclear Fusion

As the reactor runs and ${}^{235}\text{U}$ is split, some of the excess neutrons are absorbed by ${}^{238}\text{U}$ to produce ${}^{239}\text{Pu}$. The ${}^{239}\text{Pu}$ is then separated out and used to fuel another reactor. Such a reactor thus “breeds” nuclear fuel as it operates.

Although breeder reactors are now used in France, the United States is proceeding slowly with their development because of their controversial nature. One problem involves the hazards in handling plutonium, which flames on contact with air and is very toxic.

Fusion

Large quantities of energy are also produced by the fusion of two light nuclei. In fact, stars produce their energy through nuclear fusion. Our sun, which presently consists of 73% hydrogen, 26% helium, and 1% other elements, gives off vast quantities of energy from the fusion of protons to form helium:



Intense research is under way to develop a feasible fusion process because of the ready availability of many light nuclides (deuterium, ${}^2\text{H}$, in seawater, for example) that can serve as fuel in fusion reactors. The major stumbling block is that high temperatures are required to initiate fusion. The forces that bind nucleons together to form a nucleus are effective only at *very small* distances ($\sim 10^{-15}$ cm). Thus, for two protons to bind together and thereby release energy, they must get very close together. But protons, because they are identically charged, repel each other electrostatically. This means that to get two protons (or two deuterons) close enough to bind together (the nuclear binding force is *not* electrostatic), they must be “shot” at each other at speeds high enough to overcome the electrostatic repulsion.

The electrostatic repulsion forces between two ${}^1\text{H}$ nuclei are so great that a temperature of 4×10^7 K is required to give them velocities large enough to cause them to collide with sufficient energy that the nuclear forces can bind the particles together and thus release the binding energy. This situation is represented in Fig. 18.16.

Currently, scientists are studying two types of systems to produce the extremely high temperatures required: high-powered lasers and heating by electric currents. At present, many technical problems remain to be solved, and it is not clear which method will prove more useful or when fusion might become a practical energy source. However, there is still hope that fusion will be a major energy source sometime in the future.

18.7 Effects of Radiation

Everyone knows that being hit by a train is very serious. The problem is the energy transfer involved. In fact, any source of energy is potentially harmful to organisms. Energy transferred to cells can break chemical bonds and cause malfunctioning of the cell systems. This fact is behind the concern about the ozone layer in the earth’s upper atmosphere, which screens out high-energy ultraviolet radiation from the sun. Radioactive elements, which are sources of high-energy particles, are also potentially hazardous, although the effects are usually quite subtle. The reason for the subtlety of radiation damage is that even though high-energy particles are involved, the quantity of energy actually deposited in tissues *per event* is quite small. However, the resulting damage is no less real, although the effects may not be apparent for years.

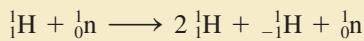
The ozone layer is discussed in Section 20.5.



CHEMICAL IMPACT

Nuclear Physics: An Introduction

Nuclear physics is concerned with the fundamental nature of matter. The central focuses of this area of study are the relationship between a quantity of energy and its mass, given by $E = mc^2$, and the fact that matter can be converted from one form (energy) to another (particulate) in particle accelerators. Collisions between high-speed particles have produced a dazzling array of new particles—hundreds of them. These events can best be interpreted as conversions of kinetic energy into particles. For example, a collision of sufficient energy between a proton and a neutron can produce four particles: two protons, one antiproton, and a neutron:



where ${}_{-1}^{-1}\text{H}$ is the symbol for an *antiproton*, which has the same mass as a proton but the opposite charge. This process is a little like throwing one baseball at a very high speed into another and having the energy of the collision converted into two additional baseballs.

The results of such accelerator experiments have led scientists to postulate the existence of three types of forces important in the nucleus: the *strong force*, the *weak force*, and the *electromagnetic force*. Along with the *gravitational force*, these forces are thought to account for all types of interactions found in matter. These forces are believed to be generated by the exchange of particles between the interacting pieces of matter. For example, gravitational forces are

thought to be carried by particles called *gravitons*. The electromagnetic force (the classical electrostatic force between charged particles) is assumed to be exerted through the exchange of *photons*. The strong force, not charge-related and effective only at very short distances ($\sim 10^{-13}$ cm), is postulated to involve the exchange of particles called *gluons*. The weak force is 100 times weaker than the strong force and seems to be exerted through the exchange of two types of large particles, the W (has a mass 70 times the proton mass) and the Z (has a mass 90 times the proton mass).

The particles discovered have been classified into several categories. Three of the most important classes are as follows:

1. *Hadrons* are particles that respond to the strong force and have internal structure.
2. *Leptons* are particles that do not respond to the strong force and have no internal structure.
3. *Quarks* are particles with no internal structure that are thought to be the fundamental constituents of hadrons. Neutrons and protons are hadrons that are thought to be composed of three quarks each.

The world of particle physics appears mysterious and complicated. For example, particle physicists have discovered new properties of matter they call “color,” “charm,”

Radiation damage to organisms can be classified as somatic or genetic damage. **Somatic damage** is damage to the organism itself, resulting in sickness or death. The effects may appear almost immediately if a massive dose of radiation is received; for smaller doses, damage may appear years later, usually in the form of cancer. **Genetic damage** is damage to the genetic machinery, which produces malfunctions in the offspring of the organism.

The biologic effects of a particular source of radiation depend on several factors:

1. *The energy of the radiation.* The higher the energy content of the radiation, the more damage it can cause. Radiation doses are measured in **rods** (which is short for *radiation absorbed dose*), where 1 rad corresponds to 10^{-2} J of energy deposited per kilogram of tissue.
2. *The penetrating ability of the radiation.* The particles and rays produced in radioactive processes vary in their abilities to penetrate human tissue: γ rays are highly penetrating, β particles can penetrate approximately 1 cm, and α particles are stopped by the skin.
3. *The ionizing ability of the radiation.* Extraction of electrons from biomolecules to form ions is particularly detrimental to their functions. The ionizing ability of radiation

and “strangeness” and have postulated conservation laws involving these properties. This area of science is extremely important because it should help us to understand the interactions of matter in a more elegant and unified way. For example, the classification of force into four categories is probably necessary only because we do not understand the true nature of forces. All forces may be special cases of a single, all-pervading force field that governs all of nature. In fact, Einstein spent the last 30 years of his

life looking for a way to unify the gravitational and electromagnetic forces—without success. Physicists may now be on the verge of accomplishing what Einstein failed to do.

Although the practical aspects of the work in nuclear physics are not yet totally apparent, a more fundamental understanding of the way nature operates could lead to presently undreamed-of devices for energy production and communication, which could revolutionize our lives.



(left) An aerial view of Fermilab, a high-energy particle accelerator in Batavia, Illinois.
(right) The accelerator tunnel at Fermilab.



varies dramatically. For example, γ rays penetrate very deeply but cause only occasional ionization. On the other hand, α particles, although not very penetrating, are very effective at causing ionization and produce a dense trail of damage. Thus ingestion of an α -particle producer, such as plutonium, is particularly damaging.

4. *The chemical properties of the radiation source.* When a radioactive nuclide is ingested into the body, its effectiveness in causing damage depends on its residence time. For example, ^{85}Kr and ^{90}Sr are both β -particle producers. However, since krypton is chemically inert, it passes through the body quickly and does not have much time to do damage. Strontium, being chemically similar to calcium, can collect in bones, where it may cause leukemia and bone cancer.

Because of the differences in the behavior of the particles and rays produced by radioactive decay, both the energy dose of the radiation and its effectiveness in causing biologic damage must be taken into account. The **rem** (which is short for roentgen equivalent for man) is defined as follows:

$$\text{Number of rems} = (\text{number of rads}) \times \text{RBE}$$

where RBE represents the relative effectiveness of the radiation in causing biologic damage.

TABLE 18.6 Effects of Short-Term Exposures to Radiation

Dose (rem)	Clinical Effect
0–25	Nondetectable
25–50	Temporary decrease in white blood cell counts
100–200	Strong decrease in white blood cell counts
500	Death of half the exposed population within 30 days after exposure

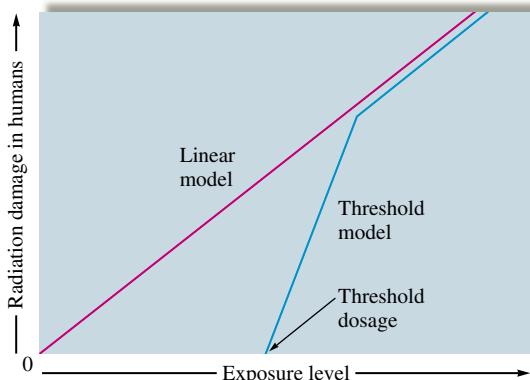
TABLE 18.7 Typical Radiation Exposures for a Person Living in the United States (1 millirem = 10^{-3} rem)

	Exposure (millirems/year)
Cosmic radiation	50
From the earth	47
From building materials	3
In human tissues	21
Inhalation of air	5
<i>Total from natural sources</i>	126
X-ray diagnosis	50
Radiotherapy	10
Internal diagnosis/therapy	1
Nuclear power industry	0.2
TV tubes, industrial wastes, etc.	2
Radioactive fallout	4
<i>Total from human activities</i>	67
<i>Total</i>	193

Table 18.6 shows the physical effects of short-term exposure to various doses of radiation, and Table 18.7 gives the sources and amounts of radiation exposure for a typical person in the United States. Note that natural sources contribute about twice as much as human activities to the total exposure. However, although the nuclear industry contributes only a small percentage of the total exposure, the major controversy associated with nuclear power plants is the *potential* for radiation hazards. These arise mainly from two sources: accidents allowing the release of radioactive materials and improper disposal of the radioactive products in spent fuel elements. The radioactive products of the fission of ^{235}U , although only a small percentage of the total products, have half-lives of several hundred years and remain dangerous for a long time. Various schemes have been advanced for the disposal of these wastes. The one that seems to hold the most promise is the incorporation of the wastes into ceramic blocks and the burial of these blocks in geologically stable formations. At present, however, no disposal method has been accepted, and nuclear wastes continue to accumulate in temporary storage facilities.

