CHEMISTRY 103 PRINCIPLES OF CHEMISTRY

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SUNY Adirondack Queensbury Campus Chemistry 103: Principles of Chemistry

Remixed and Customized for SUNY Adirondack Queensbury Campus by Carlisle J. E. D'Souza



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This text addresses the basic concepts course of modern chemistry for students with little or no previous preparation. Topics include atomic and molecular structure, stoichiometry, physical states of matter, solutions, acids and bases, and an introduction to organic chemistry (hydrocarbons).

FRONT MATTER

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1: CHEMISTRY AND MEASUREMENTS

The study of chemistry will open your eyes to a fascinating world. Chemical processes are continuously at work all around us. They happen as you cook and eat food, strike a match, shampoo your hair, and even read this page. Chemistry is called the central science because a knowledge of chemical principles is essential for other sciences. You might be surprised at the extent to which chemistry pervades your life.

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1: CHEMISTRY AND MEASUREMENTS

The study of chemistry will open your eyes to a fascinating world. Chemical processes are continuously at work all around us. They happen as you cook and eat food, strike a match, shampoo your hair, and even read this page. Chemistry is called the central science because a knowledge of chemical principles is essential for other sciences. You might be surprised at the extent to which chemistry pervades your life.

1.1: PRELUDE TO CHEMISTRY, MATTER, AND MEASUREMENT

Quantities and measurements are as important in our everyday lives as they are in medicine. The posted speed limits on roads and highways, such as 55 miles per hour (mph), are quantities we might encounter all the time. Both parts of a quantity, the amount (55) and the unit (mph), must be properly communicated to prevent potential problems. In chemistry, as in any technical endeavor, the proper expression of quantities is a necessary fundamental skill.

1.2: WHAT IS CHEMISTRY?

Chemistry is the study of matter—what it consists of, what its properties are, and how it changes. Being able to describe the ingredients in a cake and how they change when the cake is baked is called chemistry. Matter is anything that has mass and takes up space—that is, anything that is physically real.

1.3: MEASUREMENTS

Chemists measure the properties of matter and express these measurements as quantities. A quantity is an amount of something and consists of a number and a unit. The number tells us how many (or how much), and the unit tells us what the scale of measurement is. For example, when a distance is reported as "5 kilometers," we know that the quantity has been expressed in units of kilometers and that the number of kilometers is 5.

1.4: EXPRESSING NUMBERS - SCIENTIFIC NOTATION

Scientific notation is a system for expressing very large or very small numbers in a compact manner. It uses the idea that such numbers can be rewritten as a simple number multiplied by 10 raised to a certain exponent, or power. Scientific notation expressed numbers using powers of 10.

1.5: EXPRESSING NUMBERS - SIGNIFICANT FIGURES

Significant figures properly report the number of measured and estimated digits in a measurement. There are rules for applying significant figures in calculations.

1.6: THE INTERNATIONAL SYSTEM OF UNITS

Recognize the SI base units. Combining prefixes with base units creates new units of larger or smaller sizes.

1.7: CONVERTING UNITS

The ability to convert from one unit to another is an important skill. A unit can be converted to another unit of the same type with a conversion factor.

1.8: CHEMISTRY, MATTER, AND MEASUREMENT (EXERCISES)

These are homework exercises to accompany Chapter 1 of the Ball et al. "The Basics of GOB Chemistry" Textmap.

1.9: CHEMISTRY, MATTER, AND MEASUREMENT (SUMMARY)

To ensure that you understand the material in this chapter, you should review the meanings of the bold terms in the following summary and ask yourself how they relate to the topics in the chapter.



1.1: PRELUDE TO CHEMISTRY, MATTER, AND MEASUREMENT

In April 2003, the US Pharmacopeia, a national organization that establishes quality standards for medications, reported a case in which a physician ordered "morphine [a powerful painkiller] 2–3 mg IV [intravenously] every 2–3 hours for pain." A nurse misread the dose as "23 mg" and thus administered approximately 10 times the proper amount to an 8-year-old boy with a broken leg. The boy stopped breathing but was successfully resuscitated and left the hospital three days later.

Quantities and measurements are as important in our everyday lives as they are in medicine. The posted speed limits on roads and highways, such as 55 miles per hour (mph), are quantities we might encounter all the time. Both parts of a quantity, the amount (55) and the unit (mph), must be properly communicated to prevent potential problems. In chemistry, as in any technical endeavor, the proper expression of quantities is a necessary fundamental skill. As we begin our journey into chemistry, we will learn this skill so that errors—from homework mistakes to traffic tickets to more serious consequences—can be avoided.



1.2: WHAT IS CHEMISTRY?

LEARNING OBJECTIVES

- 1. Define chemistry in relation to other sciences.
- 2. Identify the general steps in the scientific method.

Chemistry is the study of matter—what it consists of, what its properties are, and how it changes. Being able to describe the ingredients in a cake and how they change when the cake is baked is called chemistry. Matter is anything that has mass and takes up space—that is, anything that is physically real. Some things are easily identified as matter—this book, for example. Others are not so obvious. Because we move so easily through air, we sometimes forget that it, too, is matter.

Chemistry is one branch of science. Science is the process by which we learn about the natural universe by observing, testing, and then generating models that explain our observations. Because the physical universe is so vast, there are many different branches of science (Figure 1.2.1). Thus, chemistry is the study of matter, biology is the study of living things, and geology is the study of rocks and the earth. Mathematics is the language of science, and we will use it to communicate some of the ideas of chemistry.



Figure 1.2.1: The Relationships between Some of the Major Branches of Science. Chemistry lies more or less in the middle, which emphasizes its importance to many branches of science.

Although we divide science into different fields, there is much overlap among them. For example, some biologists and chemists work in both fields so much that their work is called biochemistry. Similarly, geology and chemistry overlap in the field called geochemistry. Figure 1.2.1 shows how many of the individual fields of science are related.

There are many other fields of science in addition to the ones listed here.

ALCHEMY

As our understanding of the universe has changed over time, so has the practice of science. Chemistry in its modern form, based on principles that we consider valid today, was developed in the 1600s and 1700s. Before that, the study of matter was known as *alchemy* and was practiced mainly in China, Arabia, Egypt, and Europe.

Alchemy was a somewhat mystical and secretive approach to learning how to manipulate matter. Practitioners, called alchemists, thought that all matter was composed of different proportions of the four basic elements—fire, water, earth, and air—and believed that if you changed the relative proportions of these elements in a substance, you could change the substance. The long-standing attempts to "transmute" common metals into gold represented one goal of alchemy. Alchemy's other major goal was to synthesize the philosopher's stone, a material that could impart long life—even immortality. Alchemists used symbols to represent substances,





Which fields of study are branches of science? Explain.

a. sculpture

b. astronomy

Answer a

Sculpture is not considered a science because it is not a study of some aspect of the natural universe.

Answer b

Astronomy is the study of stars and planets, which are part of the natural universe. Astronomy is therefore a field of science.

Exercise 1.2.1

Which fields of study are branches of science?

a. physiology (the study of the function of an animal's or a plant's body)

- b. geophysics
- c. agriculture
- d. politics

How do scientists work? Generally, they follow a process called the scientific method. The scientific method is an organized procedure for learning answers to questions and making explanations for observations. To find the answer to a question (for example, "Why do birds fly toward Earth's equator during the cold months?"), a scientist goes through the following steps, which are also illustrated in Figure 1.2.2







Figure 1.2.2: The General Steps of the Scientific Method. After an observation is made or a question is identified, a hypothesis is made and experiments are designed to test the hypothesis.

The steps may not be as clear-cut in real life as described here, but most scientific work follows this general outline.

- 1. **Propose a hypothesis.** A scientist generates a testable idea, or hypothesis, to try to answer a question or explain an observation about how the natural universe works. Some people use the word *theory* in place of hypothesis, but the word hypothesis is the proper word in science. For scientific applications, the word theory is a general statement that describes a large set of observations and data. A theory represents the highest level of scientific understanding.
- 2. **Test the hypothesis.** A scientist evaluates the hypothesis by devising and carrying out experiments to test it. If the hypothesis passes the test, it may be a proper answer to the question. If the hypothesis does not pass the test, it may not be a good answer.
- 3. **Refine the hypothesis if necessary.** Depending on the results of experiments, a scientist may want to modify the hypothesis and then test it again. Sometimes the results show the original hypothesis to be completely wrong, in which case a scientist will have to devise a new hypothesis.

Not all scientific investigations are simple enough to be separated into these three discrete steps. But these steps represent the general method by which scientists learn about our natural universe.

CONCEPT REVIEW EXERCISES

- 1. Define science and chemistry.
- 2. Name the steps of the scientific method.

ANSWERS

- 1. Science is a process by which we learn about the natural universe by observing, testing, and then generating models that explain our observations. Chemistry is the study of matter.
- 2. propose a hypothesis, test the hypothesis, and refine the hypothesis if necessary

KEY TAKEAWAYS

- Chemistry is the study of matter and how it behaves.
- The scientific method is the general process by which we learn about the natural universe.



1.3: MEASUREMENTS

LEARNING OBJECTIVES

• To express quantities properly, using a number and a unit.

A coffee maker's instructions tell you to fill the coffeepot with 4 cups of water and use 3 scoops of coffee. When you follow these instructions, you are measuring. When you visit a doctor's office, a nurse checks your temperature, height, weight, and perhaps blood pressure (Figure 1.3.1); the nurse is also measuring.



Figure 1.3.1: Measuring Blood Pressure. A nurse or a doctor measuring a patient's blood pressure is taking a measurement. Figure used with permission from Wikipedia.

Chemists measure the properties of matter using a variety of devices or measuring tools, many of which are similar to those used in everyday life. Rulers are used to measure length, balances (scales) are used to measure mass (weight), and graduated cylinders or pipettes are used to measure volume. Measurements made using these devices are expressed as quantities. A **quantity** is an amount of something and consists of a **number** and a **unit**. The number tells us how many (or how much), and the unit tells us what the scale of measurement is. For example, when a distance is reported as "5 kilometers," we know that the quantity has been expressed in units of kilometers and that the number of kilometers is 5. If you ask a friend how far he or she walks from home to school, and the friend answers "12" without specifying a unit, you do not know whether your friend walks—for example, 12 miles, 12 kilometers, 12 furlongs, or 12 yards. <u>Both a number and a unit must be included to express a quantity properly</u>.

To understand chemistry, we need a clear understanding of the units chemists work with and the rules they follow for expressing numbers. The next two sections examine the rules for expressing numbers.

Example 1.3.1

Identify the *number* and the *unit* in each quantity.

- a. one dozen eggs
- b. 2.54 centimeters
- c. a box of pencils
- d. 88 meters per second

Answer a

The number is one, and the unit is dozen eggs.

Answer b

The number is 2.54, and the unit is centimeter.

Answer c

The number 1 is implied because the quantity is only *a* box. The unit is box of pencils.

Answer d

The number is 88, and the unit is meters per second. Note that in this case the unit is actually a combination of two units: meters and seconds.



$\mathsf{Exercise} \ 1.3.1$

Identify the *number* and the *unit* in each quantity.

- a. 99 bottles of soda
- b. 60 miles per hour
- c. 32 fluid ounces
- d. 98.6 degrees Fahrenheit

CONCEPT REVIEW EXERCISE

1. What are the two necessary parts of a quantity?

ANSWER

1. The two necessary parts are the number and the unit.

KEY TAKEAWAY

• Identify a quantity properly with a number and a unit.



1.4: EXPRESSING NUMBERS - SCIENTIFIC NOTATION

LEARNING OBJECTIVES

• To express a large number or a small number in scientific notation.

The instructions for making a pot of coffee specified 3 scoops (rather than 12,000 grounds) because any measurement is expressed more efficiently with units that are appropriate in size. In science, however, we often must deal with quantities that are extremely small or incredibly large. For example, you may have 5,000,000,000,000 red blood cells in a liter of blood, and the diameter of an iron atom is 0.000000014 inches. Numbers with many zeros can be cumbersome to work with, so scientists use scientific notation.

Scientific notation is a system for expressing very large or very small numbers in a compact manner. It uses the idea that such numbers can be rewritten as a simple number multiplied by 10 raised to a certain exponent, or power.

Let us look first at very large numbers. Suppose a spacecraft is 1,500,000 miles from Mars. The number 1,500,000 can be thought of as follows:

$$1.5 \times \underbrace{1,000,000}_{10 \times 10 \times 10 \times 10 \times 10 \times 10} = 1.5 \times 10^{6}$$

That is, 1,500,000 is the same as 1.5 times 1 million, and 1 million is $10 \times 10 \times 10 \times 10 \times 10 \times 10 \times 10$ (which is read as "ten to the sixth power"). Therefore, 1,500,000 can be rewritten as 1.5 times 10^6 , or 1.5×10^6 . The distance of the spacecraft from Mars can therefore be expressed as 1.5×10^6 miles.

Recall that:

- $10^0 = 1$
- $10^1 = 10$
- $10^2 = 100$
- $10^3 = 1,000$
- 10⁴ = 10,000
- and so forth

The standard convention for expressing numbers in scientific notation is to write a single *nonzero* first digit, a decimal point, and the rest of the digits, excluding any trailing zeros (see rules for significant figures in the next section for more details on what to exclude). This number is followed by a multiplication sign and then by 10 raised to the power necessary to reproduce the original number. For example, although 1,500,000 can also be written as $15. \times 10^5$ (which would be $15. \times 100,000$), the convention is to have only one digit before the decimal point. How do we know to what power 10 is raised? The power is the number of places you have to move the decimal point to the *left* to place it after the <u>first digit</u>, so that the number being multiplied is *between 1 and 10*:

$1,500,000 = 1.5 \times 10^{6}$

Example 1.4.1: Scientific Notation

Express each number in scientific notation.

- a. 67,000,000,000
- b. 1,689

c. 12.6

Answer a

Moving the decimal point 10 places to the left gives 6.7×10^{10} .

Answer b

The decimal point is assumed to be at the end of the number, so moving it three places to the left gives 1.689×10^3 .

Answer c

In this case, we need to move the decimal point only one place to the left, which yields 1.26×10^1 .

EXERCISE 1.4.1

Express each number in scientific notation.



a. 1,492

b. 102,000,000

c. 101,325

To change **scientific notation** to **standard notation**, we reverse the process, moving the decimal point to the right. Add zeros to the end of the number being converted, if necessary, to produce a number of the proper magnitude.

Example 1.4.2

Express each number in standard, or nonscientific, notation.

a. 5.27×10^4

b. 1.0008 × 10⁶

Answer a

Rather than moving the decimal to the left, we move it four places to the right and add zeros to give 52,700.

Answer b

Moving the decimal six places to the right gives 1,000,800.

Exercise 1.4.2

Express each number in scientific notation.

- a. 0.000006567
- b. -0.0004004
- c. 0.00000000000123

Answer a

Move the decimal point six places to the right to get 6.567×10^{-6} .

Answer b

Move the decimal point four places to the right to get -4.004×10^{-4} . The negative sign on the number itself does not affect how we apply the rules of scientific notation.

Answer c

Move the decimal point 13 places to the right to get 1.23×10^{-13} .

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Express each number in standard, or nonscientific, notation.

a. $6.98 imes 10^8$

b. $1.005 imes 10^2$

We can also use scientific notation to express numbers whose magnitudes are less than 1. For example, the quantity 0.006 centimeters can be expressed as follows:

$$6 \times \underbrace{\frac{1}{1,000}}_{10} = 6 \times 10^{-3}$$

$$\underbrace{\frac{1}{10} \times \frac{1}{10} \times \frac{1}{10}}_{10^{-3}}$$

That is, 0.006 centimeters is the same as 6 *divided by* one thousand, which is the same as 6 *divided* by 10 x 10 x 10 or 6 *times* 10^{-3} (which is read as "ten to the negative third power"). Therefore, 0.006 centimeters can be rewritten as 6 times 10^{-3} , or 6 × 10^{-3} centimeters.

Recall that:

- $10^{-1} = 1/10$
- $10^{-2} = 1/100$
- $10^{-3} = 1/1,000$
- $10^{-4} = 1/10,000$



- $10^{-5} = 1/100,000$
- and so forth

We use a negative number as the power to indicate the number of places we have to move the decimal point to the right to make it follow the first nonzero digit so that the number is between 1 and 10. This is illustrated as follows:

 $0.006 = 6 \times 10^{-3}$

In scientific notation, numbers with a magnitude greater than one have a positive power, while numbers with a magnitude less than one have a negative power.

Exercise 1.4.3

Express each number in scientific notation. a. 0.000355 b. 0.314159

As with numbers with positive powers of 10, when changing from scientific notation to standard notation, we reverse the process.

Example 1.4.4				
Express each number in standard notation.				
a. 6.22×10^{-2}				
b. 9.9×10^{-9}				
Answer a				
0.0622				
Answer b				
0.000000099				
Exercise 1.4.4				
Express each number in standard notation.				
a. 9.98×10^{-5}				
b. 5.109×10^{-8}				

Although calculators can show 8 to 10 digits in their display windows, that is not always enough when working with very large or very small numbers. For this reason, many calculators are designed to handle scientific notation. The method for entering scientific notation differs for each calculator model, so take the time to learn how to do it properly on your calculator, *asking your instructor for assistance if necessary*. If you do not learn to enter scientific notation into your calculator properly, you will not get the correct final answer when performing a calculation.

CONCEPT REVIEW EXERCISES

- 1. Why it is easier to use scientific notation to express very large or very small numbers?
- 2. What is the relationship between how many places a decimal point moves and the power of 10 used in changing a conventional number into scientific notation?

ANSWERS

- 1. Scientific notation is more convenient than listing a large number of zeros.
- 2. The number of places the decimal point moves equals the power of 10—positive if the decimal point moves to the left and negative if the decimal point moves to the right.

KEY TAKEAWAY

• Large or small numbers are expressed in scientific notation, which use powers of 10.



1.5: EXPRESSING NUMBERS - SIGNIFICANT FIGURES

LEARNING OBJECTIVES

- Understand the importance of significant figures in measured numbers.
- Identify the number of significant figures in a reported value.
- Use significant figures correctly in arithmetical operations.

Scientists have established certain conventions for communicating the degree of **precision** of a measurement, which is dependent on the measuring device used. Imagine, for example, that you are using a meterstick to measure the width of a table. The centimeters (cm) marked on the meterstick, tell you how many *centimeters* wide the table is. Many metersticks also have markings for millimeters (mm), so we can measure the table to the nearest *millimeter*. Most metersticks do not have any smaller (or more precise) markings indicated, so you cannot report the measured width of the table any more precise than to the nearest millimeter. However, you can *estimate* one past the smallest marking, in this case the millimeter, to the next decimal place in the measurement (Figure 1.5.1).



Figure 1.5.1: Measuring an Object to the Correct Number of Digits. How many digits should be reported for the length of this object? The concept of **significant figures** takes this limitation into account. The significant figures of a measured quantity are defined as all the digits known with *certainty* (those indicated by the markings on the measuring device) *and* the first uncertain, or estimated, digit (one digit past the smallest marking on the measuring device). It makes no sense to report any digits after the first uncertain one, so it is the last digit reported in a measurement. Zeros are used when needed to place the significant figures in their correct positions. Thus, zeros are sometimes counted as significant figures but are sometimes only used as placeholders.

"Sig figs" is a common abbreviation for significant figures.

Consider the earlier example of measuring the width of a table with a meterstick. If the table is measured and reported as being 1,357 mm wide, the number 1,357 has four significant figures. The 1 (thousands place), the 3 (hundreds place), and the 5 (tens place) are certain; the 7 (ones place) is assumed to have been estimated. It would make no sense to report such a measurement as 1,357.0 (five Sig Figs) or 1,357.00 (six Sig Figs) because that would suggest the measuring device was able to determine the width to the nearest tenth or hundredth of a millimeter, when in fact it shows only tens of millimeters and therefore the ones place was estimated.

On the other hand, if a measurement is reported as 150 mm, the 1 (hundreds) and the 5 (tens) are known to be significant, but how do we know whether the zero is or is not significant? The measuring device could have had marks indicating every 100 mm or marks indicating every 10 mm. How can you determine if the zero is significant (the estimated digit), or if the 5 is significant and the zero a value placeholder?

The **rules** for deciding which digits in a measurement are significant are as follows:

- 1. All nonzero digits are significant. In 1,357 mm, all the digits are significant.
- 2. Sandwiched (or embedded) zeros, those between significant digits, are significant. Thus, 405 g has four significant figures.
- 3. *Leading zeros*, which are zeros at the beginning of a decimal number less than 1, are not significant. In 0.000458 mL, the first four digits are leading zeros and are not significant. The zeros serve only to put the digits 4, 5, and 8 in the correct decimal positions. This number has three significant figures.
- 4. *Trailing zeros*, which are zeros at the end of a number, are significant only if the number has a decimal point. Thus, in 1,500 m, the two trailing zeros are not significant because the number is written without a decimal point; the number has two significant figures. However, in 1,500.00 m, all six digits are significant because the number has a decimal point.

Example 1.5.1

How many significant figures does each number have?

a. 6,798,000



- b. 6,000,798 c. 6,000,798.00
- d. 0.0006798

Answer a

four (by rules 1 and 4)

Answer b

seven (by rules 1 and 2)

Answer c

nine (by rules 1, 2, and 4)

Answer d

four (by rules 1 and 3)

Exercise 1.5.1

How many significant figures does each number have? a. 2.1828 b. 0.005505 c. 55,050

d. 5

e. 500

COMBINING NUMBERS

It is important to be aware of significant figures when you are mathematically manipulating numbers. For example, dividing 125 by 307 on a calculator gives 0.4071661238... to an infinite number of digits. But do the digits in this answer have any practical meaning, especially when you are starting with numbers that have only three significant figures each? It should make sense that the final calculated number can be no more precise than the original numbers used in the calculation. When performing mathematical operations, there are two rules for limiting the number of significant figures in an answer—one rule is for addition and subtraction, and one rule is for multiplication and division.

For addition or subtraction, the rule is to stack all the numbers with their decimal points aligned and then limit (round to) the answer's significant figures to the rightmost column for which all the numbers have significant figures. Consider the following:

56.789 + 102.2 + 1,300.099 = 1,459.088 ↓ Limit to this column

The arrow points to the rightmost column in which all the numbers have significant figures—in this case, the tenths place. Therefore, we will limit our final answer to the tenths place. Is our final answer therefore 1,459.0? No, because when we drop digits from the end of a number, we also have to round the number. Notice that the first dropped digit, in the hundredths place, is 8. This suggests that the answer is actually closer to 1,459.1 than it is to 1,459.0, so we need to round up to 1,459.1. The standard rules for rounding numbers are simple: If the first dropped digit is 5 or higher, round up. If the first dropped digit is lower than 5, do not round up.

For multiplication or division, the rule is to count the number of significant figures in each number being multiplied or divided and then limit the significant figures in the answer to the lowest count. An example is as follows:

$$\underbrace{38.65 \times 105.93}_{4 \text{ sig figs}} = \underbrace{4,094.1945}_{7 \text{ reduce to 4 sig figs}}$$

The final answer, limited to four significant figures, is 4,094. The first digit dropped is 1, so we do not round up.