Even if a satisfactory method for permanent disposal of nuclear wastes is found, there will continue to be concern about the effects of exposure to low levels of radiation. Exposure is inevitable from natural sources such as cosmic rays and radioactive minerals, and many people are also exposed to low levels of radiation from reactors, radioactive tracers, or diagnostic X rays. Currently, we have little reliable information on the long-term effects of low-level exposure to radiation.

Two models of radiation damage, illustrated in Fig. 18.17, have been proposed: the *linear model* and the *threshold model*. The linear model postulates that damage from radiation is proportional to the dose, even at low levels of exposure. Thus any exposure is dangerous. The threshold model, on the other hand, assumes that no significant damage occurs below a certain exposure, called the *threshold exposure*. Note that if the linear model is correct, radiation exposure should be limited to a bare minimum (ideally at the natural levels). If the threshold model is correct, a certain level of radiation exposure beyond natural levels can be tolerated. Most scientists feel that since there is little evidence available to evaluate these models, it is safest to assume that the linear hypothesis is correct and to minimize radiation exposure.

**FIGURE 18.17**

The two models for radiation damage. In the linear model, even a small dosage causes a proportional risk. In the threshold model, risk begins only after a certain dosage.

Key Terms

neutron
proton
nucleon
atomic number
mass number
isotopes
nuclide

Section 18.1

thermodynamic stability
kinetic stability
radioactive decay
beta (β) particle
zone of stability
alpha (α) particle
 α -particle production
spontaneous fission
 β -particle production
gamma (γ) ray
positron production
electron capture
decay series

Section 18.2

rate of decay
half-life

Section 18.3

nuclear transformation
particle accelerator
cyclotron
linear accelerator
transuranium elements

Section 18.4

Geiger–Müller counter (Geiger counter)
scintillation counter
radiocarbon dating (carbon-14 dating)
radiotracers

Section 18.5

mass defect
binding energy

Section 18.6

fusion
fission
chain reaction
subcritical reaction
critical reaction
supercritical reaction
critical mass
reactor core
moderator
control rods
breeder reactor

Section 18.7

somatic damage
genetic damage
rad
rem

For Review

Radioactivity

- Certain nuclei decay spontaneously into more stable nuclei
- Types of radioactive decay:
 - α -particle (${}^4_2\text{He}$) production
 - β -particle (${}^0_{-1}\text{e}$) production
 - Positron (${}^0_1\text{e}$) production
 - γ rays are usually produced in a radioactive decay event
- A decay series involves several radioactive decays to finally reach a stable nuclide
- Radioactive decay follows first-order kinetics
 - Half-life of a radioactive sample: the time required for half of the nuclides to decay
- The transuranium elements (those beyond uranium in the periodic table) can be synthesized by particle bombardment of uranium or heavier elements
- Radiocarbon dating employs the ${}^{14}_6\text{C}/{}^{12}_6\text{C}$ ratio in an object to establish its date of origin

Thermodynamic stability of a nucleus

- Compares the mass of a nucleus to the sum of the masses of its component nucleons
- When a system gains or loses energy, it also gains or loses mass as described by the relationship $E = mc^2$
- The difference between the sum of the masses of the component nucleons and the actual mass of a nucleus (called the mass defect) can be used to calculate the nuclear binding energy

Nuclear energy production

- Fusion: the process of combining two light nuclei to form a heavier, more stable nucleus
- Fission: the process of splitting a heavy nucleus into two lighter, more stable nuclei
 - Current nuclear power reactors employ controlled fission to produce energy

Radiation damage

- Radiation can cause direct (somatic) damage to a living organism or genetic damage to the organism's offspring
- The biologic effects of radiation depend on the energy, the penetrating ability, the ionizing ability of the radiation, and the chemical properties of the nuclide producing the radiation

REVIEW QUESTIONS

1. Define or illustrate the following terms:
 - a. thermodynamic stability
 - b. kinetic stability
 - c. radioactive decay
 - d. beta-particle production
 - e. alpha-particle production
 - f. positron production
 - g. electron capture
 - h. gamma-ray emissions

In radioactive decay processes, A and Z are conserved. What does this mean?
2. Figure 18.1 illustrates the zone of stability. What is the zone of stability? Stable light nuclides have about equal numbers of neutrons and protons. What happens to the neutron-to-proton ratio for stable nuclides as the number of protons

increases? Nuclides that are not already in the zone of stability undergo radioactive processes to get to the zone of stability. If a nuclide has too many neutrons, which process(es) can the nuclide undergo to become more stable? Answer the same question for a nuclide having too many protons.

3. All radioactive decay processes follow first-order kinetics. What does this mean? What happens to the rate of radioactive decay as the number of nuclides is halved? Write the first-order rate law and the integrated first-order rate law. Define the terms in each equation. What is the half-life equation for radioactive decay processes? How does the half-life depend on how many nuclides are present? Are the half-life and rate constant k directly related or inversely related?
4. What is a nuclear transformation? How do you balance nuclear transformation reactions? Particle accelerators are used to perform nuclear transformations. What is a particle accelerator?
5. What is a Geiger counter and how does it work? What is a scintillation counter and how does it work? Radiotracers are used in the medical sciences to learn about metabolic pathways. What are radiotracers? Explain why ^{14}C and ^{32}P radioactive nuclides would be very helpful in learning about metabolic pathways. Why is I-131 useful for diagnosis of diseases of the thyroid? How could you use a radioactive nuclide to demonstrate that chemical equilibrium is a dynamic process?
6. Explain the theory behind carbon-14 dating. What assumptions must be made and what problems arise when using carbon-14 dating?

The decay of uranium-238 to lead-206 is also used to estimate the age of objects. Specifically, ^{206}Pb -to- ^{238}U ratios allow dating of rocks. Why is the ^{238}U decay to ^{206}Pb useful for dating rocks but worthless for dating objects 10,000 years old or younger? Similarly, why is carbon-14 dating useful for dating objects 10,000 years old or younger but worthless for dating rocks?

7. Define *mass defect* and *binding energy*. How do you determine the mass defect for a nuclide? How do you convert the mass defect into the binding energy for a nuclide? Iron-56 has the largest binding energy per nucleon among all known nuclides. Is this good or bad for iron-56? Explain.
8. Define *fission* and *fusion*. How does the energy associated with fission or fusion processes compare to the energy changes associated with chemical reactions? Fusion processes are more likely to occur for lighter elements, whereas fission processes are more likely to occur for heavier elements. Why? (*Hint:* Reference Figure 18.10.) The major stumbling block for turning fusion reactions into a feasible source of power is the high temperature required to initiate a fusion reaction. Why are elevated temperatures necessary to initiate fusion reactions but not fission reactions?
9. The fission of U-235 is used exclusively in nuclear power plants located in the United States. There are many different fission reactions of U-235, but all the fission reactions are self-sustaining chain reactions. Explain. Differentiate between the terms *critical*, *subcritical*, and *supercritical*. What is the critical mass? How does a nuclear power plant produce electricity? What are the purposes of the moderator and the control rods in a fission reactor? What are some problems associated with nuclear reactors? What are breeder reactors? What are some problems associated with breeder reactors?
10. The biological effects of a particular source of radiation depend on several factors. List some of these factors. Even though ^{85}Kr and ^{90}Sr are both beta-particle emitters, the dangers associated with the decay of ^{90}Sr are much greater than those linked to ^{85}Kr . Why? Although gamma rays are far more penetrating than alpha particles, the latter are more likely to cause damage to an organism. Why? Which type of radiation is more effective at promoting the ionization of biomolecules?

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide*.

Questions

1. When nuclei undergo nuclear transformations, γ rays of characteristic frequencies are observed. How does this fact, along with other information in the chapter on nuclear stability, suggest that a quantum mechanical model may apply to the nucleus?
2. There is a trend in the United States toward using coal-fired power plants to generate electricity rather than building new nuclear fission power plants. Is the use of coal-fired power plants without risk? Make a list of the risks to society from the use of each type of power plant.
3. Which type of radioactive decay has the net effect of changing a neutron into a proton? Which type of decay has the net effect of turning a proton into a neutron?
4. What is annihilation in terms of nuclear processes?
5. What are transuranium elements and how are they synthesized?
6. Scientists have estimated that the earth's crust was formed 4.3 billion years ago. The radioactive nuclide ^{176}Lu , which decays to ^{176}Hf , was used to estimate this age. The half-life of ^{176}Lu is 37 billion years. How are ratios of ^{176}Lu to ^{176}Hf utilized to date very old rocks?
7. Why are the observed energy changes for nuclear processes so much larger than the energy changes for chemical and physical processes?
8. Natural uranium is mostly nonfissionable ^{238}U ; it contains only about 0.7% of fissionable ^{235}U . For uranium to be useful as a nuclear fuel, the relative amount of ^{235}U must be increased to about 3%. This is accomplished through a gas diffusion process. In the diffusion process, natural uranium reacts with fluorine to form a mixture of $^{238}\text{UF}_6(g)$ and $^{235}\text{UF}_6(g)$. The fluoride mixture is then enriched through a multistage diffusion process to produce a 3% ^{235}U nuclear fuel. The diffusion process utilizes Graham's law of effusion (see Chapter 5, Section 5.7). Explain how Graham's law of effusion allows natural uranium to be enriched by the gaseous diffusion process.
9. Strontium-90 and radon-222 both pose serious health risks. ^{90}Sr decays by β -particle production and has a relatively long half-life (28.8 yr). Radon-222 decays by alpha-particle production and has a relatively short half-life (3.82 days). Explain why each decay process poses health risks.
10. A recent study concluded that any amount of radiation exposure can cause biological damage. Explain the differences between the two models of radiation damage, the linear model and the threshold model.

Exercises

In this section similar exercises are paired.

Radioactive Decay and Nuclear Transformations

11. Write balanced equations for each of the processes described below.
 - a. Chromium-51, which targets the spleen and is used as a tracer in studies of red blood cells, decays by electron capture.
 - b. Iodine-131, used to treat hyperactive thyroid glands, decays by producing a β particle.
12. Write balanced equations for each of the processes described below.
 - a. Phosphorus-32, which accumulates in the liver, decays by β -particle production.
 - b. Uranium-235, which is used in atomic bombs, decays initially by α -particle production.
13. Write an equation describing the radioactive decay of each of the following nuclides. (The particle produced is shown in parentheses, except for electron capture, where an electron is a reactant.)
 - a. ^{68}Ga (electron capture)
 - c. ^{212}Fr (α)
 - b. ^{62}Cu (positron)
 - d. ^{129}Sb (β)
14. In each of the following nuclear reactions, supply the missing particle.

a. $^{73}\text{Ga} \rightarrow ^{73}\text{Ge} + ?$	c. $^{205}\text{Bi} \rightarrow ^{205}\text{Pb} + ?$
b. $^{192}\text{Pt} \rightarrow ^{188}\text{Os} + ?$	d. $^{241}\text{Cm} + ? \rightarrow ^{241}\text{Am}$
15. The radioactive isotope ^{247}Bk decays by a series of α -particle and β -particle productions, taking ^{247}Bk through many transformations to end up as ^{207}Pb . In the complete decay series, how many α particles and β particles are produced?
16. One type of commercial smoke detector contains a minute amount of radioactive americium-241 (^{241}Am), which decays by α -particle production. The α particles ionize molecules in the air, allowing it to conduct an electric current. When smoke particles enter, the conductivity of the air is changed and the alarm buzzes.
 - a. Write the equation for the decay of ^{241}Am by α -particle production.
 - b. The complete decay of ^{241}Am involves successively α , α , β , α , β , α , α , β , α , and β production. What is the final stable nucleus produced in this decay series?
 - c. Identify the 11 intermediate nuclides.
17. There are four stable isotopes of iron with mass numbers 54, 56, 57, and 58. There are also two radioactive isotopes: iron-53 and iron-59. Predict modes of decay for these two isotopes. (See Table 18.2.)
18. The only stable isotope of fluorine is fluorine-19. Predict possible modes of decay for fluorine-21, fluorine-18, and fluorine-17.
19. In 1994 it was proposed (and eventually accepted) that element 106 be named seaborgium, Sg, in honor of Glenn T. Seaborg, discoverer of the transuranium elements.
 - a. ^{263}Sg was produced by the bombardment of ^{249}Cf with a beam of ^{18}O nuclei. Complete and balance an equation for this reaction.
 - b. ^{263}Sg decays by α emission. What is the other product resulting from the α decay of ^{263}Sg ?
20. Many elements have been synthesized by bombarding relatively heavy atoms with high-energy particles in particle accelerators. Complete the following nuclear reactions, which have been used to synthesize elements.
 - a. _____ + $^4_2\text{He} \rightarrow ^{243}_{97}\text{Bk} + ^1_0\text{n}$
 - b. $^{238}_{92}\text{U} + ^{12}_{6}\text{C} \rightarrow$ _____ + $6 ^1_0\text{n}$
 - c. $^{249}_{98}\text{Cf} +$ _____ $\rightarrow ^{260}_{105}\text{Db} + 4 ^1_0\text{n}$
 - d. $^{249}_{98}\text{Cf} + ^{10}_{5}\text{B} \rightarrow ^{257}_{103}\text{Lr} +$ _____

Chapter Eighteen The Nucleus: A Chemist's View

Kinetics of Radioactive Decay

- 21.** The rate constant for a certain radioactive nuclide is $1.0 \times 10^{-3} \text{ h}^{-1}$. What is the half-life of this nuclide?
- 22.** Americium-241 is widely used in smoke detectors. The radiation released by this element ionizes particles that are then detected by a charged-particle collector. The half-life of ^{241}Am is 432.2 years, and it decays by emitting alpha particles. How many alpha particles are emitted each second by a 5.00-g sample of ^{241}Am ?
- 23.** Krypton consists of several radioactive isotopes, some of which are listed in the following table.

Half-life	
Kr-73	27 s
Kr-74	11.5 min
Kr-76	14.8 h
Kr-81	2.1×10^5 yr

- Which of these isotopes is most stable and which isotope is “hottest”? How long does it take for 87.5% of each isotope to decay?
- 24.** Radioactive copper-64 decays with a half-life of 12.8 days.
- What is the value of k in s^{-1} ?
 - A sample contains 28.0 mg ^{64}Cu . How many decay events will be produced in the first second? Assume the atomic mass of ^{64}Cu is 64.0.
 - A chemist obtains a fresh sample of ^{64}Cu and measures its radioactivity. She then determines that to do an experiment, the radioactivity cannot fall below 25% of the initial measured value. How long does she have to do the experiment?
- 25.** Phosphorus-32 is a commonly used radioactive nuclide in biochemical research, particularly in studies of nucleic acids. The half-life of phosphorus-32 is 14.3 days. What mass of phosphorus-32 is left from an original sample of 175 mg of $\text{Na}_3^{32}\text{PO}_4$ after 35.0 days? Assume the atomic mass of ^{32}P is 32.0.
- 26.** The curie (Ci) is a commonly used unit for measuring nuclear radioactivity: 1 curie of radiation is equal to 3.7×10^{10} decay events per second (the number of decay events from 1 g of radium in 1 s).
- What mass of $\text{Na}_2^{38}\text{SO}_4$ has an activity of 10.0 mCi? Sulfur-38 has an atomic mass of 38.0 and a half-life of 2.87 h.
 - How long does it take for 99.99% of a sample of sulfur-38 to decay?
- 27.** The first atomic explosion was detonated in the desert north of Alamogordo, New Mexico, on July 16, 1945. What fraction of the strontium-90 ($t_{1/2} = 28.8$ years) originally produced by that explosion still remains as of July 16, 2006?
- 28.** Iodine-131 is used in the diagnosis and treatment of thyroid disease and has a half-life of 8.1 days. If a patient with thyroid disease consumes a sample of Na^{131}I containing 10 μg of ^{131}I , how long will it take for the amount of ^{131}I to decrease to 1/100 of the original amount?
- 29.** The Br-82 nucleus has a half-life of 1.0×10^3 min. If you wanted 1.0 g of Br-82 and the delivery time was 3.0 days, what

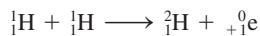
mass of NaBr should you order (assuming all of the Br in the NaBr was Br-82)?

- 30.** Fresh rainwater or surface water contains enough tritium (^3H) to show 5.5 decay events per minute per 100. g of water. Tritium has a half-life of 12.3 years. You are asked to check a vintage wine that is claimed to have been produced in 1946. How many decay events per minute should you expect to observe in 100. g of that wine?
- 31.** A living plant contains approximately the same fraction of carbon-14 as in atmospheric carbon dioxide. Assuming that the observed rate of decay of carbon-14 from a living plant is 13.6 counts per minute per gram of carbon, how many counts per minute per gram of carbon will be measured from a 15,000-year-old sample? Will radiocarbon dating work well for small samples of 10 mg or less? (For ^{14}C , $t_{1/2} = 5730$ years.)
- 32.** Assume a constant $^{14}\text{C}/^{12}\text{C}$ ratio of 13.6 counts per minute per gram of living matter. A sample of a petrified tree was found to give 1.2 counts per minute per gram. How old is the tree? ($t_{1/2} = ^{14}\text{C} = 5730$ years.)
- 33.** A rock contains 0.688 mg of ^{206}Pb for every 1.000 mg of ^{238}U present. Assuming that no lead was originally present, that all the ^{206}Pb formed over the years has remained in the rock, and that the number of nuclides in intermediate stages of decay between ^{238}U and ^{206}Pb is negligible, calculate the age of the rock. (For ^{238}U , $t_{1/2} = 4.5 \times 10^9$ years.)
- 34.** The mass ratios of ^{40}Ar to ^{40}K also can be used to date geologic materials. Potassium-40 decays by two processes:
- $${}_{19}^4\text{K} + {}_0^1\text{e} \longrightarrow {}_{18}^4\text{Ar} \quad (10.7\%) \quad t_{1/2} = 1.27 \times 10^9 \text{ years}$$
- $${}_{19}^4\text{K} \longrightarrow {}_{20}^4\text{Ca} + {}_0^1\text{e} \quad (89.3\%)$$
- Why are $^{40}\text{Ar}/^{40}\text{K}$ ratios used to date materials rather than $^{40}\text{Ca}/^{40}\text{K}$ ratios?
 - What assumptions must be made using this technique?
 - A sedimentary rock has an $^{40}\text{Ar}/^{40}\text{K}$ ratio of 0.95. Calculate the age of the rock.
 - How will the measured age of a rock compare to the actual age if some ^{40}Ar escaped from the sample?
- ### Energy Changes in Nuclear Reactions
- 35.** The sun radiates 3.9×10^{23} J of energy into space every second. What is the rate at which mass is lost from the sun?
- 36.** The earth receives 1.8×10^{14} kJ/s of solar energy. What mass of solar material is converted to energy over a 24-h period to provide the daily amount of solar energy to the earth? What mass of coal would have to be burned to provide the same amount of energy? (Coal releases 32 kJ of energy per gram when burned.)
- 37.** Many transuranium elements, such as plutonium-232, have very short half-lives. (For ^{232}Pu , the half-life is 36 minutes.) However, some, like protactinium-231 (half-life = 3.34×10^4 years), have relatively long half-lives. Use the masses given in the following table to calculate the change in energy when 1 mol of ^{232}Pu nuclei and 1 mol of ^{231}Pa nuclei are each formed from their respective number of protons and neutrons.

Atom or Particle	Atomic Mass
Neutron	1.67493×10^{-24} g
Proton	1.67262×10^{-24} g
Electron	9.10939×10^{-28} g
Pu-232	3.85285×10^{-22} g
Pa-231	3.83616×10^{-22} g

(Since the masses of ^{232}Pu and ^{231}Pa are atomic masses, they each include the mass of the electrons present. The mass of the nucleus will be the atomic mass minus the mass of the electrons.)

38. The most stable nucleus in terms of binding energy per nucleon is ^{56}Fe . If the atomic mass of ^{56}Fe is 55.9349 amu, calculate the binding energy per nucleon for ^{56}Fe .
39. Calculate the binding energy in J/nucleon for carbon-12 (atomic mass 12.0000) and uranium-235 (atomic mass 235.0439). The atomic mass of ^1H is 1.00782 amu and the mass of a neutron is 1.00866 amu. The most stable nucleus known is ^{56}Fe (see Exercise 38). Would the binding energy per nucleon for ^{56}Fe be larger or smaller than that of ^{12}C or ^{235}U ? Explain.
40. Calculate the binding energy per nucleon for ^2H and ^3H . The atomic masses are ^2H , 2.01410, and ^3H , 3.01605.
41. The mass defect for a Li-6 nucleus is -0.03434 g/mol. Calculate the atomic mass of Li-6.
42. The binding energy per nucleon for Mg-27 is 1.326×10^{-12} J/nucleon. Calculate the atomic mass of Mg-27.
43. Calculate the amount of energy released per gram of hydrogen nuclei reacted for the following reaction. The atomic masses are ^1H , 1.00782 amu, ^2H , 2.01410 amu, and an electron, 5.4858×10^{-4} amu. (Hint: Think carefully about how to account for the electron mass.)