Scientific notation provides a way of communicating significant figures without ambiguity. You simply include all the significant figures in the leading number. For example, the number 450 has two significant figures and would be written in scientific notation as



 4.5×10^2 , whereas 450.0 has four significant figures and would be written as 4.500×10^2 . In scientific notation, all reported digits are significant.

Example 1.5.2

Write the answer for each expression using scientific notation with the appropriate number of significant figures.

- a. 23.096 × 90.300
- b. 125 × 9.000
- c. 1,027 + 610 + 363.06

Answer a

The calculator answer is 2,085.5688, but we need to round it to five significant figures. Because the first digit to be dropped (in the hundredths place) is greater than 5, we round up to 2,085.6, which in scientific notation is 2.0856×10^3 .

Answer b

The calculator gives 1,125 as the answer, but we limit it to three significant figures and convert into scientific notation: 1.13×10^3 .

Answer c

The calculator gives 2,000.06 as the answer, but because 610 has its farthest-right significant figure in the tens column, our answer must be limited to the tens position: 2.0×10^3 .

Exercise 1.5.2

Write the answer for each expression using scientific notation with the appropriate number of significant figures.

- a. 217 ÷ 903
- b. 13.77 + 908.226 + 515
- c. 255.0 99
- d. 0.00666 × 321

Remember that calculators do not understand significant figures. *You* are the one who must apply the rules of significant figures to a result from your calculator.

CONCEPT REVIEW EXERCISES

- 1. Explain why the concept of significant figures is important in scientific measurements.
- 2. State the rules for determining the significant figures in a measurement.
- 3. When do you round a number up, and when do you not round a number up?

ANSWERS

- 1. Significant figures represent all the known digits of a measurement plus the first estimated one. It gives information about how precise the measuring device and measurement is.
- 2. All nonzero digits are significant; zeros between nonzero digits are significant; zeros at the end of a nondecimal number or the beginning of a decimal number are not significant; zeros at the end of a decimal number are significant.
- 3. Round up only if the first digit dropped is 5 or higher.

KEY TAKEAWAYS

- Significant figures properly report the number of measured and estimated digits in a measurement.
- There are rules for applying significant figures in calculations.



1.6: THE INTERNATIONAL SYSTEM OF UNITS

LEARNING OBJECTIVES

• To recognize the SI base units and explain the system of prefixes used with them.

People who live in the United States measure weight in pounds, height in feet and inches, and a car's speed in miles per hour. In contrast, chemistry and other branches of science use the International System of Units (also known as **SI** after *Système Internationale d'Unités*), which was established so that scientists around the world could communicate efficiently with each other. Many countries have also adopted SI units for everyday use as well. The United States is one of the few countries that has not.

BASE SI UNITS

Base (or basic) units, are the fundamental units of SI. There are seven base units, which are listed in Table 1.6.1, Chemistry uses five of the base units: the mole for amount, the kilogram for mass, the meter for length, the second for time, and the kelvin for temperature. The degree Celsius (°C) is also commonly used for temperature. The numerical relationship between kelvins and degrees Celsius is as follows:

$$K = C + 273$$
 (1.6.1)

Property	Unit	Abbreviation
length	meter	m
mass	kilogram	kg
time	second	S
amount	mole	mol
temperature	kelvin	K
electrical current	ampere	amp
luminous intensity	candela	cd

Table 1.6.1: The Seven Base SI Units

The United States uses the English (sometimes called Imperial) system of units for many quantities. Inches, feet, miles, gallons, pounds, and so forth, are all units connected with the English system of units. There have been many mistakes due to the improper conversion of units between the SI and English systems.

The size of each base unit is defined by international convention. For example, the *kilogram* is defined as the quantity of mass of a special metal cylinder kept in a vault in France (Figure 1.6.1). The other base units have similar definitions and standards. The sizes of the base units are not always convenient for all measurements. For example, a meter is a rather large unit for describing the width of something as narrow as human hair. Instead of reporting the diameter of hair as 0.00012 m or as 1.2×10^{-4} m using scientific notation as discussed in section 1.4, SI also provides a series of **prefixes** that can be attached to the units, creating units that are larger or smaller by powers of 10.



Figure 1.6.1: The Kilogram. The standard for the kilogram is a platinum-iridium cylinder kept in a special vault in France. Source: Photo reproduced by permission of the Bureau International des Poids et Mesures, who retain full internationally protected copyright. Common prefixes and their multiplicative factors are listed in Table 1.6.2 (Perhaps you have already noticed that the base unit *kilogram* is a combination of a prefix, kilo- meaning 1,000 ×, and a unit of mass, the gram.) Some prefixes create a multiple of the



original unit: 1 kilogram equals 1,000 grams, and 1 megameter equals 1,000,000 meters. Other prefixes create a fraction of the original unit. Thus, 1 centimeter equals 1/100 of a meter, 1 millimeter equals 1/1,000 of a meter, 1 microgram equals 1/1,000,000 of a gram, and so forth.

Table 1.6.2: Prefixes Used with SI Units			
Prefix	Abbreviation	Multiplicative Factor	Multiplicative Factor in Scientific Notation
giga-	G	1,000,000,000 ×	$10^9 \times$
mega-	М	1,000,000 ×	$10^6 \times$
kilo-	k	1,000 ×	$10^3 \times$
deca-	D	10 ×	$10^1 \times$
deci-	d	1/10 ×	$10^{-1} \times$
centi-	С	1/100 ×	$10^{-2} \times$
milli-	m	1/1,000 ×	$10^{-3} \times$
micro-	μ*	1/1,000,000 ×	$10^{-6} \times$
nano-	n	1/1,000,000,000 ×	$10^{-9} \times$
	*The letter u is the Greek lowercase letter for m and is called "mu," which is pronounced "myoo."		

Both SI units and prefixes have abbreviations, and the combination of a prefix abbreviation with a base unit abbreviation gives the abbreviation for the modified unit. For example, kg is the abbreviation for kilogram. We will be using these abbreviations throughout this book.

WHAT IS THE DIFFERENCE BETWEEN "MASS" AND "WEIGHT"?

The mass of a body is a measure of its inertial property or how much matter it contains. The weight of a body is a measure of the force exerted on it by gravity or the force needed to support it. Gravity on earth gives a body a downward acceleration of about 9.8 m/s². In common parlance, weight is often used as a synonym for mass in weights and measures. For instance, the verb "to weigh" means "to determine the mass of" or "to have a mass of." The incorrect use of weight in place of mass should be phased out, and the term mass used when mass is meant. The SI unit of mass is the kilogram (kg). In science and technology, the weight of a body in a particular reference frame is defined as the force that gives the body an acceleration equal to the local acceleration of free fall in that reference frame. Thus, the SI unit of the quantity weight defined in this way (force) is the newton (N).

DERIVED SI UNITS

Derived units are combinations of SI base units. Units can be multiplied and divided, just as numbers can be multiplied and divided. For example, the area of a square having a side of 2 cm is 2 cm \times 2 cm, or 4 cm² (read as "four centimeters squared" or "four square centimeters"). Notice that we have squared a length unit, the centimeter, to get a derived unit for area, the square centimeter.

Volume is an important quantity that uses a derived unit. **Volume** is the amount of space that a given substance occupies and is defined geometrically as length × width × height. Each distance can be expressed using the meter unit, so volume has the derived unit m × m × m, or m³ (read as "meters cubed" or "cubic meters"). A cubic meter is a rather large volume, so scientists typically express volumes in terms of 1/1,000 of a cubic meter. This unit has its own name—the liter (L). A liter is a little larger than 1 US quart in volume. (Table 1.6.3 gives approximate equivalents for some of the units used in chemistry.)

Table 1.6.3: Approximate Equivalents to Some SI Units $1 \text{ m} \approx 39.36 \text{ in.} \approx 3.28 \text{ ft} \approx 1.09 \text{ yd}$

1 cm ≈ 2.54 in.
$1 \text{ km} \approx 0.62 \text{ mi}$
1 kg ≈ 2.20 lb
$1 \text{ lb} \approx 454 \text{ g}$
$1 \text{ L} \approx 1.06 \text{ qt}$
$1 \text{ qt} \approx 0.946 \text{ L}$

As shown in Figure 1.6.2 a liter is also 1,000 cm³. By definition, there are 1,000 mL in 1 L, so 1 milliliter and 1 cubic centimeter represent the same volume.

$$1 mL = 1 cm^3$$
 (1.6.2)





Figure 1.6.2: Units of Volume. A liter (L) is defined as a cube 10 cm (1/10th of a meter) on a side. A milliliter (mL), 1/1,000th of a liter, is equal to 1 cubic centimeter.

Example 1.6.1

Give the abbreviation for each unit and define the abbreviation in terms of the base unit.

a. kiloliter

- b. microsecond
- c. decimeter
- d. nanogram

Answer a

The abbreviation for a kiloliter is kL. Because kilo means "1,000 ×," 1 kL equals 1,000 L.

Answer b

The abbreviation for microsecond is µs. Micro implies 1/1,000,000th of a unit, so 1 µs equals 0.000001 s.

Answer c

The abbreviation for decimeter is dm. Deci means 1/10th, so 1 dm equals 0.1 m.

Answer d

The abbreviation for nanogram is ng and equals 0.00000001 g.

Exercise 1.6.1

Give the abbreviation for each unit and define the abbreviation in terms of the base unit.

- a. kilometer
- b. milligram
- c. nanosecond
- d. centiliter

Energy, another important quantity in chemistry, is the ability to perform work, such as moving a box of books from one side of a room to the other side. It has a derived unit of kg•m²/s². (The dot between the kg and m units implies the units are multiplied together.) Because this combination is cumbersome, this collection of units is redefined as a **joule** (J). An older unit of energy, but likely more familiar to you, the calorie (cal), is also widely used. There are 4.184 J in 1 cal. Energy changes occur during all chemical processes and will be discussed in a later chapter.

TO YOUR HEALTH: ENERGY AND FOOD

The food in our diet provides the energy our bodies need to function properly. The energy contained in food could be expressed in joules or calories, which are the conventional units for energy, but the food industry prefers to use the kilocalorie and refers to it as the Calorie (with a capital C). The average daily energy requirement of an adult is about 2,000–2,500 Calories, which is 2,000,000–2,500,000 calories (with a lowercase c).

If we expend the same amount of energy that our food provides, our body weight remains stable. If we ingest more Calories from food than we expend, however, our bodies store the extra energy in high-energy-density compounds, such as fat, and we gain weight. On the other hand, if we expend more energy than we ingest, we lose weight. Other factors affect our weight as well—genetic, metabolic, behavioral, environmental, cultural factors—but dietary habits are among the most important.



In 2008 the US Centers for Disease Control and Prevention issued a report stating that 73% of Americans were either overweight or obese. More alarmingly, the report also noted that 19% of children aged 6–11 and 18% of adolescents aged 12–19 were overweight —numbers that had tripled over the preceding two decades. Two major reasons for this increase are excessive calorie consumption (especially in the form of high-fat foods) and reduced physical activity. Partly because of that report, many restaurants and food companies are working to reduce the amounts of fat in foods and provide consumers with more healthy food options.

Density is defined as the mass of an object divided by its volume; it describes the amount of matter contained in a given amount of space.

density =
$$\frac{\text{mass}}{\text{volume}}$$
 (1.6.3)

Thus, the units of density are the units of mass divided by the units of volume: g/cm³ or g/mL (for solids and liquids), g/L (for gases), kg/m³, and so forth. For example, the density of water is about 1.00 g/cm³, while the density of mercury is 13.6 g/mL. (Remember that 1 mL equals 1 cm³.) Mercury is over 13 times as dense as water, meaning that it contains over 13 times the amount of matter in the same amount of space. The density of air at room temperature is about 1.3 g/L.

Example 1.6.2: Density of Bone

What is the density of a section of bone if a 25.3 cm³ sample has a mass of 27.8 g?

SOLUTION

Because density is defined as the mass of an object divided by its volume, we can set up the following relationship:

$$ext{density} = rac{mass}{volume} \ = rac{27.8 \ g}{25.3 \ cm^3} \ = 1.10 \ g/cm^3$$

Note that we have limited our final answer to three significant figures.

Exercise 1.6.2: Density of Oxygen

What is the density of oxygen gas if a 15.0 L sample has a mass of 21.7 g?

CONCEPT REVIEW EXERCISES

- 1. What is the difference between a base unit and a derived unit? Give two examples of each type of unit.
- 2. Do units follow the same mathematical rules as numbers do? Give an example to support your answer.

ANSWERS

1. Base units are the seven fundamental units of SI; derived units are constructed by making combinations of the base units; base units: kilograms and meters (answers will vary); derived units: grams per milliliter and joules (answers will vary).

2. yes; $mL \times \frac{g}{mL} = g~~(\text{answers will vary})$

KEY TAKEAWAYS

- Recognize the SI base units and derived units.
- Combining prefixes with base units creates new units of larger or smaller sizes.



1.7: CONVERTING UNITS

LEARNING OBJECTIVES

• To convert a value reported in one unit to a corresponding value in a different unit.

The ability to convert from one unit to another is an important skill. For example, a nurse with 50 mg aspirin tablets who must administer 0.2 g of aspirin to a patient needs to know that 0.2 g equals 200 mg, so 4 tablets are needed. Fortunately, there is a simple way to convert from one unit to another.

CONVERSION FACTORS

If you learned the SI units and prefixes described, then you know that 1 cm is 1/100th of a meter.

$$1 \text{ cm} = \frac{1}{100} \text{ m}$$
 (1.7.1)

or

$$100 \text{ cm} = 1 \text{ m}$$
 (1.7.2)

Suppose we divide both sides of the equation by 1 m (both the number *and* the unit):

$$\frac{100 \text{ cm}}{1 \text{ m}} = \frac{1 \text{ m}}{1 \text{ m}} \tag{1.7.3}$$

As long as we perform the same operation on both sides of the equals sign, the expression remains an equality. Look at the right side of the equation; it now has the same quantity in the numerator (the top) as it has in the denominator (the bottom). Any fraction that has the same quantity in the numerator has a value of 1:

same quantity
$$< \frac{100 \text{ cm}}{1 \text{ m}} = 1$$

We know that 100 cm *is* 1 m, so we have the same quantity on the top and the bottom of our fraction, although it is expressed in different units. A fraction that has equivalent quantities in the numerator and the denominator but expressed in *different units* is called a **conversion factor**.

Here is a simple example. How many centimeters are there in 3.55 m? Perhaps you can determine the answer in your head. If there are 100 cm in every meter, then 3.55 m equals 355 cm. To solve the problem more formally with a conversion factor, we first write the quantity we are given, 3.55 m. Then we multiply this quantity by a conversion factor, which is the same as multiplying it by 1. We can write 1 as $\frac{100 \text{ cm}}{1 \text{ m}}$ and multiply:

$$3.55 \text{ m} \times \frac{100 \text{ cm}}{1 \text{ m}}$$
 (1.7.4)

The 3.55 m can be thought of as a fraction with a 1 in the denominator. Because m, the abbreviation for meters, occurs in both the numerator *and* the denominator of our expression, they cancel out:

$$\frac{3.55 \text{ yr}}{1} \times \frac{100 \text{ cm}}{1 \text{ yr}}$$
(1.7.5)

The final step is to perform the calculation that remains once the units have been canceled:

$$\frac{3.55}{1} \times \frac{100 \text{ cm}}{1} = 355 \text{ cm}$$
(1.7.6)

In the final answer, we omit the 1 in the denominator. Thus, by a more formal procedure, we find that 3.55 m equals 355 cm. A generalized description of this process is as follows:

$$quantity (in old units) \times conversion factor = quantity (in new units)$$

You may be wondering why we use a seemingly complicated procedure for a straightforward conversion. In later studies, the conversion problems you will encounter *will not always be so simple*. If you can master the technique of applying conversion factors, you will be able to solve a large variety of problems.



In the previous example (Equation 1.7.6), we used the fraction $\frac{100 \text{ cm}}{1 \text{ m}}$ as a conversion factor. Does the conversion factor $\frac{1 \text{ m}}{100 \text{ cm}}$ also equal 1? Yes, it does; it has the same quantity in the numerator as in the denominator (except that they are expressed in different units). Why did we not use *that* conversion factor? If we had used the second conversion factor, the original unit would not have canceled, and the result would have been meaningless. Here is what we would have gotten:

$$3.55 \text{ m} \times \frac{1 \text{ m}}{100 \text{ cm}} = 0.0355 \frac{\text{m}^2}{\text{cm}}$$
 (1.7.7)

For the answer to be meaningful, we have to *construct the conversion factor in a form that causes the original unit to cancel out*. Figure 1.7.1 shows a concept map for constructing a proper conversion.



Figure 1.7.1: A Concept Map for Conversions. This is how you construct a conversion factor to convert from one unit to another.

SIGNIFICANT FIGURES IN CONVERSIONS

How do conversion factors affect the determination of significant figures? Numbers in conversion factors based on prefix changes, such as kilograms to grams, are *not* considered in the determination of significant figures in a calculation because the numbers in such conversion factors are exact. **Exact numbers** are *defined* or *counted* numbers, not measured numbers, and can be considered as having an infinite number of significant figures. (In other words, 1 kg is exactly 1,000 g, by the definition of kilo-.) Counted numbers are also exact. If there are 16 students in a classroom, the number 16 is exact. In contrast, conversion factors that come from measurements (such as density, as we will see shortly) or are approximations have a limited number of significant figures and should be considered in determining the significant figures of the final answer.

Example 1.7.1

- a. The average volume of blood in an adult male is 4.7 L. What is this volume in milliliters?
- b. A hummingbird can flap its wings once in 18 ms. How many seconds are in 18 ms?

SOLUTION

a. We start with what we are given, 4.7 L. We want to change the unit from liters to milliliters. There are 1,000 mL in 1 L. From this relationship, we can construct two conversion factors:

$$\frac{1 \text{ L}}{1,000 \text{ mL}}$$
 or $\frac{1,000 \text{ mL}}{1 \text{ L}}$

We use the conversion factor that will cancel out the original unit, liters, and introduce the unit we are converting to, which is milliliters. The conversion factor that does this is the one on the right.

Because the numbers in the conversion factor are exact, we do not consider them when determining the number of significant figures in the final answer. Thus, we report two significant figures in the final answer.

b. We can construct two conversion factors from the relationships between milliseconds and seconds:

$$\frac{1,000 \text{ ms}}{1 \text{ s}}$$
 or $\frac{1 \text{ s}}{1,000 \text{ ms}}$

To convert 18 ms to seconds, we choose the conversion factor that will cancel out milliseconds and introduce seconds. The conversion factor on the right is the appropriate one. We set up the conversion as follows:

18
$$\text{ms} \times \frac{1 \text{ s}}{1,000 \text{ ms}} = 0.018 \text{ s}$$



The conversion factor's numerical values do not affect our determination of the number of significant figures in the final answer.

EXERCISE 1.7.1

Perform each conversion.

a. 101,000 ns to seconds

b. 32.08 kg to grams

CONVERSION FACTORS FROM DIFFERENT UNITS

Conversion factors can also be constructed for converting between different kinds of units. For example, density can be used to convert between the mass and the volume of a substance. Consider mercury, which is a liquid at room temperature and has a density of 13.6 g/mL. The density tells us that 13.6 g of mercury have a volume of 1 mL. We can write that relationship as follows:

13.6 g mercury = 1 mL mercury

This relationship can be used to construct two conversion factors:

$$\frac{13.6 \text{ g}}{1 \text{ mL}} \text{ and } \frac{1 \text{ mL}}{13.6 \text{ g}}$$
(1.7.8)

Which one do we use? It depends, as usual, on the units we need to cancel and introduce. For example, suppose we want to know the mass of 16 mL of mercury. We would use the conversion factor that has milliliters on the bottom (so that the milliliter unit cancels) and grams on top so that our final answer has a unit of mass:

$$\begin{array}{c} 16 \hspace{0.2cm} \text{ps} \not \hspace{0.2cm} \times \frac{13.6 \hspace{0.2cm} \text{g}}{1 \hspace{0.2cm} \text{ps} \not \hspace{0.2cm} } \\ \approx 220 \hspace{0.2cm} \text{g} \end{array} \\ \approx 220 \hspace{0.2cm} \text{g} \end{array}$$

In the last step, we limit our final answer to two significant figures because the volume quantity has only two significant figures; the 1 in the volume unit is considered an exact number, so it does not affect the number of significant figures. The other conversion factor would be useful if we were given a mass and asked to find volume, as the following example illustrates.

Density can be used as a conversion factor between mass and volume.

Example 1.7.2: Mercury Thermometer

A mercury thermometer for measuring a patient's temperature contains 0.750 g of mercury. What is the volume of this mass of mercury?

SOLUTION

Because we are starting with grams, we want to use the conversion factor that has grams in the denominator. The gram unit will cancel algebraically, and milliliters will be introduced in the numerator.

$$\begin{array}{ll} 0.750 \hspace{0.2cm} \not \hspace{0.2cm} \not \hspace{0.2cm} \times \frac{1 \hspace{0.2cm} \mathrm{mL}}{13.6 \hspace{0.2cm} \not \hspace{0.2cm} \not \hspace{0.2cm}} \\ \approx 0.0551 \hspace{0.2cm} \mathrm{mL} \end{array}$$

We have limited the final answer to three significant figures.

Exercise 1.7.2

What is the volume of 100.0 g of air if its density is 1.3 g/L?

LOOKING CLOSER: DENSITY AND THE BODY

The densities of many components and products of the body have a bearing on our health.

Bones. Bone density is important because bone tissue of lower-than-normal density is mechanically weaker and susceptible to breaking. The density of bone is, in part, related to the amount of calcium in one's diet; people who have a diet deficient in calcium, which is an important component of bones, tend to have weaker bones. Dietary supplements or adding dairy products to the diet seems to help strengthen bones. As a group, women experience a decrease in bone density as they age. It has been estimated that fully half of women over age 50 suffer from excessive bone loss, a condition known as osteoporosis. Exact bone densities vary



within the body, but for a healthy 30-year-old female, it is about 0.95–1.05 g/cm³. Osteoporosis is diagnosed if the bone density is below 0.6–0.7 g/cm³.

Urine. The density of urine can be affected by a variety of medical conditions. Sufferers of diabetes produce an abnormally large volume of urine with a relatively low density. In another form of diabetes, called diabetes mellitus, there is excess glucose dissolved in the urine, so that the density of urine is abnormally high. The density of urine may also be abnormally high because of excess protein in the urine, which can be caused by congestive heart failure or certain renal (kidney) problems. Thus, a urine density test can provide clues to various kinds of health problems. The density of urine is commonly expressed as a specific gravity, which is a unitless quantity defined as

$\frac{\text{density of some material}}{\text{density of water}}$

Normal values for the specific gravity of urine range from 1.002 to 1.028.

Body Fat. The overall density of the body is one indicator of a person's total body fat. Fat is less dense than muscle and other tissues, so as it accumulates, the overall density of the body decreases. Measurements of a person's weight and volume provide the overall body density, which can then be correlated to the percentage of body fat. (The body's volume can be measured by immersion in a large tank of water. The amount of water displaced is equal to the volume of the body.)