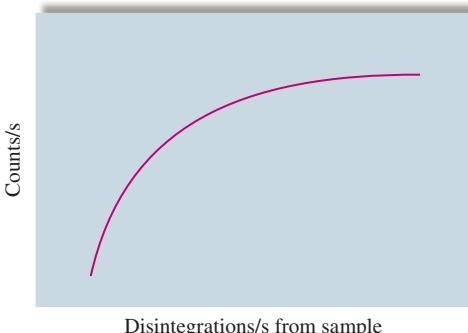
44. The easiest fusion reaction to initiate is



Calculate the energy released per ${}^4_2\text{He}$ nucleus produced and per mole of ${}^4_2\text{He}$ produced. The atomic masses are ^2H , 2.01410; ^3H , 3.01605; and ${}^4_2\text{He}$, 4.00260. The masses of the electron and neutron are 5.4858×10^{-4} and 1.00866 amu, respectively.

Detection, Uses, and Health Effects of Radiation

45. The typical response of a Geiger–Müller tube is shown below. Explain the shape of this curve.



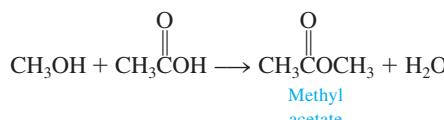
46. When using a Geiger–Müller counter to measure radioactivity, it is necessary to maintain the same geometrical orientation between the sample and the Geiger–Müller tube to compare different measurements. Why?

47. Photosynthesis in plants can be represented by the following overall reaction:



Algae grown in water containing some ^{18}O (in H_2^{18}O) evolve oxygen gas with the same isotopic composition as the oxygen in the water. When algae growing in water containing only ^{16}O were furnished carbon dioxide containing ^{18}O , no ^{18}O was found to be evolved from the oxygen gas produced. What conclusions about photosynthesis can be drawn from these experiments?

48. Consider the following reaction to produce methyl acetate:



When this reaction is carried out with CH_3OH containing oxygen-18, the water produced does not contain oxygen-18. Explain.

49. U-235 undergoes many different fission reactions. For one such reaction, when U-235 is struck with a neutron, Ce-144 and Sr-90 are produced along with some neutrons and electrons. How many neutrons and β -particles are produced in this fission reaction?
50. Breeder reactors are used to convert the nonfissionable nuclide $^{238}_{92}\text{U}$ to a fissionable product. Neutron capture of the $^{238}_{92}\text{U}$ is followed by two successive beta decays. What is the final fissionable product?

51. Which do you think would be the greater health hazard: the release of a radioactive nuclide of Sr or a radioactive nuclide of Xe into the environment? Assume the amount of radioactivity is the same in each case. Explain your answer on the basis of the chemical properties of Sr and Xe. Why are the chemical properties of a radioactive substance important in assessing its potential health hazards?

52. Consider the following information:
- The layer of dead skin on our bodies is sufficient to protect us from most α -particle radiation.
 - Plutonium is an α -particle producer.
 - The chemistry of Pu^{4+} is similar to that of Fe^{3+} .
 - Pu oxidizes readily to Pu^{4+} .

Why is plutonium one of the most toxic substances known?

Additional Exercises

53. Predict whether each of the following nuclides is stable or unstable (radioactive). If the nuclide is unstable, predict the type of radioactivity you would expect it to exhibit.
- $^{45}_{19}\text{K}$
 - $^{56}_{26}\text{Fe}$
 - $^{20}_{11}\text{Na}$
 - $^{194}_{81}\text{Tl}$
54. At a flea market, you've found a very interesting painting done in the style of Rembrandt's "dark period" (1642–1672). You suspect that you really do not have a genuine Rembrandt, but you take it to the local university for testing. Living wood shows a carbon-14

Chapter Eighteen The Nucleus: A Chemist's View

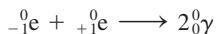
activity of 15.3 counts per minute per gram. Your painting showed a carbon-14 activity of 15.1 counts per minute per gram. Could it be a genuine Rembrandt?

55. Define "third-life" in a similar way to "half-life" and determine the "third-life" for a nuclide that has a half-life of 31.4 years.

56. A proposed system for storing nuclear wastes involves storing the radioactive material in caves or deep mine shafts. One of the most toxic nuclides that must be disposed of is plutonium-239, which is produced in breeder reactors and has a half-life of 24,100 years. A suitable storage place must be geologically stable long enough for the activity of plutonium-239 to decrease to 0.1% of its original value. How long is this for plutonium-239?

57. During World War II, tritium (${}^3\text{H}$) was a component of fluorescent watch dials and hands. Assume you have such a watch that was made in January 1944. If 17% or more of the original tritium was needed to read the dial in dark places, until what year could you read the time at night? (For ${}^3\text{H}$, $t_{1/2} = 12.3$ yr.)

58. A positron and an electron can annihilate each other on colliding, producing energy as photons:



Assuming that both γ rays have the same energy, calculate the wavelength of the electromagnetic radiation produced.

59. A small atomic bomb releases energy equivalent to the detonation of 20,000 tons of TNT; a ton of TNT releases 4×10^9 J of energy when exploded. Using 2×10^{13} J/mol as the energy released by fission of ${}^{235}\text{U}$, approximately what mass of ${}^{235}\text{U}$ undergoes fission in this atomic bomb?

60. During the research that led to production of the two atomic bombs used against Japan in World War II, different mechanisms for obtaining a supercritical mass of fissionable material were investigated. In one type of bomb, a "gun" shot one piece of fissionable material into a cavity containing another piece of fissionable material. In the second type of bomb, the fissionable material was surrounded with a high explosive that, when detonated, compressed the fissionable material into a smaller volume. Discuss what is meant by critical mass, and explain why the ability to achieve a critical mass is essential to sustaining a nuclear reaction.

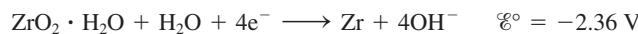
61. Using the kinetic molecular theory (Section 5.6), calculate the root mean square velocity and the average kinetic energy of ${}^1\text{H}$ nuclei at a temperature of 4×10^7 K. (See Exercise 44 for the appropriate mass values.)

Challenge Problems

62. A 0.20-mL sample of a solution containing ${}^3\text{H}$ that produces 3.7×10^3 cps is injected into the bloodstream of an animal. After allowing circulatory equilibrium to be established, a 0.20-mL sample of blood is found to have an activity of 20. cps. Calculate the blood volume of the animal.

63. A 0.10-cm³ sample of a solution containing a radioactive nuclide (5.0×10^3 counts per minute per milliliter) is injected into a rat. Several minutes later 1.0 cm³ of blood is removed. The blood shows 48 counts per minute of radioactivity. Calculate the volume of blood in the rat. What assumptions must be made in performing this calculation?

64. Zirconium is one of the few metals that retains its structural integrity upon exposure to radiation. The fuel rods in most nuclear reactors therefore are often made of zirconium. Answer the following questions about the redox properties of zirconium based on the half-reaction



a. Is zirconium metal capable of reducing water to form hydrogen gas at standard conditions?

b. Write a balanced equation for the reduction of water by zirconium.

c. Calculate \mathcal{E}° , ΔG° , and K for the reduction of water by zirconium metal.

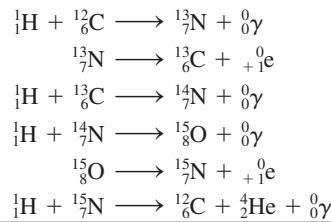
d. The reduction of water by zirconium occurred during the accidents at Three Mile Island in 1979. The hydrogen produced was successfully vented and no chemical explosion occurred. If 1.00×10^3 kg of Zr reacts, what mass of H₂ is produced? What volume of H₂ at 1.0 atm and 1000°C is produced?

e. At Chernobyl in 1986, hydrogen was produced by the reaction of superheated steam with the graphite reactor core:

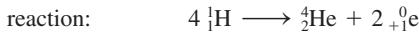


It was not possible to prevent a chemical explosion at Chernobyl. In light of this, do you think it was a correct decision to vent the hydrogen and other radioactive gases into the atmosphere at Three Mile Island? Explain.

65. In addition to the process described in the text, a second process called the *carbon–nitrogen cycle* occurs in the sun:



Overall



a. What is the catalyst in this process?

b. What nucleons are intermediates?

c. How much energy is released per mole of hydrogen nuclei in the overall reaction? (The atomic masses of ${}_{-1}^1\text{H}$ and ${}_{2}^{4}\text{He}$ are 1.00782 and 4.00260, respectively.)

66. The most significant source of natural radiation is radon-222. ${}^{222}\text{Rn}$, a decay product of ${}^{238}\text{U}$, is continuously generated in the earth's crust, allowing gaseous Rn to seep into the basements of buildings. Because ${}^{222}\text{Rn}$ is an α -particle producer with a relatively short half-life of 3.82 days, it can cause biological damage when inhaled.

a. How many α particles and β particles are produced when ${}^{238}\text{U}$ decays to ${}^{222}\text{Rn}$? What nuclei are produced when ${}^{222}\text{Rn}$ decays?

b. Radon is a noble gas so one would expect it to pass through the body quickly. Why is there a concern over inhaling ${}^{222}\text{Rn}$?

c. Another problem associated with ${}^{222}\text{Rn}$ is that the decay of ${}^{222}\text{Rn}$ produces a more potent α -particle producer ($t_{1/2} = 3.11\text{ min}$) that is a solid. What is the identity of the solid? Give the balanced equation of this species decaying by α -particle production. Why is the solid a more potent α -particle producer?

- d.** The U.S. Environmental Protection Agency (EPA) recommends that ^{222}Rn levels not exceed 4 pCi per liter of air ($1 \text{ Ci} = 1 \text{ curie} = 3.7 \times 10^{10}$ decay events per second; $1 \text{ pCi} = 1 \times 10^{-12} \text{ Ci}$). Convert 4.0 pCi per liter of air into concentrations units of ^{222}Rn atoms per liter of air and moles of ^{222}Rn per liter of air.
- 67.** To determine the K_{sp} value of Hg_2I_2 , a chemist obtained a solid sample of Hg_2I_2 in which some of the iodine is present as radioactive ^{131}I . The count rate of the Hg_2I_2 sample is 5.0×10^{11} counts per minute per mole of I. An excess amount of $\text{Hg}_2\text{I}_2(s)$ is placed into some water, and the solid is allowed to come to equilibrium with its respective ions. A 150.0-mL sample of the saturated solution is withdrawn and the radioactivity measured at 33 counts per minute. From this information, calculate the K_{sp} value for Hg_2I_2 .
- $$\text{Hg}_2\text{I}_2(s) \rightleftharpoons \text{Hg}_2^{2+}(aq) + 2\text{I}^-(aq) \quad K_{\text{sp}} = [\text{Hg}_2^{2+}][\text{I}^-]^2$$
- 68.** Estimate the temperature needed to achieve the fusion of deuterium to make an alpha particle. The energy required can be estimated from Coulomb's law [use the form $E = 9.0 \times 10^9 (Q_1 Q_2 / r)$, using $Q = 1.6 \times 10^{-19} \text{ C}$ for a proton, and $r = 2 \times 10^{-15} \text{ m}$ for the helium nucleus; the unit for the proportionality constant in Coloumb's law is $\text{J} \cdot \text{m/C}^2$.]
- 69.** A recently reported synthesis of the transuranium element bohrium (Bh) involved the bombardment of berkelium-249 with neon-22 to produce bohrium-267. Write a nuclear reaction for this synthesis. The half-life of bohrium-267 is 15.0 seconds. If 199 atoms of bohrium-267 could be synthesized, how much time would elapse before only 11 atoms of bohrium-267 remain? What is the expected electron configuration of elemental bohrium?
- 70.** Radioactive cobalt-60 is used to study defects in vitamin B_{12} absorption because cobalt is the metallic atom at the center of the vitamin B_{12} molecule. The nuclear synthesis of this cobalt isotope involves a three-step process. The overall reaction is iron-58 reacting with two neutrons to produce cobalt-60 along with the emission of another particle. What particle is emitted in this nuclear synthesis? What is the binding energy in J per nucleon for the cobalt-60 nucleus (atomic masses: $^{60}\text{Co} = 59.9338 \text{ amu}$; $^1\text{H} = 1.00782 \text{ amu}$). What is the de Broglie wavelength of the emitted particle if it has a velocity equal to $0.90c$ where c is the speed of light?



Get help understanding core concepts and visualizing molecular-level interactions, and practice problem solving, by visiting the Online Study Center at college.hmco.com/PIC/zumdahl7e.

Integrative Problems

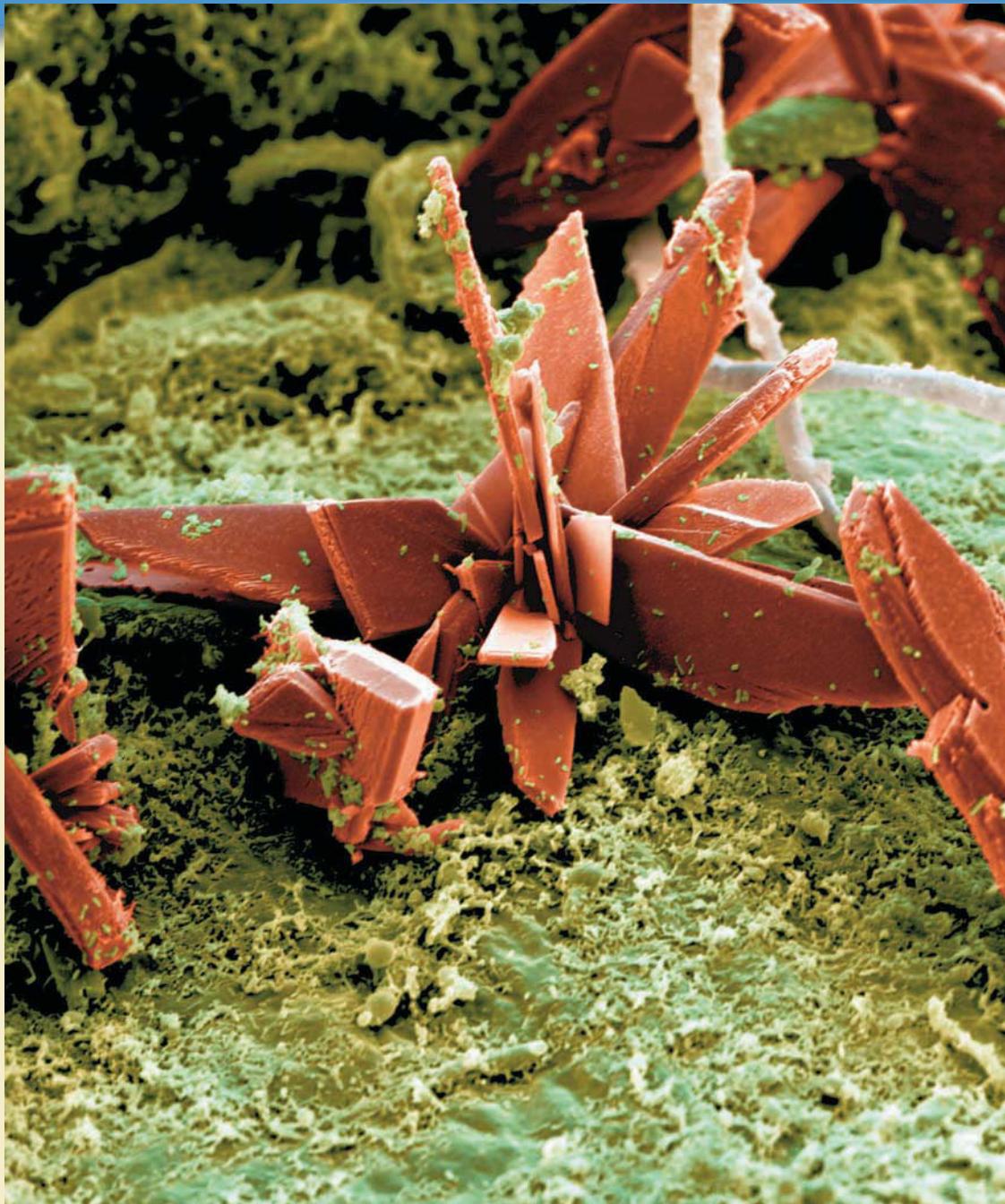
These problems require the integration of multiple concepts to find the solutions.

- 69.** A recently reported synthesis of the transuranium element bohrium (Bh) involved the bombardment of berkelium-249 with

19 The Representative Elements: Groups 1A Through 4A

Contents

- 19.1 A Survey of the Representative Elements
 - Atomic Size and Group Anomalies
 - Abundance and Preparation
- 19.2 The Group 1A Elements
- 19.3 Hydrogen
- 19.4 The Group 2A Elements
- 19.5 The Group 3A Elements
- 19.6 The Group 4A Elements



Scanning electron micrograph of calcium crystals, a representative element in Group 2A.

S

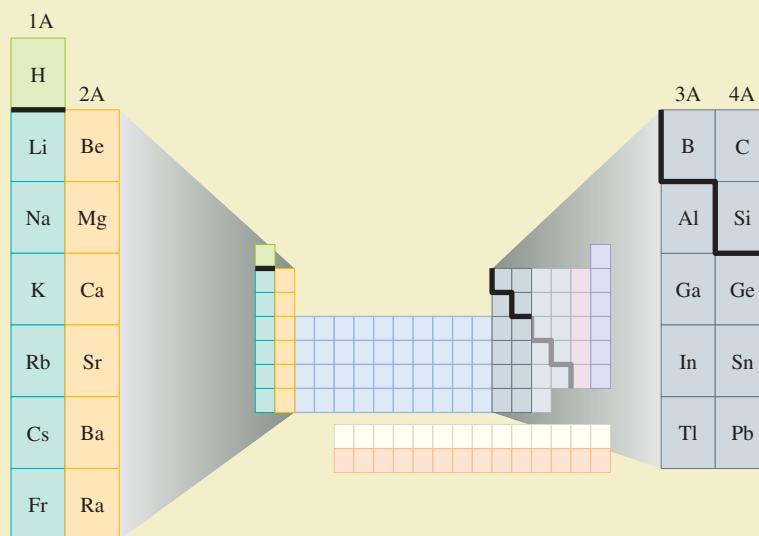
o far in this book we have covered the major principles and explored the most important models of chemistry. In particular, we have seen that the chemical properties of the elements can be explained very successfully by the quantum mechanical model of the atom. In fact, the most convincing evidence of that model's validity is its ability to relate the observed periodic properties of the elements to the number of valence electrons in their atoms.

We have learned many properties of the elements and their compounds, but we have not discussed in detail the relationship between the chemical properties of a particular element and its position on the periodic table. In this chapter and the next we will explore the chemical similarities and differences among the elements in the several groups of the periodic table and will try to interpret these data using the quantum mechanical model of the atom. In the process we will illustrate a great variety of chemical properties and further demonstrate the practical importance of chemistry.

19.1 A Survey of the Representative Elements

The traditional form of the periodic table is shown in Fig. 19.1. Recall that the **representative elements**, whose chemical properties are determined by the valence-level *s* and *p* electrons, are designated Groups 1A through 8A. The **transition metals**, in the center of the table, result from the filling of *d* orbitals. The elements that correspond to the filling of the *4f* and *5f* orbitals are listed separately as the **lanthanides** and **actinides**, respectively.

The heavy black line in Fig. 19.1 divides the metals from the nonmetals. Some elements just on either side of this line, such as silicon and germanium, exhibit both metallic and nonmetallic properties and are often called **metalloids** or **semimetals**. The fundamental chemical difference between a metal and a nonmetal is that metals tend to lose their valence electrons to form *cations*, usually with the valence-electron configuration of the noble gas from the preceding period, and nonmetals tend to gain electrons to



		Periodic Table of Elements																			
		1A		2A		Groups 3A-8A															
		Li	Be													B	C	N	O	F	
		Na	Mg													Al	Si	P	S	Cl	Ar
		K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr		
		Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe		
		Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn		
		Fr	Ra	Ac	Rf	Ha	Unh	Uns	Uno	Une	Ds	Rg	Uub	Uut	Uuq	Uup					
Lanthanides																					
Actinides																					
Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu																					
Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr																					

FIGURE 19.1

The periodic table. The elements in the A groups are the representative elements. The elements shown in pink are called *transition metals*. The dark line approximately divides the nonmetals from the metals. The elements that have both metallic and nonmetallic properties (semimetals) are shaded in blue.