PROBLEM SOLVING WITH MULTIPLE CONVERSIONS

Sometimes you will have to perform more than one conversion to obtain the desired unit. For example, suppose you want to convert 54.7 km into millimeters. You can either memorize the relationship between kilometers and millimeters, or you can do the conversion in two steps. Most people prefer to convert in steps.

To do a stepwise conversion, we first convert the given amount to the base unit. In this example, the base unit is meters. We know that there are 1,000 m in 1 km:

54.7 km
$$\times \frac{1,000 \text{ m}}{1 \text{ km}} = 54,700 \text{ m}$$

Then we take the result (54,700 m) and convert it to millimeters, remembering that there are 1,000 mm for every 1 m:

We have expressed the final answer in scientific notation.

As a shortcut, both steps in the conversion can be combined into a single, multistep expression:

54.7 kpm ×
$$\frac{1,000 \text{ ppr}}{1 \text{ kpm}}$$
 × $\frac{1,000 \text{ mm}}{1 \text{ ppr}}$ = 54,700,000 mm
= 5.47 × 10⁷ mm

Either method—one step at a time or all the steps together—is acceptable. If you do all the steps together, the restriction for the proper number of significant figures should be done after the last step. As long as the math is performed correctly, you should get the same answer no matter which method you use.

Example 1.7.3

Convert 58.2 ms to megaseconds in one multistep calculation.

SOLUTION

First, convert the given unit to the base unit—in this case, seconds—and then convert seconds to the final unit, megaseconds:

58.2
$$ms' \times \frac{js'}{1,000 ms'} \times \frac{1 \text{ Ms}}{1,000,000 s'} = 0.000000582 \text{ Ms}$$

$$= 5.82 imes 10^{-8} \ {
m mS}$$

Neither conversion factor affects the number of significant figures in the final answer.



Exercise 1.7.3

Convert 43.007 ng to kilograms in one multistep calculation.

CAREER FOCUS: PHARMACIST

A pharmacist dispenses drugs that have been prescribed by a doctor. Although that may sound straightforward, pharmacists in the United States must hold a doctorate in pharmacy and be licensed by the state in which they work. Most pharmacy programs require four years of education in a specialty pharmacy school.

Pharmacists must know a lot of chemistry and biology so they can understand the effects that drugs (which are chemicals, after all) have on the body. Pharmacists can advise physicians on the selection, dosage, interactions, and side effects of drugs. They can also advise patients on the proper use of their medications, including when and how to take specific drugs properly. Pharmacists can be found in drugstores, hospitals, and other medical facilities.

Curiously, an outdated name for pharmacist is *chemist*, which was used when pharmacists formerly did a lot of drug preparation, or *compounding*. In modern times, pharmacists rarely compound their own drugs, but their knowledge of the sciences, including chemistry, helps them provide valuable services in support of everyone's health.

KEY TAKEAWAY

• A unit can be converted to another unit of the same type with a conversion factor.

CONCEPT REVIEW EXERCISES

- 1. How do you determine which quantity in a conversion factor goes in the denominator of the fraction?
- 2. State the guidelines for determining significant figures when using a conversion factor.
- 3. Write a concept map (a plan) for how you would convert 1.0×10^{12} *nano*liters (nL) to *kilo*liters (kL).

ANSWERS

- 1. The unit you want to cancel from the numerator goes in the denominator of the conversion factor.
- 2. Exact numbers that appear in many conversion factors do not affect the number of significant figures; otherwise, the normal rules of multiplication and division for significant figures apply.



1.8: CHEMISTRY, MATTER, AND MEASUREMENT (EXERCISES)

These are homework exercises to accompany Chapter 1 of the Ball et al. "The Basics of GOB Chemistry" Textmap.

1.1: WHAT IS CHEMISTRY?

EXERCISES

- 1. Based on what you know, which fields are branches of science?
 - a. meteorology (the study of weather)
 - b. astrophysics (the physics of planets and stars)
 - c. economics (the study of money and monetary systems)
 - d. astrology (the prediction of human events based on planetary and star positions)
 - e. political science (the study of politics)
- 2. Based on what you know, which fields are a branches of science?
 - a. history (the study of past events)
 - b. ornithology (the study of birds)
 - c. paleontology (the study of fossils)
 - d. zoology (the study of animals)
 - e. phrenology (using the shape of the head to determine personal characteristics)
- 3. Which of the following are examples of matter?
 - a. a baby
 - b. an idea
 - c. the Empire State Building
 - d. an emotion
 - e. the air
 - f. Alpha Centauri, the closest known star (excluding the sun) to our solar system
- 4. Which of the following are examples of matter?
 - a. your textbook
 - b. brain cells
 - c. love
 - d. a can of soda
 - e. breakfast cereal
- 5. Suggest a name for the science that studies the physics of rocks and the earth.
- 6. Suggest a name for the study of the physics of living organisms.
- 7. Engineering is the practical application of scientific principles and discoveries to develop things that make our lives easier. Is medicine science or engineering? Justify your answer.
- 8. Based on the definition of engineering in Exercise 7, would building a bridge over a river or road be considered science or engineering? Justify your answer.
- 9. When someone says, "I have a theory that excess salt causes high blood pressure," does that person really have a theory? If it is not a theory, what is it?
- 10. When a person says, "My hypothesis is that excess calcium in the diet causes kidney stones," what does the person need to do to determine if the hypothesis is correct?
- 11. Some people argue that many scientists accept many scientific principles on faith. Using what you know about the scientific method, how might you argue against that assertion?
- 12. Most students take multiple English classes in school. Does the study of English use the scientific method?

ANSWERS

- 1. a. science
 - b. science
 - c. not science
 - d. not science
 - e. not science



- 3. a. matter
 - b. not matter
 - c. matter
 - d. not matter
 - e. matter
 - f. matter
- 5. geophysics
- 7. Medicine is probably closer to a field of engineering than a field of science, but this may be arguable. Ask your doctor.
- 9. In scientific terms, this person has a hypothesis.
- 11. Science is based on reproducible facts, not blind belief.

1.2: THE CLASSIFICATION OF MATTER

EXERCISES

- 1. Does each statement refer to a chemical property or a physical property?
 - a. Balsa is a very light wood.
 - b. If held in a flame, magnesium metal burns in air.
 - c. Mercury has a density of 13.6 g/mL.
 - d. Human blood is red.
- 2. Does each statement refer to a chemical property or a physical property?
 - a. The elements sodium and chlorine can combine to make table salt.
 - b. The metal tungsten does not melt until its temperature exceeds 3,000°C.
 - c. The ingestion of ethyl alcohol can lead to disorientation and confusion.
 - d. The boiling point of isopropyl alcohol, which is used to sterilize cuts and scrapes, is lower than the boiling point of water.
- 3. Define *element*. How does it differ from a compound?
- 4. Define *compound*. How does it differ from an element?
- 5. Give two examples of a heterogeneous mixture.
- 6. Give two examples of a homogeneous mixture.
- 7. Identify each substance as an element, a compound, a heterogeneous mixture, or a solution.
 - a. xenon, a substance that cannot be broken down into chemically simpler components
 - b. blood, a substance composed of several types of cells suspended in a salty solution called plasma
 - c. water, a substance composed of hydrogen and oxygen
- 8. Identify each substance as an element, a compound, a heterogeneous mixture, or a solution.
 - a. sugar, a substance composed of carbon, hydrogen, and oxygen
 - b. hydrogen, the simplest chemical substance
 - c. dirt, a combination of rocks and decaying plant matter
- 9. Identify each substance as an element, a compound, a heterogeneous mixture, or a solution.
 - a. air, primarily a mixture of nitrogen and oxygen
 - b. ringer's lactate, a standard fluid used in medicine that contains salt, potassium, and lactate compounds all dissolved in sterile water
 - c. tartaric acid, a substance composed of carbon, hydrogen, and oxygen
- 10. Identify each material as an element, a compound, a heterogeneous mixture, or a solution.
 - a. equal portions of salt and sand placed in a beaker and shaken up
 - b. a combination of beeswax dissolved in liquid hexane
 - c. hydrogen peroxide, a substance composed of hydrogen and oxygen
- 11. What word describes each phase change?
 - a. solid to liquid
 - b. liquid to gas
 - c. solid to gas
- 12. What word describes each phase change?



- a. liquid to solid
- b. gas to liquid
- c. gas to solid

ANSWERS

- 1. a. physical property
 - b. chemical property
 - c. physical property
 - d. physical property
- 3. An element is a substance that cannot be broken down into chemically simpler components. Compounds can be broken down into simpler substances.
- 5. a salt and pepper mix and a bowl of cereal (answers will vary)
- 7. a. element
 - b. heterogeneous mixture
 - c. compound
- 9. a. solution
 - b. solution
 - c. compound
- 11. a. melting or fusion
 - b. boiling or evaporation c. sublimation

1.3: MEASUREMENTS

EXERCISES

- 1. Why are both parts of a quantity important when describing it?
- 2. Why are measurements an important part of any branch of science, such as chemistry?
- 3. You ask a classmate how much homework your chemistry professor assigned. Your classmate answers, "twenty." Is that a proper answer? Why or why not?
- 4. Identify the number and the unit in each quantity.
 - a. five grandchildren
 - b. 16 candles
 - c. four score and seven years
 - d. 40 days and 40 nights
 - e. 12.01 grams
 - f. 9.8 meters per second squared
 - g. 55 miles per hour
 - h. 98.6 degrees Fahrenheit

ANSWERS

- 1. The number states how much, and the unit states of what. Without the number and the unit, a quantity cannot be properly communicated.
- 3. No, it is not a proper answer; you do not know whether the professor meant homework problem number 20 or 20 homework problems.

1.4: EXPRESSING NUMBERS: SCIENTIFIC NOTATION

EXERCISES

- 1. Why is scientific notation useful in expressing numbers?
- 2. What is the relationship between the power and the number of places a decimal point is moved when going from standard to scientific notation?
- 3. Express each number in scientific notation.
 - a. 0.00064



- b. 5,230,000
- c. -56,200
- d. 0.00000000220
- e. 1.0
- 4. Express each number in scientific notation.
 - a. 678
 - b. -1,061
 - c. 0.000560
 - d. 0.0000003003
 - e. 100,000,000
- 5. Express each number in standard form.
 - a. 6.72×10^4 b. 2.088×10^{-4} c. -3×10^6 d. 9.98×10^{-7}
- 6. Express each number in standard form.

a. 9.05×10^5 b. 1.0×10^{-3} c. 6.022×10^{23} d. 8.834×10^{-12}

7. Complete the following table:

Incorrect Scientific Notation	Correct Scientific Notation
$54.7 imes 10^4$	
0.0066×10^3	
$3,078 \times 10^{0}$	
Complete the following table:	

8. Complete the following table:

Incorrect Scientific Notation	Correct Scientific Notation
234.0×10^{1}	
36×10^{-4}	
0.993×10^5	

ANSWERS

- 1. Scientific notation is more convenient than listing a large number of zeros.
- 5. a. 67,200
 - b. 0.0002088 c. -3,000,000 d. 0.000000998

7.	Incorrect Scientific Notation	Correct Scientific Notation
	54.7×10^4	5.47×10^{5}
	0.0066×10^3	$6.6 imes 10^0$
	$3,078 \times 10^{0}$	3.078×10^{3}

1.5: EXPRESSING NUMBERS: SIGNIFICANT FIGURES

EXERCISES

- 1. Define *significant figures*. Why are they important?
- 2. Define the different types of zeros found in a number and explain whether or not they are significant.



3. How many significant figures are in each number?

- a. 140
- b. 0.009830
- c. 15,050
- d. 221,560,000
- e. 5.67 × 10³
- f. 2.9600×10^{-5}

4. How many significant figures are in each number?

a. 1.05 b. 9,500 c. 0.0004505 d. 0.00045050 e. 7.210 $\times 10^{6}$ f. 5.00 $\times 10^{-6}$

5. Round each number to three significant figures.

- a. 34.705
- b. 34,750
- c. 34,570

6. Round each number to four significant figures.

- a. 34,705
- b. 0.0054109
- c. 8.90443 × 10⁸

7. Perform each operation and express the answer to the correct number of significant figures.

a. 467.88 + 23.0 + 1,306 = ? b. 10,075 + 5,822.09 - 34.0 = ? c. 0.00565 + 0.002333 + 0.0991 = ?

8. Perform each operation and express the answer to the correct number of significant figures.

a. 0.9812 + 1.660 + 8.6502 = ? b. 189 + 3,201.8 - 1,100 = ? c. 675.0 - 24 + 1,190 = ?

9. Perform each operation and express the answer to the correct number of significant figures.

a. 439 × 8,767 = ? b. 23.09 ÷ 13.009 = ? c. 1.009 × 876 = ?

10. Perform each operation and express the answer to the correct number of significant figures.

a. 3.00 ÷ 1.9979 = ? b. 2,300 × 185 = ? c. 16.00 × 4.0 = ?

- 11. Use your calculator to solve each equation. Express each answer in proper scientific notation and with the proper number of significant figures. If you do not get the correct answers, you may not be entering scientific notation into your calculator properly, so ask your instructor for assistance.
 - a. $(5.6 \times 10^3) \times (9.04 \times 10^{-7}) = ?$ b. $(8.331 \times 10^{-2}) \times (2.45 \times 10^5) = ?$ c. $983.09 \div (5.390 \times 10^5) = ?$ d. $0.00432 \div (3.9001 \times 10^3) = ?$
- 12. Use your calculator to solve each equation. Express each answer in proper scientific notation and with the proper number of significant figures. If you do not get the correct answers, you may not be entering scientific notation into your calculator properly, so ask your instructor for assistance.

a. $(5.2 \times 10^6) \times (3.33 \times 10^{-2}) = ?$ b. $(7.108 \times 10^3) \times (9.994 \times 10^{-5}) = ?$ c. $(6.022 \times 10^7) \div (1.381 \times 10^{-8}) = ?$



d. $(2.997 \times 10^8) \div (1.58 \times 10^{34}) = ?$

ANSWERS

- 1. Significant figures represent all the known digits plus the first estimated digit of a measurement; they are the only values worth reporting in a measurement.
- 3. a. two
 - b. four
 - c. four
 - d. five
 - e. three
 - f. five
- 5. a. 34,700 b. 34,800
 - c. 34,600
- 7. a. 1,797
 - b. 15,863
 - c. 0.1071
- 9. a. 3,850,000 b. 1.775 c. 884
 - C. 004
- 11. a. 5.1×10^{-3} b. 2.04×10^{4}
 - c. 1.824×10^{-3}
 - d. 1.11×10^{-6}

1.6: THE INTERNATIONAL SYSTEM OF UNITS

- 1. List four base units.
- 2. List four derived units.
- 3. How many meters are in 1 km? How many centimeters are in 1 m?
- 4. How many grams are in 1 Mg? How many microliters are in 1 L?
- 5. Complete the following table:

Unit	Abbreviation
centiliter	
	ms
	cm
	kL
micrometer	
6. Complete the following table:	

Unit	Abbreviation
microliter	
kilosecond	
	dL
	ns
millimeter	

- 7. What are some appropriate units for density?
- 8. A derived unit for velocity, which is the change of position with respect to time, is meters per second (m/s). Give three other derived units for velocity.

ANSWERS

- 1. second, meter, kilogram, and kelvin (answers will vary)
- 3. 1,000; 100



CHEMISTRY

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Unit	Abbreviation
centiliter	cL
millisecond	ms
centimeter	cm
kiloliter	kL
micrometer	μm

7. grams per liter, grams per milliliter, and kilograms per liter (answers will vary)

1.7: CONVERTING UNITS

EXERCISES

- 1. Give the two conversion factors you can construct using each pair of units.
 - a. meters and kilometers
 - b. liters and microliters
 - c. seconds and milliseconds
- 2. Give the two conversion factors you can construct using each pair of units.
 - a. grams and centigrams
 - b. millimeters and meters
 - c. liters and megaliters
- 3. How many meters are in 56.2 km?
- 4. How many seconds are in 209.7 ms?
- 5. How many microliters are in 44.1 L?
- 6. How many megagrams are in 90.532 g?
- 7. Convert 109.6 kg into micrograms. Express your final answer in scientific notation.
- 8. Convert 3.8 \times 10⁵ mm into kilometers. Express your final answer in scientific notation.
- 9. Convert 3.009 \times 10⁻⁵ ML into centiliters. Express your final answer in scientific notation.
- 10. Convert 99.04 dm into micrometers. Express your final answer in scientific notation.
- 11. The density of ethyl alcohol is 0.79 g/mL. What is the mass of 340 mL of ethyl alcohol?
- 12. The density of a certain fraction of crude oil is 1.209 g/mL. What is the mass of 13,500 mL of this fraction?
- 13. The density of ethyl alcohol is 0.79 g/mL. What is the volume of 340 g of ethyl alcohol?
- 14. The density of a certain component of crude oil is 1.209 g/mL. What is the volume of 13,500 g of this component?
- 15. Vitamin C tablets can come in 500 mg tablets. How many of these tablets are needed to obtain 10 g of vitamin C?
- 16. A tablet of penicillin contains 250 mg of the antibacterial drug. A prescription contains 44 tablets. What is the total mass of penicillin in the prescription?

ANSWERS

1. a.
$$\frac{1,000 \text{ m}}{1 \text{ km}}$$
; $\frac{1 \text{ km}}{1,000 \text{ m}}$
b. $\frac{1,000,000 \ \mu\text{L}}{1 \text{ L}}$; $\frac{1 \text{ L}}{1,000,000 \ \mu\text{L}}$
c. $\frac{1,000 \text{ ms}}{1 \text{ s}}$; $\frac{1 \text{ s}}{1,000 \text{ ms}}$
3. 5.62 × 10⁴ m

- 5. $4.41 \times 10^{7} \,\mu L$
- 7. 1.096 × 10^{11} µg
- 9. 3.009×10^3 cL
- 11. 270 g
- 13. 430 mL
- 15. 20 tablets


1.8: CHAPTER SUMMARY

- 1. A sample of urine has a density of 1.105 g/cm³. What is the mass of 0.255 L of this urine?
- 2. The hardest bone in the body is tooth enamel, which has a density of 2.91 g/cm³. What is the volume, in liters, of 75.9 g of tooth enamel?
- 3. Some brands of aspirin have 81 mg of aspirin in each tablet. If a person takes 8 tablets per day, how many grams of aspirin is that person consuming every day?
- 4. The US government has a recommended daily intake (RDI) of 5 μg of vitamin D per day. (The name *recommended daily allowance* was changed to RDI in 1997.) If milk contains 1.2 μg per 8 oz glass, how many ounces of milk are needed to supply the RDI of vitamin D?
- 5. The population of the United States, according to the 2000 census, was 281.4 million people.
 - a. How many significant figures does this number have?
 - b. What is the unit in this quantity?
 - c. Express this quantity in proper scientific notation.
- 6. The United States produces 34,800,000,000 lb of sugar each year, and much of it is exported to other countries.
 - a. How many significant figures does this number have?
 - b. What is the unit in this quantity?
 - c. Express this quantity in proper scientific notation.
- 7. Construct a conversion factor that can convert from one unit to the other in each pair of units.
 - a. from millimeters to kilometers
 - b. from kilograms to micrograms
 - c. from centimeters to micrometers
- 8. Construct a conversion factor that can convert from one unit to the other in each pair of units.
 - a. from kilometers to micrometers
 - b. from decaliters to milliliters
 - c. from megagrams to milligrams
- 9. What is the density of a dextrose solution if 355 mL of the solution has a mass of 406.9 g?
- 10. What is the density of a dental amalgam (an alloy used to fill cavities) if 1.005 kg of the material has a volume of 433 mL? Express your final answer in grams per milliliter.

For Exercises 11–16, see the accompanying table for the relationships between English and SI units.

 $1~m\approx 39.36$ in. $\approx 3.28~ft\approx 1.09~yd$

- 1 cm \approx 2.54 in. 1 km \approx 0.62 mi 1 kg \approx 2.20 lb 1 lb \approx 454 g 1 L \approx 1.06 qt 1 qt \approx 0.946 L
- 11. Approximately how many inches are in 4.76 m?
- 12. Approximately how many liters are in 1 gal, which is exactly 4 qt?
- 13. Approximately how many kilograms are in a person who weighs 170 lb?
- 14. The average distance between Earth and the sun is 9.3×10^7 mi. How many kilometers is that?
- 15. Show mathematically that 1 L equals 1 dm^3 .
- 16. Show mathematically that 1 L equals 1,000 cm³.

- 1. 282 g
- 3. 650 mg
- 5. a. four significant figures
 - b. people c. 2.841 × 10⁸ people



7. a.
$$\frac{1 \text{ km}}{10^6 \text{ mm}}$$

b. $\frac{10^9 \ \mu\text{g}}{1 \text{ kg}}$
c. $\frac{10^4 \ \mu\text{m}}{1 \text{ cm}}$

- 9. 1.15 g/mL
- 11. 187 in.
- 13. 77 kg

15. 1 L = 0.001 m³ ×
$$\left(\frac{1 \text{ dm}}{0.1 \text{ m}}\right)^3 = 1 \text{ dm}^3$$



1.9: CHEMISTRY, MATTER, AND MEASUREMENT (SUMMARY)

To ensure that you understand the material in this chapter, you should review the meanings of the bold terms in the following summary and ask yourself how they relate to the topics in the chapter.

Chemistry is the study of **matter**, which is anything that has mass and takes up space. Chemistry is one branch of **science**, which is the study of the natural universe. Like all branches of science, chemistry relies on the **scientific method**, which is a process of learning about the world around us. In the scientific method, a guess or **hypothesis** is tested through experiment and measurement.

Matter can be described in a number of ways. **Physical properties** describe characteristics of a sample that do not change the chemical identity of the material (size, shape, color, and so on), while **chemical properties** describe how a sample of matter changes its chemical composition. A **substance** is any material that has the same physical and chemical properties throughout. An **element** is a substance that cannot be broken down into chemically simpler components. The smallest chemically identifiable piece of an element is an **atom**. A substance that can be broken down into simpler chemical components is a **compound**. The smallest chemically identifiable piece of a compound is a **molecule**. Two or more substances combine physically to make a **mixture**. If the mixture is composed of discrete regions that maintain their own identity, the mixture is a **heterogeneous mixture**. If the mixture is so thoroughly mixed that the different components are evenly distributed throughout, it is a **homogeneous mixture**. Another name for a homogeneous mixture is a **solution**. Substances can also be described by their **phase**: solid, liquid, or gas.

Scientists learn about the universe by making measurements of **quantities**, which consist of **numbers** (how many) and **units** (of what). The numerical portion of a quantity can be expressed using **scientific notation**, which is based on **powers**, or exponents, of 10. Large numbers have positive powers of 10, while numbers less than 1 have negative powers of 10. The proper reporting of a measurement requires proper use of **significant figures**, which are all the known digits of a measurement plus the first estimated digit. The number of figures to report in the result of a calculation based on measured quantities depends on the numbers of significant figures in those quantities. For addition and subtraction, the number of significant figures is determined by position; for multiplication and division, it is decided by the number of significant figures in the original measured values. Nonsignificant digits are dropped from a final answer in accordance with the rules of **rounding**.