Metallic character increases going down a group in the periodic table.

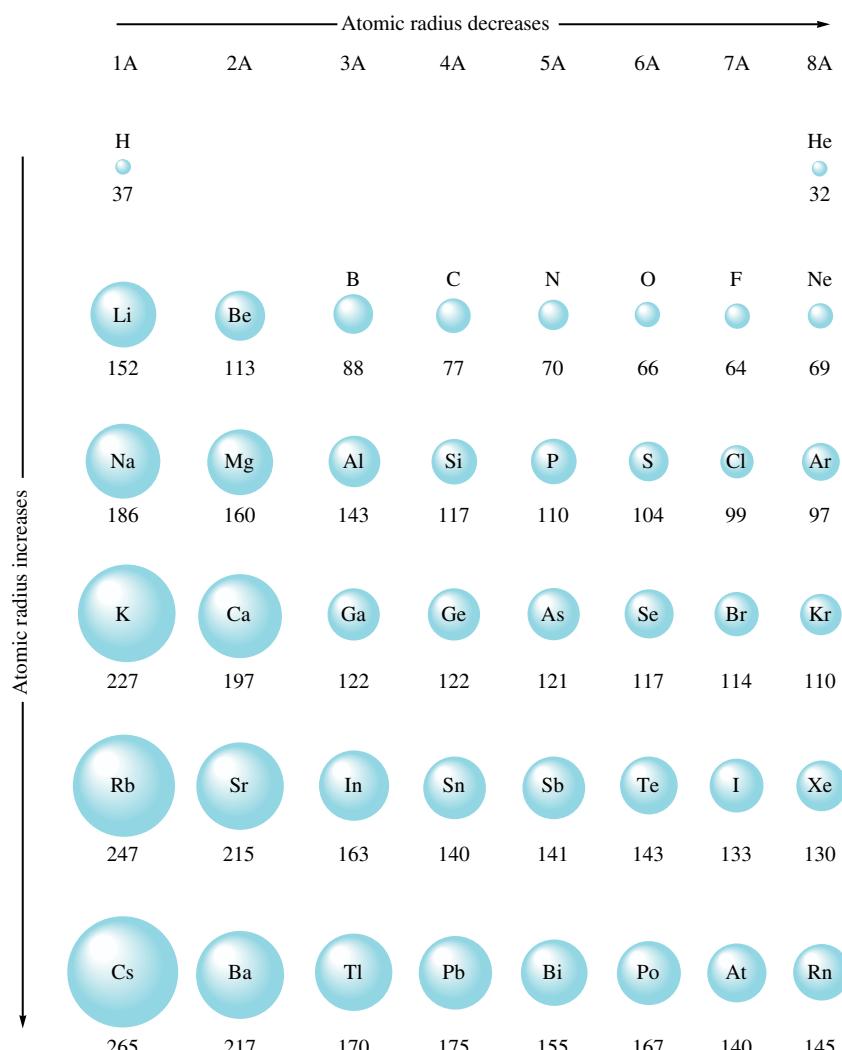
form *anions* that exhibit the electron configuration of the noble gas in the same period. Metallic character is observed to increase going down a given group, which is consistent with the trends in ionization energy, electron affinity, and electronegativity discussed earlier (see Sections 7.13 and 8.2).

Atomic Size and Group Anomalies

Although the chemical properties of the members of a group show many similarities, there are also important differences. In fact, the relatively large increase in atomic radius in going from the first to the second member of a group causes the first element to show properties that are often quite different from the others. Consequently, hydrogen, beryllium, boron, carbon, nitrogen, oxygen, and fluorine all have some properties that distinguish them from the other members of their groups. For example, in Group 1A hydrogen is a nonmetal and lithium is a very active metal. This extreme difference results primarily from the very large difference in the atomic radii of hydrogen and lithium, as shown in Fig. 19.2. The small hydrogen atom has a much greater attraction for electrons than do the larger members of Group 1A and forms covalent bonds with nonmetals; the other members of Group 1A lose their valence electrons to nonmetals to form $1+$ cations in ionic compounds.

This effect of size is also evident in other groups. For example, the oxides of the metals in Group 2A are all quite basic except for the first member of the series; beryllium oxide (BeO) is amphoteric. Recall from Section 14.10 that the basicity of an oxide depends on its ionic character. Ionic oxides contain the O^{2-} ion, which reacts with water to form two OH^- ions. All the oxides of the Group 2A metals are highly ionic except for beryllium oxide, which has considerable covalent character. The small Be^{2+} ion can effectively polarize the electron “cloud” of the O^{2-} ion, producing significant electron sharing. We see the same pattern in Group 3A, where only the small boron atom behaves as a nonmetal, or sometimes as a semimetal, and aluminum and the other members are active metals.

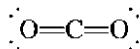
In Group 4A the effect of size is reflected in the dramatic differences between the chemistry of carbon and that of silicon. The chemistry of carbon is dominated by molecules containing chains of $\text{C}-\text{C}$ bonds, but silicon compounds mainly contain $\text{Si}-\text{O}$ bonds rather than $\text{Si}-\text{Si}$ bonds. Carbon forms a wide variety of stable compounds with strong $\text{C}-\text{C}$ single bonds. Silicon also forms compounds with chains of $\text{Si}-\text{Si}$ bonds,

**FIGURE 19.2**

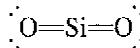
The atomic radii of some atoms in picometers.

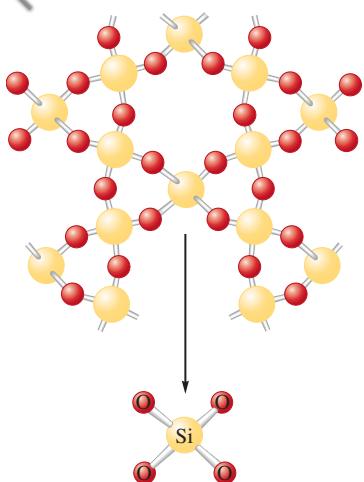
but these compounds are much more reactive than the corresponding carbon compounds. The reasons for the difference in reactivity between the carbon and silicon compounds are quite complex but are likely related to the differences in the sizes of the carbon and silicon atoms.

Carbon and silicon differ markedly in their abilities to form π bonds. As we discussed in Section 9.1, carbon dioxide is composed of discrete CO_2 molecules with the Lewis structure



where the carbon and oxygen atoms achieve the [Ne] configuration by forming π bonds. In contrast, the structure of silica (empirical formula SiO_2) is based on SiO_4 tetrahedra with Si—O—Si bridges, as shown in Fig. 19.3. The silicon 3p valence orbitals do not overlap very effectively with the smaller oxygen 2p orbitals to form π bonds; therefore, discrete SiO_2 molecules with the Lewis structure



**FIGURE 19.3**

The structure of quartz, which has the empirical formula SiO_2 . Note that the structure is based on interlocking SiO_4 tetrahedra, where each oxygen atom is shared by two silicon atoms.

are not stable. Instead, the silicon atoms achieve a noble gas configuration by forming several Si—O single bonds.

The importance of π bonding for the relatively small elements of the second period also explains the different elemental forms of the members of Groups 5A and 6A. For example, elemental nitrogen consists of very stable N_2 molecules with the Lewis structure



Elemental phosphorus forms larger aggregates of atoms, the simplest being the tetrahedral P_4 molecules found in white phosphorus (see Fig. 20.12). Like silicon atoms, the relatively large phosphorus atoms do not form strong π bonds and prefer to achieve a noble gas configuration by forming single bonds to several other phosphorus atoms. In contrast, its very strong π bonds make the N_2 molecule the most stable form of elemental nitrogen. Similarly, in Group 6A the most stable form of elemental oxygen is the O_2 molecule with a double bond, but the larger sulfur atom forms bigger aggregates, such as the cyclic S_8 molecule (see Fig. 20.16), which contains only single bonds.

The relatively large change in size in going from the first to second member of a group also has important consequences for the Group 7A elements. For example, fluorine has a smaller electron affinity than chlorine. This reversal of the expected trend can be attributed to the small fluorine $2p$ orbitals, which result in unusually large electron repulsions. The relative weakness of the bond in the F_2 molecule can be explained in terms of the repulsions among the lone pairs, shown in the Lewis structure:



The small size of the fluorine atoms allows close approach of the lone pairs, which leads to much greater repulsions than are found in the Cl_2 molecule with its much larger atoms.

Abundance and Preparation

Table 19.1 shows the distribution of elements in the earth's crust, oceans, and atmosphere. The major element is, of course, oxygen, which is found in the atmosphere as O_2 , in the oceans in H_2O , and in the earth's crust primarily in silicate and carbonate minerals. The second most abundant element, silicon, is found throughout the earth's crust in the silica and silicate minerals that form the basis of most sand, rocks, and soil. The most abundant metals, aluminum and iron, are found in ores in which they are combined with nonmetals, most commonly oxygen. One notable fact revealed by Table 19.1 is the small incidence of most transition metals. Since many of these relatively rare elements are assuming

TABLE 19.1 Distribution (Mass Percent) of the 18 Most Abundant Elements in the Earth's Crust, Oceans, and Atmosphere

Element	Mass Percent	Element	Mass Percent
Oxygen	49.2	Chlorine	0.19
Silicon	25.7	Phosphorus	0.11
Aluminum	7.50	Manganese	0.09
Iron	4.71	Carbon	0.08
Calcium	3.39	Sulfur	0.06
Sodium	2.63	Barium	0.04
Potassium	2.40	Nitrogen	0.03
Magnesium	1.93	Fluorine	0.03
Hydrogen	0.87	All others	0.49
Titanium	0.58		

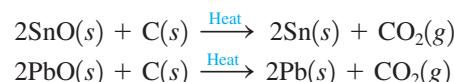
TABLE 19.2 Abundance of Elements in the Human Body

Major Elements	Mass Percent	Trace Elements (in alphabetical order)
Oxygen	65.0	Arsenic
Carbon	18.0	Chromium
Hydrogen	10.0	Cobalt
Nitrogen	3.0	Copper
Calcium	1.4	Fluorine
Phosphorus	1.0	Iodine
Magnesium	0.50	Manganese
Potassium	0.34	Molybdenum
Sulfur	0.26	Nickel
Sodium	0.14	Selenium
Chlorine	0.14	Silicon
Iron	0.004	Vanadium
Zinc	0.003	

increasing importance in our high-technology society, it is possible that the control of transition metal ores may ultimately have more significance for world politics than the control of petroleum supplies.