Chemistry uses SI, a system of units based on seven **basic units**. The most important ones for chemistry are the units for length, mass, amount, time, and temperature. Basic units can be combined with numerical prefixes to change the size of the units. They can also be combined with other units to make **derived units**, which are used to express other quantities such as **volume**, **density**, or **energy**. A formal conversion from one unit to another uses a **conversion factor**, which is constructed from the relationship between the two units. Numbers in conversion factors may affect the number of significant figures in a calculated quantity, depending on whether the conversion factor is **exact**. Conversion factors can be applied in separate computations, or several can be used at once in a single, longer computation.



2: MATTER AND ENERGY

Energy is the ability to do work. You can understand what this means by thinking about yourself when you feel "energetic." You feel ready to go—to jump up and get something done. When you have a lot of energy, you can perform a lot of work. By contrast, if you do not feel energetic, you have very little desire to do much of anything. This description is not only applicable to you but also to all physical and chemical processes.

2.1: THE CLASSIFICATION OF MATTER

Matter can be described with both physical properties and chemical properties. Matter can be identified as an element, a compound, or a mixture.

2.2: SOLIDS AND LIQUIDS

Solids and liquids are phases that have their own unique properties.

2.3: PRELUDE TO ENERGY AND CHEMICAL PROCESSES

Metabolism is the collective term for the chemical reactions that occur in cells and provide energy to keep cells alive. Some of the energy from metabolism is in the form of heat, and some animals use this heat to regulate their body temperatures. Such warm-blooded animals are called endotherms. In endotherms, problems with metabolism can lead to fluctuations in body temperature. When humans get sick, for instance, our body temperatures can rise higher than normal; we develop a fever.

2.4: ENERGY AND ITS UNITS

Energy is the ability to do work. Heat is the transfer of energy due to temperature differences. Energy and heat are expressed in units of joules.

2.5: HEAT

Heat transfer is related to temperature change. Heat is equal to the product of the mass, the change in temperature, and a proportionality constant called the specific heat.

2.6: PHASE CHANGES

There is an energy change associated with any phase change. There is an energy change associated with any phase change.

2.7: ENERGY AND CHEMICAL PROCESSES (EXERCISES)

Problems and Solutions to accompany the chapter.

2.8: ENERGY AND CHEMICAL PROCESSES (SUMMARY)

To ensure that you understand the material in this chapter, you should review the meanings of the following bold terms in the following summary and ask yourself how they relate to the topics in the chapter.



2.1: THE CLASSIFICATION OF MATTER

LEARNING OBJECTIVES

- Use physical and chemical properties, including phase, to describe matter.
- Identify a sample of matter as an element, a compound, or a mixture.

Part of understanding matter is being able to describe it. One way chemists describe matter is to assign different kinds of properties to different categories.

PHYSICAL AND CHEMICAL PROPERTIES

The properties that chemists use to describe matter fall into two general categories. **Physical properties** are characteristics that describe matter. They include characteristics such as size, shape, color, and mass. These characteristics can be observed or measured without changing the *identity* of the matter in question. **Chemical properties** are characteristics that describe how matter changes its chemical structure or composition. An example of a chemical property is flammability—a material's ability to burn—because burning (also known as combustion) changes the chemical composition of a material. The observation of chemical properties involves a *chemical change* of the matter in question, resulting in matter with a different *identity* and different physical and chemical properties.

ELEMENTS AND COMPOUNDS

Any sample of matter that has the *same physical and chemical properties throughout* the sample is called a **substance**. There are two types of substances. A substance that cannot be broken down into chemically simpler components is called an **element**. Aluminum, which is used in soda cans and is represented by the symbol Al, is an element. A substance that can be broken down into chemically simpler components (because it consists of more than one element) is called a **compound**. Water is a compound composed of the elements hydrogen and oxygen and is described by the chemical formula, H_2O . Today, there are about 118 elements in the known universe. In contrast, scientists have identified tens of millions of different compounds to date.

Sometimes the word *pure* is used to describe a substance, but this is not absolutely necessary. By definition, any single substance, element or compound is *pure*.

The smallest part of an element that maintains the identity of that element is called an **atom**. Atoms are extremely tiny; to make a line of iron atoms that is 1 inch long, you would need approximately 217 million iron atoms. The smallest part of a compound that maintains the identity of that compound is called a **molecule**. Molecules are composed of two or more different atoms that are attached together and behave as a unit. Scientists usually work with millions and millions of atoms and molecules at a time. When a scientist is working with large numbers of atoms or molecules at a time, the scientist is studying the *macroscopic viewpoint* of the universe. However, scientists can also describe chemical events on the level of individual atoms or molecules, which is referred to as the *microscopic viewpoint*. We will see examples of both macroscopic and microscopic viewpoints throughout this book (Figure 2.1.1).



Figure 2.1.1: How Many Particles Are Needed for a Period in a Sentence? Although we do not notice it from a macroscopic perspective, matter is composed of microscopic particles so tiny that billions of them are needed to make a speck we can see with the naked eye. The \times 25 and \times 400,000,000 indicate the number of times the image is magnified.

MIXTURES

A material composed of two or more substances is a **mixture**. In a mixture, the individual substances maintain their chemical identities. Many mixtures are obvious combinations of two or more substances, such as a mixture of sand and water. Such mixtures are called **heterogeneous mixtures**. In some mixtures, the components are so intimately combined that they act like a single substance (even though they are not). Mixtures with a consistent or uniform composition throughout are called **homogeneous mixtures** (or solutions). For example, when sugar is dissolved in water to form a liquid solution, the individual properties of the components cannot be distinguished. Other examples or homogenous mixtures include solid solutions, like the metal alloy steel, and gaseous solutions, like air which is a mixture of mainly nitrogen and oxygen.



Example 2.1.1

How would a chemist categorize each example of matter?

- a. saltwater
- b. soil
- c. water
- d. oxygen

Answer a

Saltwater acts as if it were a single substance even though it contains two substances—salt and water. Saltwater is a *homogeneous mixture*, or a solution.

Answer b

Soil is composed of small pieces of a variety of materials, so it is a *heterogeneous mixture*.

Answer c

Water is a substance; more specifically, because water is composed of hydrogen and oxygen, it is a compound.

Answer d

Oxygen, a *substance*, is an *element*.

Exercise 2.1.1

How would a chemist categorize each example of matter?

- a. coffee
- b. hydrogen
- c. an egg

PHASES OR PHYSICAL STATES OF MATTER

All matter can be further classified by one of three physical **states** or **phases**, solid, liquid or gas. These three descriptions each imply that the matter has certain physical properties when in these states. A solid has a definite shape and a definite volume. Liquids ordinarily have a definite volume but not a definite shape; they take the shape of their containers. Gases have neither a definite shape nor a definite volume, and they expand to fill their containers. We encounter matter in each phase every day; in fact, we regularly encounter water in all three phases: ice (solid), water (liquid), and steam (gas) (Figure 2.1.2).



Figure 2.1.2: Boiling Water. When liquid water boils to make gaseous water, it undergoes a phase change. Figure used with permission from Wikipedia.

We know from our experience with water that substances can change from one phase to another if the conditions are right. Typically, varying the temperature of a substance (and, less commonly, the pressure exerted on it) can cause a **phase change**, a physical process in which a substance changes from one phase to another (Figure 2.1.2). Phase changes are identified by particular names depending on what phases are involved, as summarized in Table 2.1.1.



Change	Name
solid to liquid	melting, fusion
solid to gas	sublimation
liquid to gas	boiling, evaporation
liquid to solid	solidification, freezing
gas to liquid	condensation
gas to solid	deposition





Figure 2.1.3: The Classification of Matter. Matter can be classified in a variety of ways, depending on its properties.

CONCEPT REVIEW EXERCISES

- 1. Explain the differences between the physical properties of matter and the chemical properties of matter.
- 2. What is the difference between a heterogeneous mixture and a homogeneous mixture? Give an example of each.
- 3. Give at least two examples of a phase change and state the phases involved in each.

ANSWERS

- 1. Physical properties describe the existence of matter, and chemical properties describe how substances change into other substances.
- 2. A heterogeneous mixture is obviously a mixture, such as dirt; a homogeneous mixture behaves like a single substance, such as saltwater.
- 3. solid to liquid (melting) and liquid to gas (boiling) (answers will vary)

KEY TAKEAWAYS



- Matter can be described with both physical properties and chemical properties.
- Matter can be identified as an element, a compound, or a mixture.



2.2: SOLIDS AND LIQUIDS

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FAR	2NING	() _R	1FCT	IVES

• To describe the solid and liquid phases.

Solids and liquids are collectively called *condensed phases* because their particles are in virtual contact. The two states share little else, however.

SOLIDS

In the solid state, the individual particles of a substance are in fixed positions with respect to each other because there is not enough thermal energy to overcome the intermolecular interactions between the particles. As a result, solids have a definite shape and volume. Most solids are hard, but some (like waxes) are relatively soft. Many solids composed of ions can also be quite brittle.



Figure 2.2.1: Crystalline Arrangement of Quartz crystal cluster. Some large crystals look the way they do because of the regular arrangement of atoms (ions) in their crystal structure. Image used with permission from Wikipedia.

Solids usually have their constituent particles arranged in a regular, three-dimensional array of alternating positive and negative ions called a crystal. The effect of this regular arrangement of particles is sometimes visible macroscopically, as shown in Figure 2.2.1. Some solids, especially those composed of large molecules, cannot easily organize their particles in such regular crystals and exist as amorphous (literally, "without form") solids. Glass is one example of an amorphous solid.

LIQUIDS

If the particles of a substance have enough energy to partially overcome intermolecular interactions, then the particles can move about each other while remaining in contact. This describes the liquid state. In a liquid, the particles are still in close contact, so liquids have a definite volume. However, because the particles can move about each other rather freely, a liquid has no definite shape and takes a shape dictated by its container.



Figure 2.2.2: The formation of a spherical droplet of liquid water minimizes the surface area, which is the natural result of surface tension in liquids. Image used with permission from Wikipedia.

GASES

If the particles of a substance have enough energy to completely overcome intermolecular interactions, then the particles can separate from each other and move about randomly in space. Like liquids, gases have no definite shape, but unlike solids and liquids, gases have no definite volume either.





Figure 2.2.3: A Representation of the Solid, Liquid, and Gas States. A solid has definite volume and shape, a liquid has a definite volume but no definite shape, and a gas has neither a definite volume nor shape.

The change from solid to liquid usually does not significantly change the volume of a substance. However, the change from a liquid to a gas significantly increases the volume of a substance, by a factor of 1,000 or more. Figure 2.2.3 shows the differences among solids, liquids, and gases at the molecular level, while Table 2.2.1 lists the different characteristics of these states.

Table $2.2.1$: Characteristics of the Three States of Matter				
Characteristic	Solid	Liquid	Gas	
shape	definite	indefinite	indefinite	
volume	definite	definite	indefinite	
relative intermolecular interaction strength	strong	moderate	weak	
relative particle positions	in contact and fixed in place	in contact but not fixed	not in contact, random positions	
Example 2.2.1 What state or states of matter does each statement, describe? a. This state has a definite volume. b. This state has no definite shape. c. This state allows the individual particles to move about while remaining in contact. SOLUTION a. This statement describes either the liquid state or the solid state. b. This statement describes either the liquid state or the gas state. c. This statement describes the liquid state.				
EXERCISE 2.2.1 What state or states of matter does each sta	tement describe?			
a. This state has individual particles in a fixed position with regard to each other.				

b. This state has individual particles far apart from each other in space.

c. This state has a definite shape.

LOOKING CLOSER: WATER, THE MOST IMPORTANT LIQUID

Earth is the only known body in our solar system that has liquid water existing freely on its surface. That is a good thing because life on Earth would not be possible without the presence of liquid water.

Water has several properties that make it a unique substance among substances. It is an excellent solvent; it dissolves many other substances and allows those substances to react when in solution. In fact, water is sometimes called the *universal solvent* because of this ability. Water has unusually high melting and boiling points (0°C and 100°C, respectively) for such a small molecule. The boiling points for similar-sized molecules, such as methane (BP = -162°C) and ammonia (BP = -33°C), are more than 100° lower. Though a liquid at normal temperatures, water molecules experience a relatively strong intermolecular interaction that allows them to maintain the liquid phase at higher temperatures than expected.



Unlike most substances, the solid form of water is less dense than its liquid form, which allows ice to float on water. In colder weather, lakes and rivers freeze from the top, allowing animals and plants to continue to live underneath. Water also requires an unusually large amount of energy to change temperature. While 100 J of energy will change the temperature of 1 g of Fe by 230°C, this same amount of energy will change the temperature of 1 g of H₂O by only 100°C. Thus, water changes its temperature slowly as heat is added or removed. This has a major impact on weather, as storm systems like hurricanes can be impacted by the amount of heat that ocean water can store.

Water's influence on the world around us is affected by these properties. Isn't it fascinating that such a small molecule can have such a big impact?

KEY TAKEAWAY

• Solids and liquids are phases that have their own unique properties.

CONCEPT REVIEW EXERCISE

1. How do the strengths of intermolecular interactions in solids and liquids differ?

ANSWER

1. Solids have stronger intermolecular interactions than liquids do.

EXERCISES

- 1. What are the general properties of solids?
- 2. What are the general properties of liquids
- 3. What are the general properties of gases?
- 4. What phase or phases have a definite volume? What phase or phases do not have a definite volume?
- 5. Name a common substance that forms a crystal in its solid state.
- 6. Name a common substance that forms an amorphous solid in its solid state.
- 7. Are substances with strong intermolecular interactions likely to be solids at higher or lower temperatures? Explain.
- 8. Are substances with weak intermolecular interactions likely to be liquids at higher or lower temperatures? Explain.
- 9. State two similarities between the solid and liquid states.
- 10. State two differences between the solid and liquid states.
- 11. If individual particles are moving around with respect to each other, a substance may be in either the ______ or _____ state but probably not in the ______ state.
- 12. If individual particles are in contact with each other, a substance may be in either the _____ or _____ state but probably not in the _____ state.

- 1. hard, specific volume and shape, high density, cannot be compressed
- 3. variable volume and shape, low density, compressible
- 5. sodium chloride (answers will vary)
- 7. At higher temperatures, their intermolecular interactions are strong enough to hold the particles in place.
- 9. high density; definite volume
- 11. liquid; gas; solid



2.3: PRELUDE TO ENERGY AND CHEMICAL PROCESSES

Metabolism is the collective term for the chemical reactions that occur in cells and provide energy to keep cells alive. Some of the energy from metabolism is in the form of heat, and some animals use this heat to regulate their body temperatures. Such *warm-blooded* animals are called *endotherms*. In endotherms, problems with metabolism can lead to fluctuations in body temperature. When humans get sick, for instance, our body temperatures can rise higher than normal; we develop a fever. When food is scarce (especially in winter), some endotherms go into a state of controlled decreased metabolism called *hibernation*. During hibernation, the body temperatures of these endotherms actually decrease. In hot weather or when feverish, endotherms will pant or sweat to rid their bodies of excess heat.

Endotherm	Body Temperature (°F)	Body Temperature (°C)
bird	up to 110	up to 43.5
cat	101.5	38.6
dog	102	38.9
horse	100.0	37.8
human	98.6	37.0
pig	102.5	39.2

Ectotherms, sometimes called *cold-blooded* animals, do not use the energy of metabolism to regulate body temperature. Instead, they depend on external energy sources, such as sunlight. Fish, for example, will seek out water of different temperatures to regulate body temperature. The amount of energy available is directly related to the metabolic rate of the animal. When energy is scarce, ectotherms may also hibernate.

The connection between metabolism and body temperature is a reminder that energy and chemical reactions are intimately related. A basic understanding of this relationship is especially important when those chemical reactions occur within our own bodies.



2.4: ENERGY AND ITS UNITS

LEARNING OBJECTIVES

• To define *energy* and *heat*.

Energy is the ability to do work. You can understand what this means by thinking about yourself when you feel "energetic." You feel ready to go—to jump up and get something done. When you have a lot of energy, you can perform a lot of work. By contrast, if you do not feel energetic, you have very little desire to do much of anything. This description is not only applicable to you but also to all physical and chemical processes. The quantity of work that can be done is related to the quantity of energy available to do it.

Energy can be transferred from one object to another if the objects have different temperatures. The transfer of energy due to temperature differences is called heat. For example, if you hold an ice cube in your hand, the ice cube slowly melts as energy in the form of heat is transferred from your hand to the ice. As your hand loses energy, it starts to feel cold.

Because of their interrelationships, energy, work, and heat have the same units. The SI unit of energy, work, and heat is the joule (J). A joule is a tiny amount of energy. For example, it takes about 4 J to warm 1 mL of H_2O by 1°C. Many processes occur with energy changes in thousands of joules, so the kilojoule (kJ) is also common. Another unit of energy, used widely in the health professions and everyday life, is the calorie (cal). The calorie was initially defined as the amount of energy needed to warm 1 g of H_2O by 1°C, but in modern times, the calorie is related directly to the joule, as follows:

1

$$cal = 4.184 J$$
 (2.4.1)

We can use this relationship to convert quantities of energy, work, or heat from one unit to another.

Although the joule is the proper SI unit for energy, we will use the calorie or the kilocalorie (or Calorie) in this chapter because they are widely used by health professionals.

The calorie is used in nutrition to express the energy content of foods. However, because a calorie is a rather small quantity, nutritional energies are usually expressed in kilocalories (kcal), also called Calories (capitalized; Cal). For example, a candy bar may provide 120 Cal (nutritional calories) of energy, which is equal to 120,000 cal. Figure 2.4.1 shows an example. Proteins and carbohydrates supply 4 kcal/g, while fat supplies 9 kcal/g.



Figure 2.4.1: Nutritional Energy. A sample nutrition facts label, with instructions from the U.S. Food and Drug Administration. Image used with permission from Wikipedia.

EXAMPLE 2.4.1 The energy content of a single serving of bread is 70.0 Cal. What is the energy content in calories? In joules?



SOLUTION

This is a simple conversion-factor problem. Using the relationship 1 Cal = 1,000 cal, we can answer the first question with a one-step conversion:

$$70.0 \text{ Cal} imes rac{1,000 \text{ cal}}{1 \text{ Cal}} = 70,000 \text{ cal}$$

Then we convert calories into joules

$$70,000 ext{ cal} imes rac{4.184 ext{ J}}{1 ext{ cal}} = 293,000 ext{ J}$$

and then kilojoules

$$293,000 \text{ J} imes rac{1 \text{ kJ}}{1,000 \text{ J}} = 293 \text{ kJ}$$

The energy content of bread comes mostly from carbohydrates.

Exercise 2.4.1

The energy content of one cup of honey is 1,030 Cal. What is its energy content in calories and joules?

TO YOUR HEALTH: ENERGY EXPENDITURES

Most health professionals agree that exercise is a valuable component of a healthy lifestyle. Exercise not only strengthens the body and develops muscle tone but also expends energy. After obtaining energy from the foods we eat, we need to expend that energy somehow, or our bodies will store it in unhealthy ways (e.g., fat). Like the energy content in food, the energy expenditures of exercise are also reported in kilocalories, usually kilocalories per hour of exercise. These expenditures vary widely, from about 440 kcal/h for walking at a speed of 4 mph to 1,870 kcal/h for mountain biking at 20 mph. Table 2.4.1 lists the energy expenditure for a variety of exercises.

Table 2.4.1: Energy	Expenditure of	a 180-Pound Person during Selected Exercises
		v

Exercise Energy Expended (kcal/h)	
aerobics, low-level	325
basketball	940
bike riding, 20 mph	830
golfing, with cart	220
golfing, carrying clubs	425
jogging, 7.5 mph	950
racquetball	740
skiing, downhill	520
soccer	680
walking upstairs	1,200
yoga	280

Because some forms of exercise use more energy than others, anyone considering a specific exercise regimen should consult with his or her physician first.

SUMMARY

Energy is the ability to do work. Heat is the transfer of energy due to temperature differences. Energy and heat are expressed in units of joules.

CONCEPT REVIEW EXERCISES

- 1. What is the relationship between energy and heat?
- 2. What units are used to express energy and heat?

ANSWERS

- 1. Heat is the exchange of energy from one part of the universe to another. Heat and energy have the same units.
- 2. Joules and calories are the units of energy and heat.

EXERCISES

- 1. Define energy.
- 2. What is heat?



- 3. What is the relationship between a calorie and a joule? Which unit is larger?
- 4. What is the relationship between a calorie and a kilocalorie? Which unit is larger?
- 5. Express 1,265 cal in kilocalories and in joules.
- 6. Express 9,043.3 J in calories and in kilocalories.
- 7. One kilocalorie equals how many kilojoules?
- 8. One kilojoule equals how many kilocalories?
- 9. Many nutrition experts say that an average person needs 2,000 Cal per day from his or her diet. How many joules is this?
- 10. Baby formula typically has 20.0 Cal per ounce. How many ounces of formula should a baby drink per day if the RDI is 850 Cal?

- 1. Energy is the ability to do work.
- 3. 1 cal = 4.184 J; the calorie is larger.
- 5. 1.265 kcal; 5,293 J
- 7. 1 kcal = 4.184 kJ
- 9. $8.4 \times 10^{6} \text{ J}$



2.5: HEAT

LEARNING OBJECTIVES

• To relate heat transfer to temperature change.

Heat is a familiar manifestation of energy. When we touch a hot object, energy flows from the hot object into our fingers, and we perceive that incoming energy as the object being "hot." Conversely, when we hold an ice cube in our palms, energy flows from our hand into the ice cube, and we perceive that loss of energy as "cold." In both cases, the temperature of the object is different from the temperature of our hand, so we can conclude that differences in temperatures are the ultimate cause of heat transfer.

Suppose we consider the transfer of heat from the opposite perspective—namely, what happens to a system that gains or loses heat? Generally, the system's temperature changes. (We will address a few exceptions later.) The greater the original temperature difference, the greater the transfer of heat, and the greater the ultimate temperature change. The relationship between the amount of heat transferred and the temperature change can be written as

heat
$$\propto \Delta T$$
 (2.5.1)

where \propto means "is proportional to" and ΔT is the change in temperature of the system. Any change in a variable is always defined as "the final value minus the initial value" of the variable, so ΔT is $T_{\text{final}} - T_{\text{initial}}$. In addition, the greater the mass of an object, the more heat is needed to change its temperature. We can include a variable representing mass (*m*) to the proportionality as follows:

heat
$$\propto m\Delta T$$
 (2.5.2)

To change this proportionality into an equality, we include a proportionality constant. The proportionality constant is called the specific heat and is commonly symbolized by *c*:

$$heat = mc\Delta T \tag{2.5.3}$$

Every substance has a characteristic specific heat, which is reported in units of cal/g•°C or cal/g•K, depending on the units used to express ΔT . The specific heat of a substance is the amount of energy that must be transferred to or from 1 g of that substance to change its temperature by 1°. Table 2.5.1 lists the specific heats for various materials.

Substance	c (cal/g•°C)
aluminum (Al)	0.215
aluminum oxide (Al ₂ O ₃)	0.305
benzene (C ₆ H ₆)	0.251
copper (Cu)	0.092
ethanol (C_2H_6O)	0.578
hexane (C ₆ H ₁₄)	0.394
hydrogen (H ₂)	3.419
ice [H ₂ O(s)]	0.492
iron (Fe)	0.108
iron(III) oxide (Fe ₂ O ₃)	0.156
mercury (Hg)	0.033
oxygen (O ₂)	0.219
sodium chloride (NaCl)	0.207
steam [H ₂ O(g)]	0.488
water $[H_2O(\ell)]$	1.00

Table 2.5.1: Specific Heats of Selected Substances

The proportionality constant c is sometimes referred to as the specific heat capacity or (incorrectly) the heat capacity.