The distribution of elements in living materials is very different from that found in the earth's crust. Table 19.2 shows the relative abundance of elements in the human body. Oxygen, carbon, hydrogen, and nitrogen form the basis for all biologically important molecules. The other elements, even though they are found in relatively small amounts, are often crucial for life. For example, zinc is found in over 150 different biomolecules in the human body.

Only about one-fourth of the elements occur naturally in the free state. Most are found in a combined state. The *process of obtaining a metal from its ore* is called **metallurgy**. Since the metals in ores are found in the form of cations, the chemistry of metallurgy always involves reduction of the ions to the elemental metal (with an oxidation state of zero). A variety of reducing agents can be used, but carbon is the usual choice because of its wide availability and relatively low cost. As we will see in Chapter 21, carbon is the primary reducing agent in the production of steel. Carbon also can be used to produce tin and lead from their oxides:



Hydrogen gas also can be used as a reducing agent for metal oxides, as in the production of tin:



Electrolysis is often used to reduce the most active metals. In Chapter 17 we considered the electrolytic production of aluminum metal. The alkali metals are also produced by electrolysis, usually of their molten halide salts.

The preparation of nonmetals varies widely. Elemental nitrogen and oxygen are usually obtained from the **liquefaction** of air, which is based on the principle that a real gas cools when it expands. After each expansion, part of the cooler gas is compressed, while the rest is used to carry away the heat of the compression. The compressed gas is then allowed to expand again. This cycle is repeated many times. Eventually, the remaining gas becomes cold enough to form the liquid state. Because liquid nitrogen and liquid oxygen have different boiling points, they can be separated by the distillation of liquid air. Both

Metallurgy is discussed in more detail in Chapter 21.

Carbon is the cheapest and most readily available industrial reducing agent for metallic ions.

The preparation of sulfur and the halogens is discussed in Chapter 20.

Several properties of the alkali metals are given in Table 7.8.

1A
H
Li
Na
K
Rb
Cs
Fr

substances are important industrial chemicals, ranking in the top five in terms of the amounts manufactured in the United States. Hydrogen can be obtained from the electrolysis of water, but more commonly it is obtained from the decomposition of the methane in natural gas. Sulfur is found underground in its elemental form and is recovered using the Frasch process (see Section 20.6). The halogens are obtained by oxidation of the anions from halide salts (see Section 20.7).

19.2 The Group 1A Elements

The Group 1A elements with their ns^1 valence-electron configurations are all very active metals (they lose their valence electrons very readily), except for hydrogen, which behaves as a nonmetal. We will discuss the chemistry of hydrogen in the next section. Many of the properties of the **alkali metals** have been described previously (see Section 7.13). The sources and methods of preparation of pure alkali metals are given in Table 19.3. The ionization energies, standard reduction potentials, ionic radii, and melting points for the alkali metals are listed in Table 19.4. Lepidolite, shown in Fig. 19.4, contains several pure alkali metals.

In Section 7.13 we saw that the alkali metals all react vigorously with water to release hydrogen gas:



We will reconsider this process briefly because it illustrates several important concepts. Based on the ionization energies, we might expect lithium to be the weakest of the alkali metals as a reducing agent in water. However, the standard reduction potentials indicate that it is the strongest. This reversal results mainly from the very large energy of hydration

TABLE 19.3 Sources and Methods of Preparation of the Pure Alkali Metals

Element	Source	Method of Preparation
Lithium	Silicate minerals such as spodumene, $LiAl(Si_2O_6)$	Electrolysis of molten LiCl
Sodium	NaCl	Electrolysis of molten NaCl
Potassium	KCl	Electrolysis of molten KCl
Rubidium	Impurity in lepidolite, $Li_2(F,OH)_2Al_2(SiO_3)_3$	Reduction of RbOH with Mg and H_2
Cesium	Pollucite ($Cs_4Al_4Si_9O_{26} \cdot H_2O$) and an impurity in lepidolite (see Fig. 19.4)	Reduction of CsOH with Mg and H_2

TABLE 19.4 Selected Physical Properties of the Alkali Metals

Element	Ionization Energy (kJ/mol)	Standard Reduction Potential (V) for $M^+ + e^- \rightarrow M$	Radius of M^+ (pm)	Melting Point (°C)
Lithium	520	-3.05	60	180
Sodium	495	-2.71	95	98
Potassium	419	-2.92	133	63
Rubidium	409	-2.99	148	39
Cesium	382	-3.02	169	29



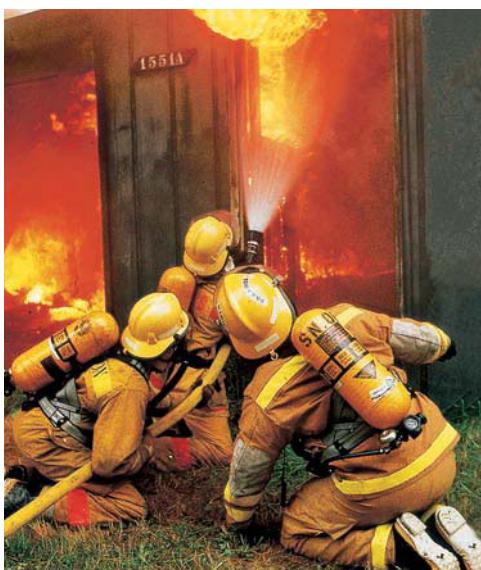
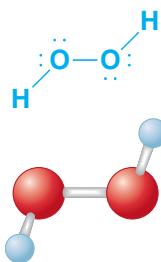
FIGURE 19.4

Lepidolite is composed mainly of lithium, aluminum, silicon, and oxygen, but it also contains significant amounts of rubidium and cesium.



Sodium reacting with water.

Hydrogen peroxide has the Lewis structure

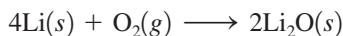


Airpacks are an essential source of oxygen for firefighters.

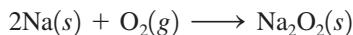
of the small Li^+ ion. Because of its relatively high charge density, the Li^+ ion very effectively attracts water molecules. A large quantity of energy is released in the process, favoring the formation of the Li^+ ion and making lithium a strong reducing agent in aqueous solution.

We also saw in Section 7.13 that lithium, although it is the strongest reducing agent, reacts more slowly with water than does sodium or potassium. From the discussions in Chapters 12 and 16, we know that the *equilibrium position* for a reaction (in this case indicated by the \mathcal{E}° values) is controlled by thermodynamic factors but that the *rate* of a reaction is controlled by kinetic factors. There is *no* direct connection between these factors. Lithium reacts more slowly with water than does sodium or potassium because as a solid it has a higher melting point than either of them. It does not become molten from the heat of reaction with water as sodium and potassium do, and thus it has a smaller area of contact with the water.

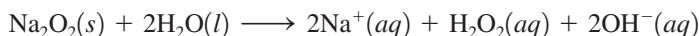
The relative ease with which the alkali metals lose electrons to form M^+ cations means that they react with nonmetals to form ionic compounds. Although we might expect the alkali metals to react with oxygen to form regular oxides of the general formula M_2O , lithium is the only one that does so in the presence of excess oxygen gas:



Sodium forms solid Na_2O if the oxygen supply is limited, but in excess oxygen it forms *sodium peroxide*:

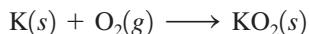


Sodium peroxide contains the basic O_2^{2-} anion and reacts with water to form hydrogen peroxide and hydroxide ions:

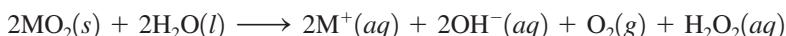


Hydrogen peroxide is a strong oxidizing agent often used as a bleach for hair and as a disinfectant.

Potassium, rubidium, and cesium react with oxygen to produce **superoxides** of the general formula MO_2 , which contains the O_2^- anion. For example, potassium reacts with oxygen as follows:



The superoxides release oxygen gas in reactions with water or carbon dioxide:

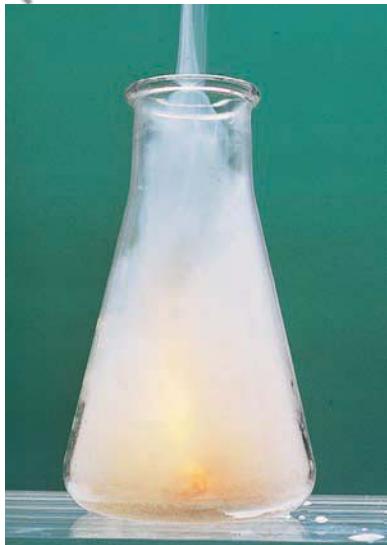


This chemistry makes superoxides very useful in the self-contained breathing apparatuses used by firefighters. These “airpacks” are also used as emergency equipment in labs and production facilities in case toxic fumes are released.

The types of compounds formed by the alkali metals with oxygen are summarized in Table 19.5. Table 19.6 summarizes some important reactions of the alkali metals.

TABLE 19.5 Types of Compounds Formed by the Alkali Metals with Oxygen

General Formula	Name	Examples
M_2O	Oxide	$\text{Li}_2\text{O}, \text{Na}_2\text{O}$
M_2O_2	Peroxide	Na_2O_2
MO_2	Superoxide	$\text{KO}_2, \text{RbO}_2, \text{CsO}_2$



Sodium reacts violently with chlorine.