The *direction* of heat flow is not shown in heat = $mc\Delta T$. If energy goes into an object, the total energy of the object increases, and the values of heat ΔT are positive. If energy is coming out of an object, the total energy of the object decreases, and the values of heat and ΔT are negative.

Example 2.5.1



What quantity of heat is transferred when a 150.0 g block of iron metal is heated from 25.0°C to 73.3°C? What is the direction of heat flow?

SOLUTION

We can use heat = $mc\Delta T$ to determine the amount of heat, but first we need to determine ΔT . Because the final temperature of the iron is 73.3°C and the initial temperature is 25.0°C, ΔT is as follows:

$$egin{aligned} \Delta T = T_{final} - T_{initial} \ &= 73.3^{o}C - 25.0^{o}C \ &= 48.3^{o}C \end{aligned}$$

The mass is given as 150.0 g, and Table 2.5.1 gives the specific heat of iron as 0.108 cal/g•°C. Substitute the known values into heat = $mc\Delta T$ and solve for amount of heat:

$${
m heat} = (150.0~{
m g}) \left(0.108~{{
m cal}\over {
m g}\cdot{}^{\circ}{
m C}}
ight) (48.3^{\circ}{
m C}) = 782~{
m cal}$$

Note how the gram and °C units cancel algebraically, leaving only the calorie unit, which is a unit of heat. Because the temperature of the iron increases, energy (as heat) must be flowing *into* the metal.

Exercise 2.5.1

What quantity of heat is transferred when a 295.5 g block of aluminum metal is cooled from 128.0°C to 22.5°C? What is the direction of heat flow?

Example 2.5.2

A 10.3 g sample of a reddish-brown metal gave off 71.7 cal of heat as its temperature decreased from 97.5°C to 22.0°C. What is the specific heat of the metal? Can you identify the metal from the data in Table 2.5.1?

SOLUTION

The question gives us the heat, the final and initial temperatures, and the mass of the sample. The value of ΔT is as follows:

$$\Delta T = T_{\text{final}} - T_{\text{initial}} = 22.0^{\circ}\text{C} - 97.5^{\circ}\text{C} = -75.5^{\circ}\text{C}$$

If the sample gives off 71.7 cal, it loses energy (as heat), so the value of heat is written as a negative number, -71.7 cal. Substitute the known values into heat = $mc\Delta T$ and solve for *c*:

$$-71.7 \text{ cal} = (10.3 \text{ g})(c)(-75.5^{\circ}\text{C})$$
$$c = \frac{-71.7 \text{ cal}}{(10.3 \text{ g})(-75.5^{\circ}\text{C})}$$
$$c = 0.0923 \text{ cal/g} \cdot ^{\circ}\text{C}$$

This value for specific heat is very close to that given for copper in Table 2.5.1.

Exercise 2.5.2

A 10.7 g crystal of sodium chloride (NaCl) had an initial temperature of 37.0°C. What is the final temperature of the crystal if 147 cal of heat were supplied to it?

SUMMARY

Heat transfer is related to temperature change.

CONCEPT REVIEW EXERCISE

1. Describe the relationship between heat transfer and the temperature change of an object.

ANSWER

1. Heat is equal to the product of the mass, the change in temperature, and a proportionality constant called the specific heat.

EXERCISES

1. A pot of water is set on a hot burner of a stove. What is the direction of heat flow?

2. Some uncooked macaroni is added to a pot of boiling water. What is the direction of heat flow?



- 3. How much energy in calories is required to heat 150 g of H₂O from 0°C to 100°C?
- 4. How much energy in calories is required to heat 125 g of Fe from 25°C to 150°C?
- 5. If 250 cal of heat were added to 43.8 g of Al at 22.5°C, what is the final temperature of the aluminum?
- 6. If 195 cal of heat were added to 33.2 g of Hg at 56.2°C, what is the final temperature of the mercury?
- 7. A sample of copper absorbs 145 cal of energy, and its temperature rises from 37.8°C to 41.7°C. What is the mass of the copper?
- 8. A large, single crystal of sodium chloride absorbs 98.0 cal of heat. If its temperature rises from 22.0°C to 29.7°C, what is the mass of the NaCl crystal?
- 9. If 1.00 g of each substance in Table 7.3 were to absorb 100 cal of heat, which substance would experience the largest temperature change?
- 10. If 1.00 g of each substance in Table 7.3 were to absorb 100 cal of heat, which substance would experience the smallest temperature change?
- 11. Determine the heat capacity of a substance if 23.6 g of the substance gives off 199 cal of heat when its temperature changes from 37.9°C to 20.9°C.
- 12. What is the heat capacity of gold if a 250 g sample needs 133 cal of energy to increase its temperature from 23.0°C to 40.1°C?

- 1. Heat flows into the pot of water.
- 3. 15,000 cal
- 5. 49.0°C
- 7. 404 g
- 9. Mercury would experience the largest temperature change.
- 11. 0.496 cal/g•°C



2.6: PHASE CHANGES

LEARNING OBJECTIVES

• The Learning Objective of this Module is to determine the heat associated with a phase change.

Depending on the surrounding conditions, normal matter usually exists as one of three *phases*: solid, liquid, or gas.

A phase change is a physical process in which a substance goes from one phase to another. Usually the change occurs when adding or removing heat at a particular temperature, known as the melting point or the boiling point of the substance. The melting point is the temperature at which the substance goes from a solid to a liquid (or from a liquid to a solid). The boiling point is the temperature at which a substance goes from a liquid to a gas (or from a gas to a liquid). The nature of the phase change depends on the direction of the heat transfer. Heat going *into* a substance changes it from a solid to a liquid or a liquid to a gas. Removing heat *from* a substance changes a gas to a liquid or a liquid or a solid.

Two key points are worth emphasizing. First, at a substance's melting point or boiling point, two phases can exist simultaneously. Take water (H₂O) as an example. On the Celsius scale, H₂O has a melting point of 0°C and a boiling point of 100°C. At 0°C, both the solid and liquid phases of H₂O can coexist. However, if heat is added, some of the solid H₂O will melt and turn into liquid H₂O. If heat is removed, the opposite happens: some of the liquid H₂O turns into solid H₂O. A similar process can occur at 100°C: adding heat increases the amount of gaseous H₂O, while removing heat increases the amount of liquid H₂O (Figure 2.6.1).



Figure 2.6.1: Heating curve for water. As heat is added to solid water, the temperature increases until it reaches 0 °C, the melting point. At this point, the phase change, added heat goes into changing the state from a solid to liquid. Only when this phase change is complete, the temperature can increase. Image used with permission (CC BY 3.0 Unported; Community College Consortium for Bioscience Credentials).

Water is a good substance to use as an example because many people are already familiar with it. Other substances have melting points and boiling points as well.

Second, as shown in Figure 2.6.1, the temperature of a substance does not change as the substance goes from one phase to another. In other words, phase changes are isothermal (isothermal means "constant temperature"). Again, consider H_2O as an example. Solid water (ice) can exist at 0°C. If heat is added to ice at 0°C, some of the solid changes phase to make liquid, which is also at 0°C. Remember, the solid and liquid phases of H_2O can coexist at 0°C. Only after all of the solid has melted into liquid does the addition of heat change the temperature of the substance.

For each phase change of a substance, there is a characteristic quantity of heat needed to perform the phase change per gram (or per mole) of material. The heat of fusion (ΔH_{fus}) is the amount of heat per gram (or per mole) required for a phase change that occurs at the melting point. The heat of vaporization (ΔH_{vap}) is the amount of heat per gram (or per mole) required for a phase change that occurs at the boiling point. If you know the total number of grams or moles of material, you can use the ΔH_{fus} or the ΔH_{vap} to determine the total heat being transferred for melting or solidification using these expressions:



$$heat = n \times \Delta H_{fus} \tag{2.6.1}$$

where n is the number of moles and ΔH_{fus} is expressed in energy/mole or

$$heat = m \times \Delta H_{fus} \tag{2.6.2}$$

where m is the mass in grams and ΔH_{fus} is expressed in energy/gram.

For the boiling or condensation, use these expressions:

$$ext{heat} = n imes \Delta H_{vap} aga{2.6.3}$$

where *n* is the number of moles) and ΔH_{vap} is expressed in energy/mole or

$$heat = m imes \Delta H_{vap}$$
 (2.6.4)

where *m* is the mass in grams and ΔH_{vap} is expressed in energy/gram.

Remember that a phase change depends on the direction of the heat transfer. If heat transfers in, solids become liquids, and liquids become solids at the melting and boiling points, respectively. If heat transfers out, liquids solidify, and gases condense into liquids. At these points, there are no changes in temperature as reflected in the above equations.

Example 2.6.1

How much heat is necessary to melt 55.8 g of ice (solid H₂O) at 0°C? The heat of fusion of H₂O is 79.9 cal/g.

SOLUTION

We can use the relationship between heat and the heat of fusion (Equation 2.6.1) to determine how many joules of heat are needed to melt this ice:

$$\mathrm{heat} = \mathrm{m} imes \Delta \mathrm{H}_{\mathrm{fus}}$$
 $\mathrm{heat} = (55.8 \ \) \left(rac{79.9 \ \mathrm{cal}}{\ \)}
ight) = 4,460 \ \mathrm{cal}$

Exercise 2.6.1

How much heat is necessary to vaporize 685 g of H₂O at 100°C? The heat of vaporization of H₂O is 540 cal/g.

Table 2.6.1 lists the heats of fusion and vaporization for some common substances. Note the units on these quantities; when you use these values in problem solving, make sure that the other variables in your calculation are expressed in units consistent with the units in the specific heats or the heats of fusion and vaporization.

Table 2.6.1: Heats of Fusion and Vaporization for Selected Substances				
Substance	$\Delta H_{ m fus}$ (cal/g)	$\Delta H_{\rm vap}$ (cal/g)		
aluminum (Al)	94.0	2,602		
gold (Au)	15.3	409		
iron (Fe)	63.2	1,504		
water (H ₂ O)	79.9	540		
sodium chloride (NaCl)	123.5	691		
ethanol (C ₂ H ₅ OH)	45.2	200.3		
benzene (C ₆ H ₆)	30.4	94.1		

There is also a phase change where a solid goes directly t	o a gas:	
	$\operatorname{solid} \to \operatorname{gas}$	(2.6.5)

2.6.2



This phase change is called *sublimation*. Each substance has a characteristic heat of sublimation associated with this process. For example, the heat of sublimation (ΔH_{sub}) of H₂O is 620 cal/g.

We encounter sublimation in several ways. You may already be familiar with dry ice, which is simply solid carbon dioxide (CO₂). At -78.5°C (-109°F), solid carbon dioxide sublimes, changing directly from the solid phase to the gas phase:

$$\operatorname{CO}_2(\mathrm{s}) \xrightarrow{-78.5^\circ\mathrm{C}} \operatorname{CO}_2(\mathrm{g})$$
 (2.6.6)

Solid carbon dioxide is called dry ice because it does not pass through the liquid phase. Instead, it does directly to the gas phase. (Carbon dioxide *can* exist as liquid but only under high pressure.) Dry ice has many practical uses, including the long-term preservation of medical samples.

Even at temperatures below 0°C, solid H_2O will slowly sublime. For example, a thin layer of snow or frost on the ground may slowly disappear as the solid H_2O sublimes, even though the outside temperature may be below the freezing point of water. Similarly, ice cubes in a freezer may get smaller over time. Although frozen, the solid water slowly sublimes, redepositing on the colder cooling elements of the freezer, which necessitates periodic defrosting (frost-free freezers minimize this redeposition). Lowering the temperature in a freezer will reduce the need to defrost as often.

Under similar circumstances, water will also sublime from frozen foods (e.g., meats or vegetables), giving them an unattractive, mottled appearance called freezer burn. It is not really a "burn," and the food has not necessarily gone bad, although it looks unappetizing. Freezer burn can be minimized by lowering a freezer's temperature and by wrapping foods tightly so water does not have any space to sublime into.

CONCEPT REVIEW EXERCISES

- 1. Explain what happens when heat flows into or out of a substance at its melting point or boiling point.
- 2. How does the amount of heat required for a phase change relate to the mass of the substance?

ANSWERS

- 1. The energy goes into changing the phase, not the temperature.
- 2. The amount of heat is a constant per gram of substance.

KEY TAKEAWAY

• There is an energy change associated with any phase change.

EXERCISES

- 1. How much energy is needed to melt 43.8 g of Au at its melting point of 1,064°C?
- 2. How much energy is given off when 563.8 g of NaCl solidifies at its freezing point of 801°C?
- 3. What mass of ice can be melted by 558 cal of energy?
- 4. How much ethanol (C₂H₅OH) in grams can freeze at its freezing point if 1,225 cal of heat are removed?
- 5. What is the heat of vaporization of a substance if 10,776 cal are required to vaporize 5.05 g? Express your final answer in joules per gram.
- 6. If 1,650 cal of heat are required to vaporize a sample that has a heat of vaporization of 137 cal/g, what is the mass of the sample?
- 7. What is the heat of fusion of water in calories per mole?
- 8. What is the heat of vaporization of benzene (C_6H_6) in calories per mole?
- 9. What is the heat of vaporization of gold in calories per mole?
- 10. What is the heat of fusion of iron in calories per mole?

- 1. 670 cal
- 3. 6.98 g
- 5. 8,930 J/g
- 7. 1,440 cal/mol
- 9. 80,600 cal/mol



2.7: ENERGY AND CHEMICAL PROCESSES (EXERCISES)

ADDITIONAL EXERCISES

- 1. Sulfur dioxide (SO₂) is a pollutant gas that is one cause of acid rain. It is oxidized in the atmosphere to sulfur trioxide (SO₃), which then combines with water to make sulfuric acid (H₂SO₄).
 - a. Write the balanced reaction for the oxidation of SO₂ to make SO₃. (The other reactant is diatomic oxygen.)
 - b. When 1 mol of SO₂ reacts to make SO₃, 23.6 kcal of energy are given off. If 100 lb (1 lb = 454 g) of SO₂ were converted to SO₃, what would be the total energy change?
- 2. Ammonia (NH₃) is made by the direct combination of H₂ and N₂ gases according to this reaction:

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) + 22.0 \text{ kcal}$$

a. Is this reaction endothermic or exothermic?

- b. What is the overall energy change if 1,500 g of N_2 are reacted to make ammonia?
- 3. A 5.69 g sample of iron metal was heated in boiling water to 99.8°C. Then it was dropped into a beaker containing 100.0 g of H₂O at 22.6°C. Assuming that the water gained all the heat lost by the iron, what is the final temperature of the H₂O and Fe?
- 4. A 5.69 g sample of copper metal was heated in boiling water to 99.8°C. Then it was dropped into a beaker containing 100.0 g of H_2O at 22.6°C. Assuming that the water gained all the heat lost by the copper, what is the final temperature of the H_2O and Cu?
- 5. When 1 g of steam condenses, 540 cal of energy is released. How many grams of ice can be melted with 540 cal?
- 6. When 1 g of water freezes, 79.9 cal of energy is released. How many grams of water can be boiled with 79.9 cal?
- 7. The change in energy is +65.3 kJ for each mole of calcium hydroxide [Ca(OH)₂] according to the following reaction:

$$Ca(OH)_2(s) \rightarrow CaO(s) + H_2O(g)$$

How many grams of Ca(OH)₂ could be reacted if 575 kJ of energy were available?

8. The thermite reaction gives off so much energy that the elemental iron formed as a product is typically produced in the liquid state:

$$2Al(s) + Fe_2O_3(s) \rightarrow Al_2O_3(s) + 2Fe(\ell) + 204 \text{ kcal}$$

How much heat will be given off if 250 g of Fe are to be produced?

- 9. A normal adult male requires 2,500 kcal per day to maintain his metabolism.
 - a. Nutritionists recommend that no more than 30% of the calories in a person's diet come from fat. At 9 kcal/g, what is the maximum mass of fat an adult male should consume daily?
 - b. At 4 kcal/g each, how many grams of protein and carbohydrates should an adult male consume daily?
- 10. A normal adult male requires 2,500 kcal per day to maintain his metabolism.
 - a. At 9 kcal/g, what mass of fat would provide that many kilocalories if the diet was composed of nothing but fats?
 - b. At 4 kcal/g each, what mass of protein and/or carbohydrates is needed to provide that many kilocalories?
- 11. The volume of the world's oceans is approximately $1.34\times 10^{24}\,\text{cm}^3.$
 - a. How much energy would be needed to increase the temperature of the world's oceans by 1°C? Assume that the heat capacity of the oceans is the same as pure water.
 - b. If Earth receives 6.0×10^{22} J of energy per day from the sun, how many days would it take to warm the oceans by 1°C, assuming all the energy went into warming the water?
- 12. Does a substance that has a small specific heat require a small or large amount of energy to change temperature? Explain.
- 13. Some biology textbooks represent the conversion of adenosine triphosphate (ATP) to adenosine diphosphate (ADP) and phosphate ions as follows:

ATP \rightarrow ADP + phosphate + energy

What is wrong with this reaction?

14. Assuming that energy changes are additive, how much energy is required to change 15.0 g of ice at -15°C to 15.0 g of steam at 115°C? (Hint: you will have five processes to consider.)

- 1. a. $2SO_2 + O_2 \rightarrow 2SO_3$ b. 16,700 kcal
- 3. about 23.1°C



- 5. 6.76 g
- 7. 652 g
- 9. a. 83.3 g b. 438 g
- 11. a. 1.34 × 10²⁴ cal b. 93 days
- 13. A reactant is missing: H₂O is missing.7



2.8: ENERGY AND CHEMICAL PROCESSES (SUMMARY)

To ensure that you understand the material in this chapter, you should review the meanings of the following bold terms in the following summary and ask yourself how they relate to the topics in the chapter.

Energy is the ability to do work. The transfer of energy from one place to another is **heat**. Heat and energy are measured in units of **joules**, **calories**, or kilocalories (equal to 1,000 calories). The amount of heat gained or lost when the temperature of an object changes can be related to its mass and a constant called the **specific heat** of the substance.

The transfer of energy can also cause a substance to change from one phase to another. During the transition, called a **phase change**, heat is either added or lost. Despite the fact that heat is going into or coming out of a substance during a phase change, the temperature of the substance does not change until the phase change is complete; that is, phase changes are **isothermal**. Analogous to specific heat, a constant called the **heat of fusion** of a substance describes how much heat must be transferred for a substance to melt or solidify (that is, to change between solid and liquid phases), while the **heat of vaporization** describes the amount of heat transferred in a boiling or condensation process (that is, to change between liquid and gas phases).

Every chemical change is accompanied by an energy change. This is because the interaction between atoms bonding to each other has a certain **bond energy**, the energy required to break the bond (called **lattice energy** for ionic compounds), and the bond energies of the reactants will not be the same as the bond energies of the products. Reactions that give off energy are called **exothermic**, while reactions that absorb energy are called **endothermic**. Energy-level diagrams can be used to illustrate the energy changes that accompany chemical reactions.

Even complex biochemical reactions have to follow the rules of simple chemistry, including rules involving energy change. Reactions of **carbohydrates** and **proteins** provide our bodies with about 4 kcal of energy per gram, while **fats** provide about 9 kcal per gram.



3: ELEMENTS, ATOMS, AND THE PERIODIC TABLE

Just as a language has an alphabet from which words are built, chemistry has an alphabet from which matter is described. However, the chemical alphabet is larger than the one we use for spelling. You may have already figured out that the chemical alphabet consists of the chemical elements. Their role is central to chemistry, for they combine to form the millions and millions of known compounds.

3.1: PRELUDE TO ELEMENTS, ATOMS, AND THE PERIODIC TABLE

The hardest material in the human body is tooth enamel. It has to be hard so that our teeth can serve us for a lifetime of biting and chewing; however, tough as it is, tooth enamel is susceptible to chemical attack. Acids found in some foods or made by bacteria that feed on food residues on our teeth are capable of dissolving enamel. Unprotected by enamel, a tooth will start to decay, thus developing cavities and other dental problems.

3.2: THE ELEMENTS

All matter is composed of elements. Chemical elements are represented by a one- or two-letter symbol.

3.3: ATOMIC THEORY

Atoms are the ultimate building blocks of all matter. The modern atomic theory establishes the concepts of atoms and how they compose matter.

3.4: THE STRUCTURE OF ATOMS

Atoms are composed of three main subatomic particles: protons, neutrons, and electrons. Protons and neutrons are grouped together in the nucleus of an atom, while electrons orbit about the nucleus.

3.5: NUCLEI OF ATOMS

Elements can be identified by their atomic number and mass number. Isotopes are atoms of the same element that have different masses.

3.6: ATOMIC MASSES

Atoms have a mass that is based largely on the number of protons and neutrons in their nucleus.

3.7: ARRANGEMENTS OF ELECTRONS

Electrons are organized into shells and subshells about the nucleus of an atom.

3.8: THE PERIODIC TABLE

The chemical elements are arranged in a chart called the periodic table. Some characteristics of the elements are related to their position on the periodic table.

3.9: ELEMENTS, ATOMS, AND THE PERIODIC TABLE (EXERCISES)

These are homework exercises to accompany Chapter 2 of the Ball et al. "The Basics of GOB Chemistry" Textmap.

3.10: ELEMENTS, ATOMS, AND THE PERIODIC TABLE (SUMMARY)

To ensure that you understand the material in this chapter, you should review the meanings of the following bold terms and ask yourself how they relate to the topics in the chapter.



3.1: PRELUDE TO ELEMENTS, ATOMS, AND THE PERIODIC TABLE

The hardest material in the human body is tooth enamel. It has to be hard so that our teeth can serve us for a lifetime of biting and chewing; however, tough as it is, tooth enamel is susceptible to chemical attack. Acids found in some foods or made by bacteria that feed on food residues on our teeth are capable of dissolving enamel. Unprotected by enamel, a tooth will start to decay, thus developing cavities and other dental problems.

In the early 1900s, a dentist in Colorado Springs, Colorado, noted that many people who lived in the area had brown-stained teeth that, while unsightly, were surprisingly resistant to decay. After years of study, excess fluorine compounds in the drinking water were discovered to be the cause of both these effects. Research continued, and in the 1930s, the US Public Health Service found that low levels of fluorine in water would provide the benefit of resisting decay without discoloring teeth.

The protective effects of fluorine have a simple chemical explanation. Tooth enamel consists mostly of a mineral called hydroxyapatite, which is composed of calcium, phosphorus, oxygen, and hydrogen. We know now that fluorine combines with hydroxyapatite to make fluorapatite, which is more resistant to acidic decay than hydroxyapatite is. Currently about 50% of the US population drinks water that has some fluorine added (in the form of sodium fluoride, NaF) to reduce tooth decay. This intentional fluoridation, coupled with the use of fluoride-containing toothpastes and improved oral hygiene, has reduced tooth decay by as much as 60% in children. The nationwide reduction of tooth decay has been cited as an important public health advance in history. (Another important advance was the eradication of polio.)



3.2: THE ELEMENTS

LEARNING OBJECTIVES

- Define a chemical element and give examples of the abundance of different elements.
- Represent a chemical element with a chemical symbol.

An element is a substance that cannot be broken down into simpler chemical substances. There are about 90 naturally occurring elements known on Earth. Using technology, scientists have been able to create nearly 30 additional elements that do not occur in nature. Today, chemistry recognizes 118 elements—some of which were created an atom at a time. Figure 3.2.1 shows some of the chemical elements.



Figure 3.2.1: Samples of Elements. Gold is a yellowish solid, iron is a silvery solid, while mercury is a silvery liquid at room temperature. © Thinkstock

ABUNDANCE

The elements vary widely in abundance. In the universe as a whole, the most common element is hydrogen (about 90% of atoms), followed by helium (most of the remaining 10%). All other elements are present in relatively minuscule amounts, as far as we can detect.

Earth's	s Crust	Earth (overall)
Element	Percentage	Element	Percentage
oxygen	46.1	iron	34.6
silicon	28.2	oxygen	29.5
aluminum	8.23	silicon	15.2
iron	5.53	magnesium	12.7
calcium	4.15	nickel	2.4
sodium	2.36	sulfur	1.9
magnesium	2.33	all others	3.7
potassium	2.09		
titanium	0.565		
hydrogen	0.14		
phosphorus	0.105		
all others	0.174		

Table 3.2.1: Elemental Composition of Earth

Source: D. R. Lide, ed. CRC Handbook of Chemistry and Physics, 89th ed. (Boca Raton, FL: CRC Press, 2008–9), 14–17.

On the planet Earth, however, the situation is rather different. Oxygen makes up 46.1% of the mass of Earth's crust (the relatively thin layer of rock forming Earth's surface), mostly in combination with other elements, while silicon makes up 28.5%. Hydrogen, the most



abundant element in the universe, makes up only 0.14% of Earth's crust. Table 3.2.1 lists the relative abundances of elements on Earth as a whole and in Earth's crust. Table 3.2.2 lists the relative abundances of elements in the human body. If you compare Table 3.2.1 and Table 3.2.2 you will find disparities between the percentage of each element in the human body and on Earth. Oxygen has the highest percentage in both cases, but carbon, the element with the second highest percentage in the body, is relatively rare on Earth and does not even appear as a separate entry in Table 3.2.1; carbon is part of the 0.174% representing "other" elements. How does the human body concentrate so many apparently rare elements?

Table 3.2.2: Elemental Composition of a Human Body			
Element	Percentage by Mass		
oxygen	61		
carbon	23		
hydrogen	10		
nitrogen	2.6		
calcium	1.4		
phosphorus	1.1		
sulfur	0.20		
potassium	0.20		
sodium	0.14		
chlorine	0.12		
magnesium	0.027		
silicon	0.026		
iron	0.006		
fluorine	0.0037		
zinc	0.0033		
all others	0.174		

Source: D. R. Lide, ed. CRC Handbook of Chemistry and Physics, 89th ed. (Boca Raton, FL: CRC Press, 2008–9), 7-24.

The relative amounts of elements in the body have less to do with their abundances on Earth than with their availability in a form we can assimilate. We obtain oxygen from the air we breathe and the water we drink. We also obtain hydrogen from water. On the other hand, although carbon is present in the atmosphere as carbon dioxide, and about 80% of the atmosphere is nitrogen, we obtain those two elements from the food we eat, not the air we breathe.

LOOKING CLOSER: PHOSPHOROUS, THE CHEMICAL BOTTLENECK

There is an element that we need more of in our bodies than is proportionately present in Earth's crust, and *this* element is not easily accessible. Phosphorus makes up 1.1% of the human body but only 0.105% of Earth's crust. We need phosphorus for our bones and teeth, and it is a crucial component of all living cells. Unlike carbon, which can be obtained from carbon dioxide, there is no phosphorus compound present in our surroundings that can serve as a convenient source. Phosphorus, then, is nature's bottleneck. Its availability limits the amount of life our planet can sustain.

Higher forms of life, such as humans, can obtain phosphorus by selecting a proper diet (plenty of protein); but lower forms of life, such as algae, must absorb it from the environment. When phosphorus-containing detergents were introduced in the 1950s, wastewater from normal household activities greatly increased the amount of phosphorus available to algae and other plant life. Lakes receiving this wastewater experienced sudden increases in growth of algae. When the algae died, concentrations of bacteria that ate the dead algae increased. Because of the large bacterial concentrations, the oxygen content of the water dropped, causing fish to die in large numbers. This process, called *eutrophication*, is considered a negative environmental impact.



Today, many detergents are made without phosphorus so the detrimental effects of eutrophication are minimized. You may even see statements to that effect on detergent boxes. It can be sobering to realize how much impact a single element can have on life—or the ease with which human activity can affect the environment.

NAMES AND SYMBOLS

Each element has a name. Some of these names date from antiquity, while others are quite new. Today, the names for new elements are proposed by their discoverers but must be approved by the International Union of Pure and Applied Chemistry, an international organization that makes recommendations concerning all kinds of chemical terminology.

Today, new elements are usually named after famous scientists.

The names of the elements can be cumbersome to write in full, especially when combined to form the names of compounds. Therefore, each element name is abbreviated as a one- or two-letter chemical symbol. By convention, the first letter of a chemical symbol is a capital letter, while the second letter (if there is one) is a lowercase letter. The first letter of the symbol is usually the first letter of the element's name, while the second letter is some other letter from the name. Some elements have symbols that derive from earlier, mostly Latin names, so the symbols may not contain any letters from the English name. Table 3.2.3 lists the names and symbols of some of the most familiar elements.

aluminum	Al	magnesium	Mg
argon	Ar	manganese	Mn
arsenic	As	mercury	Hg*
barium	Ba	neon	Ne
bismuth	Bi	nickel	Ni
boron	В	nitrogen	Ν
bromine	Br	oxygen	0
calcium	Ca	phosphorus	Р
carbon	С	platinum	Pt
chlorine	Cl	potassium	K*
chromium	Cr	silicon	Si
copper	Cu*	silver	Ag*
fluorine	F	sodium	Na*
gold	Au*	strontium	Sr
helium	He	sulfur	S
hydrogen	Н	tin	Sn*
iron	Fe	tungsten	W [†]
iodine	Ι	uranium	U
lead	Pb*	zinc	Zn
lithium	Li	zirconium	Zr
*The symbol comes from the Latin name of element.			
[†] The symbol for tungsten comes from its German name— <i>wolfram</i> .			

Element names in languages other than English are often close to their Latin names. For example, gold is *oro* in Spanish and *or* in French (close to the Latin *aurum*), tin is *estaño* in Spanish (compare to *stannum*), lead is *plomo* in Spanish and *plomb* in French (compare to *plumbum*), silver is *argent* in French (compare to *argentum*), and iron is *fer* in French and *hierro* in Spanish (compare to *ferrum*). The closeness is even more apparent in pronunciation than in spelling.

Example 3.2.1

Write the chemical symbol for each element without consulting Table 3.2.3 "Element Names and Symbols".

- a. bromine
- b. boron
- c. carbon
- d. calcium
- e. gold

Answer a

Br



Answer b		
В		
Answer c		
С		
Answer d		
Ca		
Answer e		
Au		

Exercise 3.2.1

Write the chemical symbol for each element without consulting Table 3.2.3

a. manganese

b. magnesium

c. neon

d. nitrogen

e. silver

$\mathsf{Example} \ 3.2.2$

What element is represented by each chemical symbol?

a. Na

b. Hg

c. P d. K

e. I

Answer a

sodium Answer b

mercury

Answer c

phosphorus

Answer d

potassium

Answer e

iodine

Exercise 3.2.2

What element is represented by each chemical symbol?

a. Pb

b. Sn

c. U d. O

e. F

CONCEPT REVIEW EXERCISES

1. What is an element?

2. Give some examples of how the abundance of elements varies.

3. Why are chemical symbols so useful? What is the source of the letter(s) for a chemical symbol?



- 1. An element is the basic chemical building block of matter; it is the simplest chemical substance.
- 2. Elements vary from being a small percentage to more than 30% of the atoms around us.
- 3. Chemical symbols are useful to concisely represent the elements present in a substance. The letters usually come from the name of the element.

KEY TAKEAWAYS

- All matter is composed of elements.
- Chemical elements are represented by a one- or two-letter symbol.

CONTRIBUTORS

• Anonymous



3.3: ATOMIC THEORY

LEARNING OBJECTIVES

- Explain how all matter is composed of atoms.
- Describe the modern atomic theory.

Take some aluminum foil. Cut it in half. Now you have two smaller pieces of aluminum foil. Cut one of the pieces in half again. Cut one of those smaller pieces in half again. Continue cutting, making smaller and smaller pieces of aluminum foil.

It should be obvious that the pieces are still aluminum foil; they are just becoming smaller and smaller. But how far can you take this exercise, at least in theory? Can you continue cutting the aluminum foil into halves forever, making smaller and smaller pieces? Or is there some limit, some absolute smallest piece of aluminum foil? (Thought experiments like this—and the conclusions based on them —were debated as far back as the fifth century BC.)

The modern atomic theory, proposed about 1803 by the English chemist John Dalton (Figure 3.3.1), is a fundamental concept that states that all elements are composed of atoms. Previously, we defined an atom as the smallest part of an element that maintains the identity of that element. Individual atoms are extremely small; even the largest atom has an approximate diameter of only 5.4×10^{-10} m. With that size, it takes over 18 million of these atoms, lined up side by side, to equal the width of your little finger (about 1 cm).



Figure 3.3.1 John Dalton was an English scientist who enunciated the modern atomic theory.

Most elements in their pure form exist as individual atoms. For example, a macroscopic chunk of iron metal is composed, microscopically, of individual atoms. Some elements, however, exist as groups of atoms called molecules. Several important elements exist as two-atom combinations and are called diatomic molecules. In representing a diatomic molecule, we use the symbol of the element and include the subscript 2 to indicate that two atoms of that element are joined together. The elements that exist as diatomic molecules are hydrogen (H_2), oxygen (O_2), nitrogen (N_2), fluorine (F_2), chlorine (Cl_2), bromine (Br_2), and iodine (I_2).

LOOKING CLOSER: ATOMIC THEORY

Dalton's ideas are called the *modern* atomic theory because the concept of atoms is very old. The Greek philosophers Leucippus and Democritus originally introduced atomic concepts in the fifth century BC. (The word *atom* comes from the Greek word *atomos*, which means "indivisible" or "uncuttable.") Dalton had something that the ancient Greek philosophers didn't have, however; he had experimental evidence, such as the formulas of simple chemicals and the behavior of gases. In the 150 years or so before Dalton, natural philosophy had been maturing into modern science, and the scientific method was being used to study nature. So when Dalton announced a modern atomic theory, he was proposing a fundamental theory to describe many previous observations of the natural world; he was not just participating in a philosophical discussion.



CONCEPT REVIEW EXERCISES

- 1. What is the modern atomic theory?
- 2. What are atoms?

ANSWERS

- 1. The modern atomic theory states that all matter is composed of atoms.
- 2. Atoms are the smallest parts of an element that maintain the identity of that element.

KEY TAKEAWAYS

- Atoms are the ultimate building blocks of all matter.
- The modern atomic theory establishes the concepts of atoms and how they compose matter.

CONTRIBUTORS

• Anonymous



3.4: THE STRUCTURE OF ATOMS

LEARNING OBJECTIVES

- Describe the three main subatomic particles.
- State how the subatomic particles are arranged in atoms.

There have been several minor but important modifications to Dalton's atomic theory. For one thing, Dalton considered atoms to be indivisible. We know now that atoms not only can be divided but also are composed of three different kinds of particle, *subatomic particles*, with their own properties that are different from the chemical properties of atoms.

SUBATOMIC PARTICLES

The first subatomic particle was identified in 1897 and called the electron. It is an extremely tiny particle, with a mass of about 9.109×10^{-31} kg. Experiments with magnetic fields showed that the electron has a negative electrical charge, it is *neutral*. By 1920, experimental evidence indicated the existence of a second particle. A proton has the same amount of charge as an electron, but its charge is positive, not negative. Another major difference between a proton and an electron is mass. Although still incredibly small, the mass of a proton is 1.673×10^{-27} kg, which is almost 2,000 times greater than the mass of an electron. Because opposite charges attract each other (while like charges repel each other), protons attract electrons (and vice versa).

Finally, additional experiments pointed to the existence of a third particle. Evidence produced in 1932 established the existence of the neutron, a particle with about the same mass as a proton but with no electrical charge. We understand now that all atoms can be broken down into subatomic particles: protons, neutrons, and electrons. Table 3.4.1 lists some of their important characteristics and the symbols used to represent each particle.

Particle	Symbol	Mass (kg)	Relative Mass (proton = 1)	Relative Charge
proton	p^+	1.673 × 10 ⁻²⁷	1	+1
neutron	n ⁰	1.675 × 10 ⁻²⁷	1	0
electron	e ⁻	9.109 × 10 ⁻³¹	0.00055	-1

Table 3.4.1: Properties of the Subatomic Particles

THE NUCLEUS

How are these subatomic particles arranged? Between 1909 and 1911, Ernest Rutherford, a Cambridge physicist, and his associates Hans Geiger and Ernest Marsden performed experiments that provided strong evidence concerning the internal structure of an atom. They took a very thin metal foil, such as gold or platinum, and aimed a beam of positively charged particles (called alpha particles, which are combinations of two protons and two neutrons) from a radioactive source toward the foil. Surrounding the foil was a detector —either a scintillator (a material that glows when hit by such particles) or some unexposed film (which is exposed where the particles hit it). The detector allowed the scientists to determine the distribution of the alpha particles after they interacted with the foil. Figure 3.4.1 shows a diagram of the experimental setup.





Figure 3.4.1: The Geiger-Marsden Experimental Setup. Experiments using this setup were used to investigate the structure of atoms. In this experiment, most of the particles traveled straight through the foil, but some alpha particles were deflected off to one side. Some were even deflected back toward the source. This was unexpected. Rutherford once said, "It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you." Image used with permission (CC SA-BY 3.0; Kurzon).

Rutherford proposed the following model to explain these experimental results. Protons and neutrons are concentrated in a central region he called the nucleus (plural, *nuclei*) of the atom. Electrons are outside the nucleus and orbit about it because they are attracted to the positive charge in the nucleus. Most of the mass of an atom is in the nucleus, while the orbiting electrons account for an atom's size. As a result, an atom consists largely of empty space. Rutherford called his description the "planetary model" of the atom. Figure 3.4.2shows how this model explains the experimental results.



Figure 3.4.2: Rutherford's Metal Foil Experiments. Rutherford explained the results of the metal foil experiments by proposing that most of the mass and the positive charge of an atom are located in its nucleus, while the relatively low-mass electrons orbit about the nucleus. Most alpha particles go straight through the empty space, a few particles are deflected, and fewer still ricochet back toward the source. The nucleus is much smaller proportionately than depicted here.

The planetary model of the atom replaced the plum pudding model, which had electrons floating around aimlessly like plums in a "pudding" of positive charge.

Rutherford's model is essentially the same model that we use today to describe atoms but with one important modification. The planetary model suggests that electrons occupy certain specific, circular orbits about the nucleus. We know now that this model is overly simplistic. A better description is that electrons form fuzzy clouds around nuclei. Figure 3.4.3 shows a more modern version of our understanding of atomic structure.





Figure 3.4.3: A Modern Depiction of Atomic Structure. A more modern understanding of atoms, reflected in these representations of the electron in a hydrogen atom, is that electrons occupy regions of space about the nucleus; they are not in discrete orbits like planets around the sun. (a) The darker the color, the higher the probability that an electron will be at that point. (b) In a two-dimensional cross section of the electron in a hydrogen atom, the more crowded the dots, the higher the probability that an electron will be at that point. In both (a) and (b), the nucleus is in the center of the diagram.

CONCEPT REVIEW EXERCISES

- 1. What are the charges and the relative masses of the three subatomic particles?
- 2. Describe the structure of an atom in terms of its protons, neutrons, and electrons.

ANSWERS

- 1. proton: +1, large; neutron: 0, large; electron: -1, small
- 2. Protons and neutrons are located in a central nucleus, while electrons orbit about the nucleus.

KEY TAKEAWAYS

- Atoms are composed of three main subatomic particles: protons, neutrons, and electrons.
- Protons and neutrons are grouped together in the nucleus of an atom, while electrons orbit about the nucleus.

CONTRIBUTORS

• Anonymous


3.5: NUCLEI OF ATOMS

KILLS TO DEVELOP

- Define and differentiate between the atomic number and the mass number of an element.
- Explain how isotopes differ from one another.

Now that we know how atoms are generally constructed, what do atoms of any particular element look like? How many protons, neutrons, and electrons are in a specific kind of atom? First, if an atom is electrically neutral overall, then the number of protons equals the number of electrons. Because these particles have the same but opposite charges, equal numbers cancel out, producing a neutral atom.

ATOMIC NUMBER

In the 1910s, experiments with x-rays led to this useful conclusion: the magnitude of the positive charge in the nucleus of every atom of a particular element is the same. In other words, all atoms of the same element have the same number of protons. Furthermore, different elements have a different number of protons in their nuclei, so the number of protons in the nucleus of an atom is characteristic of a particular element. This discovery was so important to our understanding of atoms that the number of protons in the nucleus of an atom is called the atomic number (Z).

For example, hydrogen has the atomic number 1; all hydrogen atoms have 1 proton in their nuclei. Helium has the atomic number 2; all helium atoms have 2 protons in their nuclei. There is no such thing as a hydrogen atom with 2 protons in its nucleus; a nucleus with 2 protons would be a helium atom. The atomic number *defines* an element. Chapter 21 lists the elements and their atomic numbers. From this table, you can determine the number of protons in the nucleus of any element. The largest atoms have over 100 protons in their nuclei.

Example 3.5.1
What is the number of protons in the nucleus of each element?
a. aluminum
b. iron
c. carbon
Answer a
According to the table, aluminum has an atomic number of 13. Therefore, every aluminum atom has 13 protons in its nucleus.
Answer b
Iron has an atomic number of 26. Therefore, every iron atom has 26 protons in its nucleus.
Answer c
Carbon has an atomic number of 6. Therefore, every carbon atom has 6 protons in its nucleus.
Exercise 3.5.1
What is the number of protons in the nucleus of each element? (Use the table in Chapter 21 "Appendix: Periodic Table of the Elements".)

a. sodium

b. oxygen

c. chlorine

How many electrons are in an atom? Previously we said that for an electrically neutral atom, the number of electrons equals the number of protons, so the total opposite charges cancel. Thus, the atomic number of an element also gives the number of electrons in an atom of that element. (Later we will find that some elements may gain or lose electrons from their atoms, so those atoms will no longer be electrically neutral. Thus we will need a way to differentiate the number of electrons for those elements.)

Example 3.5.2

How many electrons are present in the atoms of each element?

- a. sulfur
- b. tungsten
- c. argon





Answer a

The atomic number of sulfur is 16. Therefore, in a neutral atom of sulfur, there are 16 electrons.

Answer b

The atomic number of tungsten is 74. Therefore, in a neutral atom of tungsten, there are 74 electrons.

Answer c

The atomic number of argon is 18. Therefore, in a neutral atom of argon, there are 18 electrons.

Exercise 3.5.2

How many electrons are present in the atoms of each element?

- a. magnesium
- b. potassium
- c. iodine

ISOTOPES

How many neutrons are in atoms of a particular element? At first it was thought that the number of neutrons in a nucleus was also characteristic of an element. However, it was found that atoms of the same element can have *different* numbers of neutrons. Atoms of the same element (i.e., same atomic number, Z) that have different numbers of neutrons are called isotopes. For example, 99% of the carbon atoms on Earth have 6 neutrons and 6 protons in their nuclei; about 1% of the carbon atoms have 7 neutrons in their nuclei. Naturally occurring carbon on Earth, therefore, is actually a mixture of isotopes, albeit a mixture that is 99% carbon with 6 neutrons in each nucleus.

An important series of isotopes is found with hydrogen atoms. Most hydrogen atoms have a nucleus with only a single proton. About 1 in 10,000 hydrogen nuclei, however, also has a neutron; this particular isotope is called *deuterium*. An extremely rare hydrogen isotope, *tritium*, has 1 proton and 2 neutrons in its nucleus. Figure 3.5.1 compares the three isotopes of hydrogen.



Figure 3.5.1: Isotopes of Hydrogen. Most hydrogen atoms have only a proton in the nucleus (a). A small amount of hydrogen exists as the isotope deuterium, which has one proton and one neutron in its nucleus (b). A tiny amount of the hydrogen isotope tritium, with one proton and two neutrons in its nucleus, also exists on Earth (c). The nuclei and electrons are proportionately much smaller than depicted here.

The discovery of isotopes required a minor change in Dalton's atomic theory. Dalton thought that all atoms of the same element were exactly the same.

Most elements exist as mixtures of isotopes. In fact, there are currently over 3,500 isotopes known for all the elements. When scientists discuss individual isotopes, they need an efficient way to specify the number of neutrons in any particular nucleus. The *mass number* (A) of an atom is the sum of the numbers of protons and neutrons in the nucleus. Given the mass number for a nucleus (and knowing the atomic number of that particular atom), you can determine the number of neutrons by subtracting the atomic number from the mass number.

A simple way of indicating the mass number of a particular isotope is to list it as a superscript on the left side of an element's symbol. Atomic numbers are often listed as a subscript on the left side of an element's symbol. Thus, we might see

$$\begin{array}{c} \underset{\text{atomic number} \longrightarrow 56}{\text{mass number} \longrightarrow 26} Fe \\ \end{array}$$

$$(3.5.1)$$

which indicates a particular isotope of iron. The 26 is the atomic number (which is the same for all iron atoms), while the 56 is the mass number of the isotope. To determine the number of neutrons in this isotope, we subtract 26 from 56: 56 - 26 = 30, so there are 30 neutrons in this atom.

Example 3.5.3

How many protons and neutrons are in each atom?

a. ${}^{35}_{17}Cl$



b. $^{127}_{53}{ m I}$

Answer a

In ${}^{35}_{17}$ Cl there are 17 protons, and 35 – 17 = 18 neutrons in each nucleus.

Answer b

In ${}^{127}_{53}$ I there are 53 protons, and 127 – 53 = 74 neutrons in each nucleus.

Exercise 3.5.3	
How many protons and neutrons are in each atom?	
- 197 •	

a. ${}^{+9}_{79}$ 'Au b. ${}^{23}_{11}$ Na

It is not absolutely necessary to indicate the atomic number as a subscript because each element has its own unique atomic number. Many isotopes are indicated with a superscript only, such as ¹³C or ²³⁵U. You may also see isotopes represented in print as, for example, carbon-13 or uranium-235.

SUMMARY

The atom consists of discrete particles that govern its chemical and physical behavior. Each atom of an element contains the same number of protons, which is the atomic number (Z). Neutral atoms have the same number of electrons and protons. Atoms of an element that contain different numbers of neutrons are called isotopes. Each isotope of a given element has the same atomic number but a different mass number (A), which is the sum of the numbers of protons and neutrons.