TABLE 19.6 Selected Reactions of the Alkali Metals

Reaction	Comment
$2M + X_2 \rightarrow 2MX$	X_2 = any halogen molecule
$4Li + O_2 \rightarrow 2Li_2O$	Excess oxygen
$2Na + O_2 \rightarrow Na_2O_2$	
$M + O_2 \rightarrow MO_2$	$M = K, Rb, or Cs$
$2M + S \rightarrow M_2S$	
$6Li + N_2 \rightarrow 2Li_3N$	Li only
$12M + P_4 \rightarrow 4M_3P$	
$2M + H_2 \rightarrow 2MH$	
$2M + 2H_2O \rightarrow 2MOH + H_2$	
$2M + 2H^+ \rightarrow 2M^+ + H_2$	Violent reaction!

The alkali metal ions are very important for the proper functioning of biologic systems, such as nerves and muscles, and Na^+ and K^+ ions are present in all body cells and fluids. In human blood plasma the concentrations are

$$[Na^+] \approx 0.15\text{ M} \quad \text{and} \quad [K^+] \approx 0.005\text{ M}$$

For the fluids *inside* the cells the concentrations are reversed:

$$[Na^+] \approx 0.005\text{ M} \quad \text{and} \quad [K^+] \approx 0.16\text{ M}$$

Since the concentrations are so different inside and outside the cells, an elaborate mechanism is needed to transport Na^+ and K^+ ions through the cell membranes.

Recently, studies have been carried out concerning the role of the Li^+ ion in the human brain, and lithium carbonate has been used extensively in the treatment of manic-depressive patients. The Li^+ ion apparently affects the levels of neurotransmitters, molecules that assist the transmission of messages along the nerve networks. Incorrect concentrations of these molecules can lead to depression or mania.

Sample Exercise 19.1

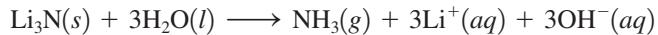
Predicting Reaction Products

Predict the products formed by the following reactants.

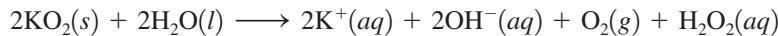
- $Li_3N(s)$ and $H_2O(l)$
- $KO_2(s)$ and $H_2O(l)$

Solution

- Solid Li_3N contains the N^{3-} anion, which has a strong attraction for three H^+ ions to form NH_3 . Thus the reaction is



- Solid KO_2 is a superoxide that characteristically reacts with water to produce O_2 , H_2O_2 , and OH^- :



See Exercises 19.17 and 19.18.

19.3 Hydrogen

Under ordinary conditions of temperature and pressure, hydrogen is a colorless, odorless gas composed of H₂ molecules. Because of its low molar mass and nonpolarity, hydrogen has a very low boiling point (−253°C) and melting point (−260°C). Hydrogen gas is highly flammable, and mixtures of air containing from 18% to 60% hydrogen by volume are explosive. In a common lecture demonstration hydrogen and oxygen gases are bubbled into soapy water. The resulting bubbles can be ignited with a candle on a long stick, giving a loud explosion.

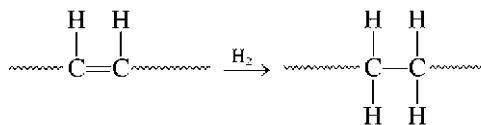
The major industrial source of hydrogen gas is the reaction of methane and water at high temperatures (800–1000°C) and high pressures (10–50 atm) with a metallic catalyst, often nickel:



Large quantities of hydrogen are also formed as a by-product of gasoline production, in which hydrocarbons with high molar masses are broken down (*cracked*) to produce smaller molecules more suitable for use as a motor fuel.

Very pure hydrogen can be produced by electrolysis of water (see Section 17.7), but this method is currently not economically feasible for large-scale production because of the relatively high cost of electricity.

The major industrial use of hydrogen is in the production of ammonia by the Haber process. Large quantities of hydrogen are also used for hydrogenating unsaturated vegetable oils (those containing carbon–carbon double bonds) to produce solid shortenings that are saturated (containing carbon–carbon single bonds):



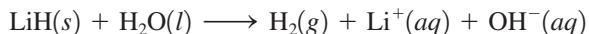
The catalysis of this process was discussed in Section 12.8.

Chemically, hydrogen behaves as a typical nonmetal, forming covalent compounds with other nonmetals and forming salts with very active metals. Binary compounds containing hydrogen are called **hydrides**, of which there are three classes. The **ionic**



(left) Hydrogen gas being used to blow soap bubbles. (right) As the bubbles float upward, they are lighted using a candle on a long pole. The orange flame is due to the heat from the reaction of hydrogen with the oxygen in the air that excites sodium ions in the soap solution.

(or **saltlike**) **hydrides** are formed when hydrogen combines with the most active metals, those from Groups 1A and 2A. Examples are LiH and CaH₂, which can best be characterized as containing hydride ions (H⁻) and metal cations. Because the presence of two electrons in the small 1s orbital produces large electron–electron repulsions and the nucleus has only a 1+ charge, the hydride ion is a strong reducing agent (easily loses electrons). For example, when ionic hydrides are placed in water, a violent reaction takes place. This reaction results in the formation of hydrogen gas, as seen in the equation



Boiling points of covalent hydrides are discussed in Section 10.1.

Covalent hydrides are formed when hydrogen combines with other nonmetals. We have encountered many of these compounds already: HCl, CH₄, NH₃, H₂O, and so on. The most important covalent hydride is water. The polarity of the H₂O molecule leads to many of water's unusual properties. Water has a much higher boiling point than is expected from its molar mass. It has a large heat of vaporization and a large heat capacity, both of which make it a very useful coolant. Water has a higher density as a liquid than as a solid. This is due to the open structure of ice, which results from maximizing the hydrogen bonding (see Fig. 19.5). Because water is an excellent solvent for ionic and polar substances, it provides an effective medium for life processes. In fact, water is one of the few covalent hydrides that is nontoxic to organisms.

The third class of hydrides, the **metallic** (or **interstitial**) **hydrides**, are formed when transition metal crystals are treated with hydrogen gas. The hydrogen molecules dissociate at the metal's surface, and the small hydrogen atoms migrate into the crystal structure to occupy holes, or interstices. These metal–hydrogen mixtures are more like solid solutions than true compounds. Palladium can absorb about 900 times its own volume of hydrogen gas. In fact, hydrogen can be purified by placing it under slight pressure in a vessel containing a thin wall of palladium. The hydrogen diffuses into and through the metal wall, leaving the impurities behind.

Although hydrogen can react with transition metals to form compounds of constant composition, most of the interstitial hydrides have variable compositions (often called *nonstoichiometric compositions*) with formulas such as LaH_{2.76} and VH_{0.56}. The compositions of the nonstoichiometric hydrides vary with the length of exposure of the metal to hydrogen gas and other factors.

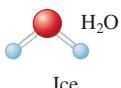
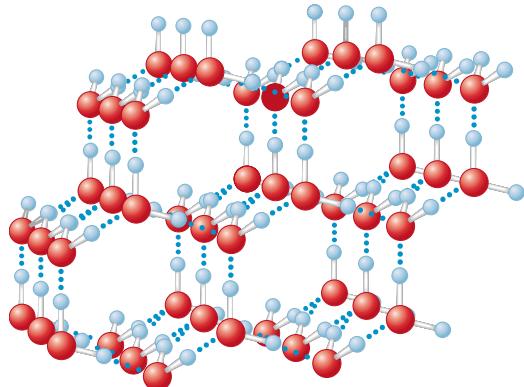


FIGURE 19.5

The structure of ice, showing the hydrogen bonding.

See Section 6.6 for a discussion of the feasibility of using hydrogen gas as a fuel.

When interstitial hydrides are heated, much of the absorbed hydrogen is expelled as hydrogen gas. Because of this behavior, these materials offer possibilities for storing hydrogen for use as a portable fuel. The internal combustion engines in current automobiles can burn hydrogen gas with little modification, but storage of enough hydrogen to provide an acceptable mileage range remains a problem. One possible solution might be to use a fuel tank containing a porous solid that includes a transition metal into which the hydrogen gas could be pumped to form the interstitial hydride. The hydrogen gas could then be released as required by the engine.

19.4 The Group 2A Elements

2A

Be

Mg

Ca

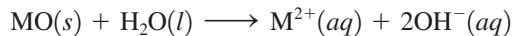
Sr

Ba

Ra

An amphoteric oxide displays both acidic and basic properties.

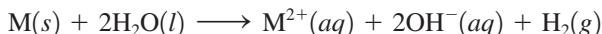
The Group 2A elements (with valence-electron configuration ns^2) are very reactive, losing their two valence electrons to nonmetals to form ionic compounds containing M^{2+} cations. These elements are commonly called the **alkaline earth metals** because of the basicity of their oxides:



Only beryllium oxide (BeO) also shows some acidic properties, such as dissolving in aqueous solutions containing hydroxide ions:



The more active alkaline earth metals react with water as the alkali metals do, producing hydrogen gas:



Calcium, strontium, and barium react vigorously at $25^\circ C$. The less easily oxidized beryllium and magnesium show no observable reaction with water at $25^\circ C$, although magnesium reacts with boiling water. Table 19.7 summarizes various properties, sources, and preparations of the alkaline earth metals.

TABLE 19.7 Selected Physical Properties, Sources, and Methods of Preparation for the Group 2A Elements

Element	Radius of M^{2+} (pm)	Ionization Energy (kJ/mol)		E° (V) for $M^{2+} + 2e^- \rightarrow M$	Source	Method of Preparation
		First	Second			
Beryllium	~30	900	1760	-1.70	Beryl ($Be_3Al_2Si_6O_{18}$)	Electrolysis of molten $BeCl_2$
Magnesium	65	738	1450	-2.37	Magnesite ($MgCO_3$), dolomite ($MgCO_3 \cdot CaCO_3$), carnallite ($MgCl_2 \cdot KCl \cdot 6H_2O$)	Electrolysis of molten $MgCl_2$
Calcium	99	590	1146	-2.76	Various minerals containing $CaCO_3$	Electrolysis of molten $CaCl_2$
Strontium	113	549	1064	-2.89	Celestite ($SrSO_4$), strontianite ($SrCO_3$)	Electrolysis of molten $SrCl_2$
Barium	135	503	965	-2.90	Baryte ($BaSO_4$), witherite ($BaCO_3$)	Electrolysis of molten $BaCl_2$
Radium	140	509	979	-2.92	Pitchblende (1 g of Ra/7 tons of ore)	Electrolysis of molten $RaCl_2$