Almost all of the mass of an atom is from the total protons and neutrons contained within a tiny (and therefore very dense) nucleus. The majority of the volume of an atom is the surrounding space in which the electrons reside. A representation of a carbon-12 atom is shown below in Figure 3.5.2



Figure 3.5.2: Formalism used for identifying specific nuclide (any particular kind of nucleus)

CONCEPT REVIEW EXERCISES

- 1. Why is the atomic number so important to the identity of an atom?
- 2. What is the relationship between the number of protons and the number of electrons in an atom?
- 3. How do isotopes of an element differ from each other?
- 4. What is the mass number of an element?



ANSWERS

- 1. The atomic number defines the identity of an element.
- 2. In an electrically neutral atom, the number of protons equals the number of electrons.
- 3. Isotopes have different numbers of neutrons in their nuclei.
- 4. The mass number is the sum of the numbers of protons and neutrons in the nucleus of an atom.

KEY TAKEAWAYS

- Elements can be identified by their atomic number and mass number.
- Isotopes are atoms of the same element that have different masses.

CONTRIBUTORS

• Anonymous



3.6: ATOMIC MASSES

LEARNING OBJECTIVES

• To define atomic mass and atomic mass unit.

Even though atoms are very tiny pieces of matter, they have mass. Their masses are so small, however, that chemists often use a unit other than grams to express them—the atomic mass unit.

The atomic mass unit (abbreviated u, although amu is also used) is defined as 1/12 of the mass of a ${}^{12}C$ atom:

$$1 u = {1 \over 12}$$
 the mass of ¹²C atom (3.6.1)

It is equal to 1.661×10^{-24} g.

Masses of other atoms are expressed with respect to the atomic mass unit. For example, the mass of an atom of 1 H is 1.008 u, the mass of an atom of 16 O is 15.995 u, and the mass of an atom of 32 S is 31.97 u. Note, however, that these masses are for particular isotopes of each element. Because most elements exist in nature as a mixture of isotopes, any sample of an element will actually be a mixture of atoms having slightly different masses (because neutrons have a significant effect on an atom's mass). How, then, do we describe the mass of a given element? By calculating an average of an element's atomic masses, weighted by the natural abundance of each isotope, we obtain a weighted average mass called the atomic mass (also commonly referred to as the *atomic weight*) of an element.

For example, boron exists as a mixture that is 19.9% 10 B and 80.1% 11 B. The atomic mass of boron would be calculated as (0.199 × 10.0 u) + (0.801 × 11.0 u) = 10.8 u. Similar average atomic masses can be calculated for other elements. Carbon exists on Earth as about 99% 12 C and about 1% 13 C, so the weighted average mass of carbon atoms is 12.01 u.

Example 3.6.1: Mass of Carbon

What is the average mass of a carbon atom in grams?

SOLUTION

This is a simple one-step conversion, similar to conversions we did in Chapter 1. We use the fact that $1 \text{ u} = 1.661 \times 10^{-24} \text{ g}$:

12.01
$$\gamma \times \frac{1.661 \times 10^{-24} \text{ g}}{1 \gamma} = 1.995 \times 10^{-23} \text{ g}$$

This is an extremely small mass, which illustrates just how small individual atoms are.

Exercise 3.6.1: Mass of Tin

What is the average mass of a tin atom in grams? The atomic mass of tin is 118.71 u.

CONCEPT REVIEW EXERCISES

- 1. Define atomic mass. Why is it considered a weighted average?
- 2. What is an atomic mass unit?

ANSWERS

- 1. The atomic mass is an average of an element's atomic masses, weighted by the natural abundance of each isotope of that element. It is a weighted average because different isotopes have different masses.
- 2. An atomic mass unit is 1/12th of the mass of a 12 C atom.

KEY TAKEAWAY

• Atoms have a mass that is based largely on the number of protons and neutrons in their nucleus.

CONTRIBUTORS

• Anonymous



3.7: ARRANGEMENTS OF ELECTRONS

LEARNING OBJECTIVES

• To describe how electrons are grouped within atoms.

Although we have discussed the general arrangement of subatomic particles in atoms, we have said little about how electrons occupy the space about the nucleus. Do they move around the nucleus at random, or do they exist in some ordered arrangement?

The modern theory of electron behavior is called quantum mechanics. It makes the following statements about electrons in atoms:

- Electrons in atoms can have only certain specific energies. We say that the energies of the electrons are quantized.
- Electrons are organized according to their energies into sets called shells (labeled by the principle quantum number, *n*).. Generally the higher the energy of a shell, the farther it is (on average) from the nucleus. Shells do not have specific, fixed distances from the nucleus, but an electron in a higher-energy shell will spend more time farther from the nucleus than does an electron in a lower-energy shell.
- Shells are further divided into subsets of electrons called subshells. The first shell has only one subshell, the second shell has two subshells, the third shell has three subshells, and so on. The subshells of each shell are labeled, in order, with the letters *s*, *p*, *d*, and *f*. Thus, the first shell has only an *s* subshell, the second shell has an *s* and a *p* subshell, the third shell has *s*, *p*, and *d* subshells, and so forth.
- Different subshells hold a different maximum number of electrons. Any *s* subshell can hold up to 2 electrons; *p*, 6; *d*, 10; and *f*, 14.

It is the arrangement of electrons into shells and subshells that most concerns us here, so we will focus on that.

We use numbers to indicate which shell an electron is in. The first shell, closest to the nucleus and with the lowest-energy electrons, is shell 1. This first shell has only one subshell, which is labeled *s* and can hold a maximum of 2 electrons. We combine the shell and subshell labels when referring to the organization of electrons about a nucleus and use a superscript to indicate how many electrons are in a subshell. Thus, because a hydrogen atom has its single electron in the *s* subshell of the first shell, we use $1s^1$ to describe the electronic structure of hydrogen. This structure is called an electron configuration. Electron configurations are shorthand descriptions of the arrangements of electrons in atoms. The electron configuration of a hydrogen atom is spoken out loud as "one-ess-one."

Helium atoms have 2 electrons. Both electrons fit into the 1*s* subshell because *s* subshells can hold up to 2 electrons; therefore, the electron configuration for helium atoms is $1s^2$ (spoken as "one-ess-two").

The 1*s* subshell cannot hold 3 electrons (because an *s* subshell can hold a maximum of 2 electrons), so the electron configuration for a lithium atom cannot be $1s^3$. Two of the lithium electrons can fit into the 1*s* subshell, but the third electron must go into the second shell. The second shell has two subshells, *s* and *p*, which fill with electrons in that order. The 2*s* subshell holds a maximum of 2 electrons, and the 2*p* subshell holds a maximum of 6 electrons. Because lithium's final electron goes into the 2*s* subshell, we write the electron configuration of a lithium atom as $1s^22s^1$.

The next largest atom, beryllium, has 4 electrons, so its electron configuration is $1s^22s^2$. Now that the 2*s* subshell is filled, electrons in larger atoms start filling the 2*p* subshell. Thus, the electron configurations for the next six atoms are as follows:

- B: $1s^22s^22p^1$
- C: $1s^2 2s^2 2p^2$
- N: $1s^2 2s^2 2p^3$
- O: $1s^2 2s^2 2p^4$
- F: $1s^2 2s^2 2p^5$
- Ne: $1s^2 2s^2 2p^6$

With neon, the 2*p* subshell is completely filled. Because the second shell has only two subshells, atoms with more electrons now must begin the third shell. The third shell has three subshells, labeled *s*, *p*, and *d*. The *d* subshell can hold a maximum of 10 electrons. The first two subshells of the third shell are filled in order—for example, the electron configuration of aluminum, with 13 electrons, is $1s^22s^22p^63s^23p^1$. However, a curious thing happens after the 3*p* subshell is filled: the 4*s* subshell begins to fill before the 3*d* subshell does. In fact, the exact ordering of subshells becomes more complicated at this point (after argon, with its 18 electrons), so we will not consider the electron configurations of larger atoms.

A fourth subshell, the f subshell, is needed to complete the electron configurations for all elements. An f subshell can hold up to 14 electrons.

EXAMPLE 3.7.1: ELECTRONIC CONFIGURATION OF PHOSPHORUS ATOMS

What is the electron configuration of a neutral phosphorus atom?

SOLUTION



A neutral phosphorus atom has 15 electrons. Two electrons can go into the 1*s* subshell, 2 can go into the 2*s* subshell, and 6 can go into the 2*p* subshell. That leaves 5 electrons. Of those 5 electrons, 2 can go into the 3*s* subshell, and the remaining 3 electrons can go into the 3*p* subshell. Thus, the electron configuration of neutral phosphorus atoms is $1s^22s^22p^63s^23p^3$.

EXERCISE 3.7.1: ELECTRONIC CONFIGURATION OF CHLORINE ATOMS

What is the electron configuration of a neutral chlorine atom?

Chemistry results from interactions between the outermost shells of electrons on different atoms. Thus, it is convenient to separate electrons into two groups. Valence shell electrons (or, more simply, the *valence electrons*) are the electrons in the highest-numbered shell, or valence shell, while core electrons are the electrons in lower-numbered shells. We can see from the electron configuration of a carbon atom $-1s^22s^22p^2$ —that it has 4 valence electrons ($2s^22p^2$) and 2 core electrons ($1s^2$).

EXAMPLE 3.7.2: COUNTING VALENCE ELECTRONS IN PHOSPHORUS ATOMS

From the electron configuration of neutral phosphorus atoms in Example 3.7.1, how many valence electrons and how many core electrons does a neutral phosphorus atom have?

SOLUTION

The highest-numbered shell is the third shell, which has 2 electrons in the 3*s* subshell and 3 electrons in the 3*p* subshell. That gives a total of 5 electrons, so neutral phosphorus atoms have 5 valence electrons. The 10 remaining electrons, from the first and second shells, are core electrons.

EXERCISE 3.7.2: COUNTING VALENCE ELECTRONS IN CHLORINE ATOMS

From the electron configuration of neutral chlorine atoms (Exercise 3.7.1), how many valence electrons and how many core electrons does a neutral chlorine atom have?

CONCEPT REVIEW EXERCISES

- 1. How are electrons organized in atoms?
- 2. What information does an electron configuration convey?
- 3. What is the difference between core electrons and valence electrons?

ANSWERS

- 1. Electrons are organized into shells and subshells around nuclei.
- 2. The electron configuration states the arrangement of electrons in shells and subshells.
- 3. Valence electrons are in the highest-numbered shell; all other electrons are core electrons.

KEY TAKEAWAY

• Electrons are organized into shells and subshells about the nucleus of an atom.



3.8: THE PERIODIC TABLE

LEARNING OBJECTIVES

- Explain how elements are organized into the periodic table.
- Describe how some characteristics of elements relate to their positions on the periodic table.

In the 19th century, many previously unknown elements were discovered, and scientists noted that certain sets of elements had similar chemical properties. For example, chlorine, bromine, and iodine react with other elements (such as sodium) to make similar compounds. Likewise, lithium, sodium, and potassium react with other elements (such as oxygen) to make similar compounds. Why is this so?

In 1864, Julius Lothar Meyer, a German chemist, organized the elements by atomic mass and grouped them according to their chemical properties. Later that decade, Dmitri Mendeleev, a Russian chemist, organized all the known elements according to similar properties. He left gaps in his table for what he thought were undiscovered elements, and he made some bold predictions regarding the properties of those undiscovered elements. When elements were later discovered whose properties closely matched Mendeleev's predictions, his version of the table gained favor in the scientific community. Because certain properties of the elements repeat on a regular basis throughout the table (that is, they are periodic), it became known as the periodic table.

Mendeleev had to list some elements out of the order of their atomic masses to group them with other elements that had similar properties.

The periodic table is one of the cornerstones of chemistry because it organizes all the known elements on the basis of their chemical properties. A modern version is shown in Figure 3.8.1 Most periodic tables provide additional data (such as atomic mass) in a box that contains each element's symbol. The elements are listed in order of atomic number.

1			B = So	lids	Hg =	= Liquid	S	Kr = Ga	ises	Pm =	= Not fo	ound in	nature				18
1 H 1.00794	2											13	14	15	16	17	2 He 4.002602
3 Li 6.941	4 Be 9.012182											5 B 10.811	C	7 N 14.00674	8 0 15.9994	9 F 18.9984032	10 Ne 20.1797
11 Na 22.989770	12 Mg 24.3050	3	4	5	6	7	8	9	10	11	12	13 Al 26.581538	14 Si 28.0855	15 P 30.973761	16 S 32.066	17 Cl 35.4527	18 Ar 39.948
19 K 39.0983	20 Ca 40.078	21 Sc 44.955910	22 Ti ^{47.867}	23 V 50.9415	24 Cr 51.9961	25 Mn 54.938049	26 Fe 55.845	27 CO 58.933200	28 Ni ^{58.6534}	29 Cu 63.545	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.92160	34 Se 78.96	35 Br 79.504	36 Kr 83.80
37 Rb 85.4678	38 Sr ^{87.62}	39 Y 88.90585	40 Zr 91.224	41 Nb 92.90638	42 Mo _{95.94}	43 TC (98)	44 Ru 101.07	45 Rh 102.90550	46 Pd 106.42	47 Ag 107.87	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.760	52 Te 127.60	53 126.90447	54 Xe 131.29
55 Cs 132.90545	56 Ba 137.327	71 Lu 174.967	72 Hf 178.49	73 Ta 180.94.79	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.217	78 Pt 195.078	79 Au 196.56655	80 Hg 200.59	81 TI 204.3833	82 Pb 207.2	83 Bi 208.58038	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	103 Lr (262)	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 Ds (269)	111 Rg (272)	112 Cn (277)	113 Uut (277)	114 Uuq (277)	115 Uup (277)	116 Uuh (277)		118 Uuo (277)
			57 La 138.9055	58 Ce 140.116	59 Pr 140.50765	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.964	64 Gd 157.25	65 Tb 158.92534	66 Dy 162.50	67 Ho 164.93032	68 Er 167.26	69 Tm 168.93421	70 Yb 173.04	
			89 Ac 232.0381	90 Th 232.0381	91 Pa 231.035888	92 U 238.0289	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	

Figure 3.8.1: A Modern Periodic Table. A modern periodic table lists elements left to right by atomic number.

FEATURES OF THE PERIODIC TABLE

Elements that have similar chemical properties are grouped in columns called groups (or families). As well as being numbered, some of these groups have names—for example, *alkali metals* (the first column of elements), *alkaline earth metals* (the second column of elements), *halogens* (the next-to-last column of elements), and *noble gases* (the last column of elements).

The word halogen comes from the Greek for "salt maker" because these elements combine with other elements to form a group of compounds called salts.

To Your Health: Radon



Radon is an invisible, odorless noble gas that is slowly released from the ground, particularly from rocks and soils whose uranium content is high. Because it is a noble gas, radon is not chemically reactive. Unfortunately, it is radioactive, and increased exposure to it has been correlated with an increased lung cancer risk.

Because radon comes from the ground, we cannot avoid it entirely. Moreover, because it is denser than air, radon tends to accumulate in basements, which if improperly ventilated can be hazardous to a building's inhabitants. Fortunately, specialized ventilation minimizes the amount of radon that might collect. Special fan-and-vent systems are available that draw air from below the basement floor, before it can enter the living space, and vent it above the roof of a house.

After smoking, radon is thought to be the second-biggest *preventable* cause of lung cancer in the United States. The American Cancer Society estimates that 10% of all lung cancers are related to radon exposure. There is uncertainty regarding what levels of exposure cause cancer, as well as what the exact causal agent might be (either radon or one of its breakdown products, many of which are also radioactive and, unlike radon, not gases). The US Environmental Protection Agency recommends testing every floor below the third floor for radon levels to guard against long-term health effects.

Each row of elements on the periodic table is called a period. Periods have different lengths; the first period has only 2 elements (hydrogen and helium), while the second and third periods have 8 elements each. The fourth and fifth periods have 18 elements each, and later periods are so long that a segment from each is removed and placed beneath the main body of the table.

Certain elemental properties become apparent in a survey of the periodic table as a whole. Every element can be classified as either a metal, a nonmetal, or a semimetal, as shown in Figure 3.8.2 A metal is a substance that is shiny, typically (but not always) silvery in color, and an excellent conductor of electricity and heat. Metals are also malleable (they can be beaten into thin sheets) and ductile (they can be drawn into thin wires). A nonmetal is typically dull and a poor conductor of electricity and heat. Solid nonmetals are also very brittle. As shown in Figure 3.8.2 metals occupy the left three-fourths of the periodic table, while nonmetals (except for hydrogen) are clustered in the upper right-hand corner of the periodic table. The elements with properties intermediate between those of metals and nonmetals are called **semimetals** (or **metalloids**). Elements adjacent to the bold line in the right-hand portion of the periodic table have semimetal properties.



Figure 3.8.2: Types of Elements. Elements are either metals, nonmetals, or semimetals. Each group is located in a different part of the periodic table.

Another way to categorize the elements of the periodic table is shown in Figure **3.8.3** The first two columns on the left and the last six columns on the right are called the main group elements. The ten-column block between these columns contains the transition metals. The two rows beneath the main body of the periodic table contain the inner transition metals. The elements in these two rows are also referred to as, respectively, the **lanthanide metals** and the **actinide metals**.





Figure 3.8.3: Special Names for Sections of the Periodic Table. Some sections of the periodic table have special names. The elements lithium, sodium, potassium, rubidium, cesium, and francium are collectively known as alkali metals.

To YOUR HEALTH: TRANSITION METALS IN THE BODY

Most of the elemental composition of the human body consists of main group elements. The first element appearing on the list that is not a main group element is iron, at 0.006 percentage by mass. Because iron has relatively massive atoms, it would appear even lower on a list organized in terms of percent by *atoms* rather than percent by mass.

Iron is a transition metal. Transition metals have interesting chemical properties, partially because some of their electrons are in *d* subshells. The chemistry of iron makes it a key component in the proper functioning of red blood cells.

Red blood cells are cells that transport oxygen from the lungs to cells of the body and then transport carbon dioxide from the cells to the lungs. Without red blood cells, animal respiration as we know it would not exist. The critical part of the red blood cell is a protein called *hemoglobin*. Hemoglobin combines with oxygen and carbon dioxide, transporting these gases from one location to another in the body. Hemoglobin is a relatively large molecule, with a mass of about 65,000 u.

The crucial atom in the hemoglobin protein is iron. Each hemoglobin molecule has four iron atoms, which act as binding sites for oxygen. It is the presence of this particular transition metal in your red blood cells that allows you to use the oxygen you inhale.

Other transition metals have important functions in the body, despite being present in low amounts. Zinc is needed for the body's immune system to function properly, as well as for protein synthesis and tissue and cell growth. Copper is also needed for several proteins to function properly in the body. Manganese is needed for the body to metabolize oxygen properly. Cobalt is a necessary component of vitamin B-12, a vital nutrient. These last three metals are not listed explicitly in Table 2.2, so they are present in the body in very small quantities. However, even these small quantities are required for the body to function properly.

The periodic table is organized on the basis of similarities in elemental properties, but what explains these similarities? It turns out that the shape of the periodic table reflects the filling of subshells with electrons, as shown in Figure 3.8.4 Starting with the first period and going from left to right, the table reproduces the order of filling of the electron subshells in atoms. Furthermore, elements in the same *group* share the same valence shell electron configuration. For example, all elements in the first column have a single *s* electron in their valence shells, so their electron configurations can be described as ns^1 (where *n* represents the shell number). This last observation is crucial. Chemistry is largely the result of interactions between the valence electrons of different atoms. Thus, atoms that have the same valence shell electron configuration will have similar chemistry.





Figure 3.8.4: The Shape of the Periodic Table. The shape of the periodic table reflects the order in which electron shells and subshells fill with electrons.

Example 3.8.1

Using the variable n to represent the number of the valence electron shell, write the valence shell electron configuration for each group.

- a. the alkaline earth metals
- b. the column of elements headed by carbon

Answer a

The alkaline earth metals are in the second column of the periodic table. This column corresponds to the *s* subshell being filled with 2 electrons. Therefore, the valence shell electron configuration is ns^2 .

Answer b

The electron configuration of carbon is $1s^22s^22p^2$. Its valence shell electron configuration is $2s^22p^2$. Every element in the same column should have a similar valence shell electron configuration, which we can represent as ns^2np^2 .

Exercise 3.8.1

Using the variable n to represent the number of the valence electron shell, write the valence shell electron configuration for each group.

a. the halogens

b. the column of elements headed by oxygen

ATOMIC RADIUS

The periodic table is useful for understanding atomic properties that show periodic trends. One such property is the atomic radius (Figure 3.8.5). As mentioned earlier, the higher the shell number, the farther from the nucleus the electrons in that shell are likely to be. In other words, the size of an atom is generally determined by the number of the valence electron shell. Therefore, as we go down a column on the periodic table, the atomic radius increases. As we go *across* a period on the periodic table, however, electrons are being added to the *same* valence shell; meanwhile, more protons are being added to the nucleus, so the positive charge of the nucleus is increasing. The increasing positive charge attracts the electrons more strongly, pulling them closer to the nucleus. Consequently, as we go across a period, the atomic radius decreases. These trends are seen clearly in Figure 3.8.5





Figure 3.8.5: Trends on the Periodic Table. The relative sizes of the atoms show several trends with regard to the structure of the periodic table. Atoms become larger going down a column and smaller going across a period. (CC BY-SA 3.0; CK-12 Foundation).

Example 3.8.2

Using the periodic table (rather than Figure 3.8.5), which atom is larger?

a. N or Bi

b. Mg or Cl

Answer a

Because Bi is below N on the periodic table and has electrons in higher-numbered shells, we expect that Bi atoms are larger than N atoms.

Answer b

Both Mg and Cl are in period 3 of the periodic table, but Cl lies farther to the right. Therefore we expect Mg atoms to be larger than Cl atoms.

Exercise 3.8.2

Using the periodic table (rather than Figure 3.8.5), which atom is larger?

a. Li or F

b. Na or K

CAREER FOCUS: CLINICAL CHEMIST

Clinical chemistry is the area of chemistry concerned with the analysis of body fluids to determine the health status of the human body. Clinical chemists measure a variety of substances, ranging from simple elements such as sodium and potassium to complex molecules such as proteins and enzymes, in blood, urine, and other body fluids. The absence or presence, or abnormally low or high amounts, of a substance can be a sign of some disease or an indication of health. Many clinical chemists use sophisticated equipment and complex chemical reactions in their work, so they not only need to understand basic chemistry, but also be familiar with special instrumentation and how to interpret test results.

CONCEPT REVIEW EXERCISES

1. How are the elements organized into the periodic table?

2. Looking at the periodic table, where do the following elements appear?





- a. the metals
- b. the nonmetals
- c. the halogens
- d. the transition metals
- 3. Describe the trends in atomic radii as related to an element's position on the periodic table.

ANSWERS

- 1. Elements are organized by atomic number.
- 2. a. the left three-quarters of the periodic table
 - b. the right quarter of the periodic table
 - c. the next-to-last column of the periodic table
 - d. the middle section of the periodic table
- 3. As you go across the periodic table, atomic radii decrease; as you go down the periodic table, atomic radii increase.

KEY TAKEAWAYS

- The chemical elements are arranged in a chart called the periodic table.
- Some characteristics of the elements are related to their position on the periodic table.



3.9: ELEMENTS, ATOMS, AND THE PERIODIC TABLE (EXERCISES)

ADDITIONAL EXERCISES

- 1. If the atomic radius of sodium atoms is 1.86×10^{-10} m, how many sodium atoms are needed to make a line that is 1.00 cm in length?
- 2. If the atomic radius of osmium atoms is 1.34×10^{-10} m, how many osmium atoms are needed to make a line that is 5.85 m in length?
- 3. What might be the electron configuration of K⁺, an atom that has lost an electron?
- 4. What might be the electron configuration of Cl⁻, an atom that has gained an additional electron?
- 5. The electron configuration of the Ti atom is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$. What is the valence shell electron configuration of Ti?
- 6. The electron configuration of the Ge atom is $1s^22s^22p^63s^23p^64s^23d^{10}4p^2$. What is the valence shell electron configuration of Ge?
- 7. What is the mass of an electron in atomic mass units?
- 8. In a footnote in this chapter, an alpha particle was defined as a particle with 2 protons and 2 neutrons. What is the mass, in grams, of an alpha particle? (Hint: what element does an alpha particle resemble?)
- 9. A sample of the nonexistent element mythium consists of 25.59% of an isotope with mass number 580, 32.74% of an isotope with mass number 581. What is the atomic mass of mythium?
- 10. Because the distribution of isotopes is different on different planets in the solar system, the average atomic mass of any element differs from planet to planet. Assume that on Mercury, a rather hot planet, there is more deuterium left in the atmosphere than on Earth, so that 92.55% of the hydrogen on Mercury is ¹H, while the remainder is ²H. What is the atomic mass of hydrogen on Mercury?
- 11. The compound that sodium makes with chlorine has sodium and chlorine atoms in a 1:1 ratio. Name two other elements that should make a compound having a 1:1 ratio of atoms with sodium.
- 12. The compound that magnesium makes with oxygen has magnesium to oxygen atoms in a 1:1 ratio. Name two other elements that should make a compound having a 1:1 ratio of atoms with magnesium.

ANSWERS

1. 5.38 × 10^7 atoms

3. $1s^22s^22p^63s^23p^6$

- 5. $4s^2$
- 7. 0.000545 u
- 9. 581.1 u
- 11. potassium and bromine (answers will vary)



3.10: ELEMENTS, ATOMS, AND THE PERIODIC TABLE (SUMMARY)

To ensure that you understand the material in this chapter, you should review the meanings of the following bold terms and ask yourself how they relate to the topics in the chapter.

An element is a substance that cannot be broken down into simpler chemical substances. Only about 90 naturally occurring elements are known. They have varying abundances on Earth and in the body. Each element has a one- or two-letter **chemical symbol**.

The **modern atomic theory** states that the smallest piece of an element is an **atom**. Individual atoms are extremely small, on the order of 10^{-10} m across. Most elements exist in pure form as individual atoms, but some exist as **diatomic molecules**. Atoms themselves are composed of subatomic particles. The **electron** is a tiny subatomic particle with a negative charge. The **proton** has a positive charge and, while small, is much larger than the electron. The **neutron** is also much larger than an electron but has no electrical charge.

Protons, neutrons, and electrons have a specific arrangement in an atom. The protons and neutrons are found in the center of the atom, grouped together into a **nucleus**. The electrons are found in fuzzy clouds around the nucleus.

Each element has a characteristic number of protons in its nucleus. This number of protons is the **atomic number** of the element. An element may have different numbers of neutrons in the nuclei of its atoms; such atoms are referred to as **isotopes**. Two isotopes of hydrogen are deuterium, with a proton and a neutron in its nucleus, and tritium, with a proton and two neutrons in its nucleus. The sum of the numbers of protons and neutrons in a nucleus is called the **mass number** and is used to distinguish isotopes from each other.

Masses of individual atoms are measured in **atomic mass units**. An atomic mass unit is equal to 1/12th of the mass of a single carbon-12 atom. Because different isotopes of an element have different masses, the **atomic mass** of an element is a weighted average of the masses of all the element's naturally occurring isotopes.

The modern theory of electron behavior is called **quantum mechanics**. According to this theory, electrons in atoms can only have specific, or **quantized**, energies. Electrons are grouped into general regions called **shells**, and within these into more specific regions called **subshells**. There are four types of subshells, and each type can hold up to a maximum number of electrons. The distribution of electrons into shells and subshells is the **electron configuration** of an atom. Chemistry typically occurs because of interactions between the electrons of the outermost shell of different atoms, called the valence shell electrons. Electrons in inner shells are called core electrons.

Elements are grouped together by similar chemical properties into a chart called the **periodic table**. Vertical columns of elements are called **groups** or **families**. Some of the groups of elements have names, like the alkali metals, the alkaline earth metals, the halogens, and the noble gases. A horizontal row of elements is called a **period**. Periods and groups have differing numbers of elements in them. The periodic table separates elements into **metals**, **nonmetals**, and **semimetals**. The periodic table is also separated into **main group elements**, **transition metals**, **lanthanide elements**, and **actinide elements**. The lanthanide and actinide elements are also referred to as **inner transition metal elements**. The shape of the periodic table reflects the sequential filling of shells and subshells in atoms.

The periodic table helps us understand trends in some of the properties of atoms. One such property is the **atomic radius** of atoms. From top to bottom of the periodic table, atoms get bigger because electrons are occupying larger and bigger shells. From left to right across the periodic table, electrons are filling the same shell but are being attracted by an increasing positive charge from the nucleus, and thus the atoms get smaller.



4: NUCLEAR CHEMISTRY

In nuclear chemistry, the composition of the nucleus and the changes that occur there are very important. Applications of nuclear chemistry may be more widespread than you realize. In this chapter, we will examine some of the basic concepts of nuclear chemistry and some of the nuclear reactions that are important in our everyday lives.

4.1: PRELUDE TO NUCLEAR CHEMISTRY

A typical smoke detector contains an electric circuit that includes two metal plates about 1 cm apart. A battery in the circuit creates a voltage between the plates. Next to the plates is a small disk containing a tiny amount (\sim 0.0002 g) of the radioactive element americium (Am). The radioactivity of the americium ionizes the air between the plates, causing a tiny current to constantly flow between them.

4.2: RADIOACTIVITY

Atoms are composed of subatomic particles—protons, neutrons, and electrons. Protons and neutrons are located in the nucleus and provide most of the mass of the atom, while electrons circle the nucleus in shells and subshells and account for an atom's size. There are three main forms of radioactive emissions and are alpha particles, beta particles, and gamma rays.

4.3: HALF-LIFE

Natural radioactive processes are characterized by a half-life, the time it takes for half of the material to decay radioactively. The amount of material left over after a certain number of half-lives can be easily calculated.

4.4: UNITS OF RADIOACTIVITY

Radioactivity can be expressed in a variety of units, including rems, rads, and curies.

4.5: USES OF RADIOACTIVE ISOTOPES

Radioactivity has several practical applications, including tracers, medical applications, dating once-living objects, and the preservation of food.

4.6: NUCLEAR ENERGY

Nuclear energy comes from tiny mass changes in nuclei as radioactive processes occur. In fission, large nuclei break apart and release energy; in fusion, small nuclei merge together and release energy.

4.7: NUCLEAR CHEMISTRY (EXERCISES)

Select problems and solutions.

4.8: NUCLEAR CHEMISTRY (SUMMARY)

Chapter summary



4.1: PRELUDE TO NUCLEAR CHEMISTRY

Most of us may not be aware of a device in our homes that guards our safety and, at the same time, depends on radioactivity to operate properly. This device is a smoke detector.

A typical smoke detector contains an electric circuit that includes two metal plates about 1 cm apart. A battery in the circuit creates a voltage between the plates. Next to the plates is a small disk containing a tiny amount (\sim 0.0002 g) of the radioactive element americium (Am). The radioactivity of the americium ionizes the air between the plates, causing a tiny current to constantly flow between them. (This constant drain on the battery explains why the batteries in smoke detectors should be replaced on a regular basis, whether the alarm has been triggered or not.)



Figure 4.1.1: Many people think of nuclear chemistry in connection with the nuclear power industry and atomic bombs but do not realize that most smoke detectors rely on nuclear chemistry and save countless lives every year. The applications of nuclear chemistry may be more widespread than you think. Image used with permission (CC BY-SA 3.0; Wile e2005).

When particles of smoke from a fire enter the smoke detector, they interfere with the ions between the metal plates, interrupting the tiny flow of current. When the current drops beneath a set value, another circuit triggers a loud alarm, warning of the possible presence of fire.

Although radioactive, the americium in a smoke detector is embedded in plastic and is not harmful unless the plastic package is taken apart, which is unlikely. Although many people experience an unfounded fear of radioactivity, smoke detectors provide an application of radioactivity that saves thousands of lives every year.



4.2: RADIOACTIVITY

LEARNING OBJECTIVES

• To define and give examples of the major types of radioactivity.

Atoms are composed of subatomic particles—protons, neutrons, and electrons. Protons and neutrons are located in the nucleus and provide most of the mass of the atom, while electrons circle the nucleus in shells and subshells and account for an atom's size. Remember, the notation for succinctly representing an isotope of a particular atom:

 ${}^{12}_{6}C$

(4.2.1)

The element in this example, represented by the symbol *C*, is carbon. Its atomic number, 6, is the lower left subscript on the symbol and is the number of protons in the atom. The mass number, the superscript to the upper left of the symbol, is the sum of the number of protons and neutrons in the nucleus of this particular isotope. In this case, the mass number is 12, which means that the number of neutrons in the atom is 12 - 6 = 6 (that is, the mass number of the atom minus the number of protons in the nucleus equals the number of neutrons). Occasionally, the atomic number is omitted in this notation because the symbol of the element itself conveys its characteristic atomic number. The two isotopes of hydrogen, ²H and ³H, are given their own names: deuterium (D) and tritium (T), respectively. Another way of expressing a particular isotope is to list the mass number after the element name, like carbon-12 or hydrogen-3.

Atomic theory in the 19th century presumed that nuclei had fixed compositions. But in 1896, the French scientist Henri Becquerel found that a uranium compound placed near a photographic plate made an image on the plate, even if the compound was wrapped in black cloth. He reasoned that the uranium compound was emitting some kind of radiation that passed through the cloth to expose the photographic plate. Further investigations showed that the radiation was a combination of particles and electromagnetic rays, with its ultimate source as the atomic nucleus. These emanations were ultimately called, collectively, radioactivity.

There are three main forms of radioactive emissions. The first is called an alpha particle, which is symbolized by the Greek letter α . An alpha particle is composed of two protons and two neutrons, and so it is the same as a helium nucleus. (We often use $\frac{4}{2}$ He to represent an alpha particle.) It has a 2+ charge. When a radioactive atom emits an alpha particle, the original atom's atomic number decreases by two (because of the loss of two protons), and its mass number decreases by four (because of the loss of four nuclear particles). We can represent the emission of an alpha particle with a chemical equation—for example, the alpha-particle emission of uranium-235 is as follows:

$${}^{235}_{92}\text{U} \to {}^{4}_{2}\text{He} + {}^{231}_{90}\text{Th}$$
(4.2.2)

How do we know that a product of the reaction is $^{231}_{90}$ Th? We use the law of conservation of matter, which says that matter cannot be created or destroyed. This means we must have the same number of protons and neutrons on both sides of the chemical equation. If our uranium nucleus loses 2 protons, there are 90 protons remaining, identifying the element as thorium. Moreover, if we lose 4 nuclear particles of the original 235, there are 231 remaining. Thus, we use subtraction to identify the isotope of the thorium atom—in this case, $^{20}_{90}$ Th.

Chemists often use the names *parent isotope* and *daughter isotope* to represent the original atom and the product other than the alpha particle. In the previous example, $^{235}_{92}$ U is the parent isotope, and $^{231}_{90}$ Th is the daughter isotope. When one element changes into another in this manner, it undergoes *radioactive decay*.

Example 4.2.1: Radon-222

Write the nuclear equation that represents the radioactive decay of radon-222 by alpha particle emission and identify the daughter isotope.

SOLUTION

Radon has an atomic number of 86, so the parent isotope is represented as ${}^{222}_{86}$ Rn. We represent the alpha particle as ${}^{4}_{2}$ He and use subtraction (222 – 4 = 218 and 86 – 2 = 84) to identify the daughter isotope as an isotope of polonium, ${}^{218}_{84}$ Po:

 $^{222}_{86}{\rm Rn} \rightarrow \, {}^{4}_{2}{\rm He} + \, {}^{218}_{84}{\rm Po}$

Exercise 4.2.1: Polonium-209

Write the nuclear equation that represents the radioactive decay of polonium-209 by alpha particle emission and identify the daughter isotope.



$${}^{14}_{6}\text{C} \rightarrow {}^{14}_{7}\text{N} + {}^{0}_{-1}\text{e}$$
 (4.2.3)

CHEMISTRY

Again, the sum of the atomic numbers is the same on both sides of the equation, as is the sum of the mass numbers. (Note that the electron is assigned an "atomic number" of 1–, equal to its charge.)

The third major type of radioactive emission is not a particle but rather a very energetic form of electromagnetic radiation called gamma rays, symbolized by the Greek letter γ . Gamma rays themselves do not carry an overall electrical charge, but they may knock electrons out of atoms in a sample of matter and make it electrically charged (for which gamma rays are termed *ionizing radiation*). For example, in the radioactive decay of radon-222, both alpha and gamma radiation are emitted, with the latter having an energy of 8.2×10^{-14} J per nucleus decayed:

$${}^{222}_{86}\text{Rn} \to {}^{218}_{84}\text{Po} + {}^{4}_{2}\text{He} + \gamma \tag{4.2.4}$$

This may not seem like much energy, but if 1 mol of radon atoms were to decay, the gamma ray energy would be 49 million kJ!

Example 4.2.2: Boron-12

Write the nuclear equation that represents the radioactive decay of boron-12 by beta particle emission and identify the daughter isotope. A gamma ray is emitted simultaneously with the beta particle.

SOLUTION

The parent isotope is ${}_{5}^{12}B$ while one of the products is an electron, ${}_{-1}^{0}e$. So that the mass and atomic numbers have the same value on both sides, the mass number of the daughter isotope must be 12, and its atomic number must be 6. The element having an atomic number of 6 is carbon. Thus, the complete nuclear equation is as follows:

$${}^{12}_{5}\text{B} \to {}^{12}_{6}\text{C} + {}^{0}_{-1}\text{e} + \gamma \tag{4.2.5}$$

The daughter isotope is ${}^{12}_{6}$ C.

Exercise 4.2.2: Iodine-131

Write the nuclear equation that represents the radioactive decay of iodine-131 by beta particle emission and identify the daughter isotope. A gamma ray is emitted simultaneously with the beta particle.

Alpha, beta, and gamma emissions have different abilities to penetrate matter. The relatively large alpha particle is easily stopped by matter (although it may impart a significant amount of energy to the matter it contacts). Beta particles penetrate slightly into matter, perhaps a few centimeters at most. Gamma rays can penetrate deeply into matter and can impart a large amount of energy into the surrounding matter. Table 4.2.1 summarizes the properties of the three main types of radioactive emissions.

Characteristic	Alpha Particles	Beta Particles	Gamma Rays
symbols	$\alpha, {}_2^4 \mathrm{He}$	β , $_{-1}^{0}$ e	γ
identity	helium nucleus	electron	electromagnetic radiation
charge	2+	1-	none
mass number	4	0	0
penetrating power	minimal (will not penetrate skin)	short (will penetrate skin and some tissues slightly)	deep (will penetrate tissues deeply)

Occasionally, an atomic nucleus breaks apart into smaller pieces in a radioactive process called *spontaneous fission* (or fission). Typically, the daughter isotopes produced by fission are a varied mix of products, rather than a specific isotope as with alpha and beta particle emission. Often, fission produces excess neutrons that will sometimes be captured by other nuclei, possibly inducing additional radioactive events. Uranium-235 undergoes spontaneous fission to a small extent. One typical reaction is



$^{235}_{~92}\mathrm{U} \rightarrow ~^{139}_{~56}\mathrm{Ba} + ~^{94}_{~36}\mathrm{Kr} + 2~^{1}_{0}\mathrm{n}$

(4.2.6)

where ${}_{0}^{1}n$ is a neutron. As with any nuclear process, the sums of the atomic numbers and the mass numbers must be the same on both sides of the equation. Spontaneous fission is found only in large nuclei. The smallest nucleus that exhibits spontaneous fission is lead-208.

Fission is the radioactive process used in nuclear power plants and one type of nuclear bomb.

KEY TAKEAWAY

The major types of radioactivity include alpha particles, beta particles, and gamma rays.



4.3: HALF-LIFE

LEARNING OBJECTIVES

- To define *half-life*.
- To determine the amount of radioactive substance remaining after a given number of half-lives.

Whether or not a given isotope is radioactive is a characteristic of that particular isotope. Some isotopes are stable indefinitely, while others are radioactive and decay through a characteristic form of emission. As time passes, less and less of the radioactive isotope will be present, and the level of radioactivity decreases. An interesting and useful aspect of radioactive decay is the **half-life**. The half-life of a radioactive isotope is the amount of time it takes for one-half of the radioactive isotope to decay. The half-life of a specific radioactive isotope is constant; it is unaffected by conditions and is independent of the initial amount of that isotope.

Consider the following example. Suppose we have 100.0 g of ³H (tritium, a radioactive isotope of hydrogen). It has a half-life of 12.3 y. After 12.3 y, half of the sample will have decayed to ³He by emitting a beta particle, so that only 50.0 g of the original ³H remains. After another 12.3 y—making a total of 24.6 y—another half of the remaining ³H will have decayed, leaving 25.0 g of ³H. After another 12.3 y—now a total of 36.9 y—another half of the remaining ³H will have decayed, leaving 12.5 g of ³H. This sequence of events is illustrated in Figure 4.3.1



Figure 4.3.1: Radioactive Decay. During each successive half-life, half of the initial amount will radioactively decay.

We can determine the amount of a radioactive isotope remaining after a given number half-lives by using the following expression:

amount remaining = initial amount
$$\times \left(\frac{1}{2}\right)^n$$
 (4.3.1)

where *n* is the number of half-lives. This expression works even if the number of half-lives is not a whole number.

Example 4.3.1: Fluorine-20

The half-life of ²⁰F is 11.0 s. If a sample initially contains 5.00 g of ²⁰F, how much ²⁰F remains after 44.0 s?

SOLUTION

If we compare the time that has passed to the isotope's half-life, we note that 44.0 s is exactly 4 half-lives, so we can use Equation ??? with n = 4. Substituting and solving results in the following:

$$egin{aligned} ext{amount remaining} &= 5.00 \ g imes \left(rac{1}{2}
ight)^4 \ &= 5.00 \ g imes rac{1}{16} \ &= 0.313 \ g \end{aligned}$$

Less than one-third of a gram of ²⁰F remains.

Exercise 4.3.1: Titanium-44

The half-life of ⁴⁴Ti is 60.0 y. A sample initially contains 0.600 g of ⁴⁴Ti. How much ⁴⁴Ti remains after 180.0 y?



Half-lives of isotopes range from fractions of a microsecond to billions of years. Table 4.3.1 lists the half-lives of some isotopes.

Table 4.3.1: Half-Lives of Various Isotopes

Isotope	Half-Life
³ Н	12.3 у
¹⁴ C	5,730 y
40 K	$1.26 \times 10^9 \mathrm{y}$
⁵¹ Cr	27.70 d
⁹⁰ Sr	29.1 у
¹³¹ I	8.04 d
²²² Rn	3.823 d
²³⁵ U	$7.04 imes 10^8 \mathrm{y}$
²³⁸ U	$4.47\times10^9\mathrm{y}$
²⁴¹ Am	432.7 у
$^{248}\mathrm{Bk}$	23.7 h
²⁶⁰ Sg	4 ms

Example 4.3.2: Iodine-125

The isotope I-125 is used in certain laboratory procedures and has a half-life of 59.4 days. If the initial activity of a sample of I-125 is 32,000 counts per minute (cpm), how much activity will be present in 178.2 days?

Solution

We begin by determining how many half-lives are represented by 178.2 days:

 $\frac{178.2~{\rm days}}{59.4~{\rm days}/{\rm half-life}}=3~{\rm half-lives}$

Then we simply count activity:

initial activity $(t_0) = 32,000$ cpm after one half-life = 16,000 cpm after two half-lives = 8,000 cpm after three half-lives = 4,000 cpm

Be sure to keep in mind that the initial count is at time zero (t_0) and we subtract from that count at the first half-life. The second half-life has an activity of half the previous count (not the initial count).

Equation 4.3.1 can be used to calculate the amount of radioactivity remaining after a given time:

$$N_t = N_0 imes (0.5)^{
m number of half-lives}$$

where $N_t =$ activity at time t and $N_0 =$ initial activity at time t = 0 .

If we have an initial activity of 42,000 cpm, what will the activity be after four half-lives?

$$egin{aligned} N_t &= N_0(0.5)^4 \ &= (42,000)\,(0.5)\,(0.5)\,(0.5)\,(0.5)\,(0.5) \ &= 2625 ext{ cpm} \end{aligned}$$





Typical radioactive decay curve.

The graph above illustrates a typical decay curve for I - 125. The activity decreases by one-half during each succeeding half-life.

LOOKING CLOSER: HALF-LIVES OF RADIOACTIVE ELEMENTS

Many people think that the half-life of a radioactive element represents the amount of time an element is radioactive. In fact, it is the time required for half—not all—of the element to decay radioactively. Occasionally, however, the daughter element is also radioactive, so its radioactivity must also be considered.

The expected working life of an ionization-type smoke detector (described in the opening essay) is about 10 years. In that time, americium-241, which has a half-life of about 432 y, loses less than 4% of its radioactivity. A half-life of 432 y may seem long to us, but it is not very long as half-lives go. Uranium-238, the most common isotope of uranium, has a half-life of about 4.5×10^9 y, while thorium-232 has a half-life of 14×10^9 y.

On the other hand, some nuclei have extremely short half-lives, presenting challenges to the scientists who study them. The longestlived isotope of lawrencium, ²⁶²Lr, has a half-life of 3.6 h, while the shortest-lived isotope of lawrencium, ²⁵²Lr, has a half-life of 0.36 s. As of this writing, the largest atom ever detected has atomic number 118, mass number 293, and a half-life of 120 ns. Can you imagine how quickly an experiment must be done to determine the properties of elements that exist for so short a time?

KEY TAKEAWAYS

- Natural radioactive processes are characterized by a half-life, the time it takes for half of the material to decay radioactively.
- The amount of material left over after a certain number of half-lives can be easily calculated.



4.4: UNITS OF RADIOACTIVITY

LEARNING OBJECTIVES

• To express amounts of radioactivity in a variety of units.

Previously, we used mass to indicate the amount of radioactive substance present. This is only one of several units used to express amounts of radiation. Some units describe the number of radioactive events occurring per unit time, while others express the amount of a person's exposure to radiation.

Perhaps the direct way of reporting radioactivity is the number of radioactive decays per second. One decay per second is called one becquerel (Bq). Even in a small mass of radioactive material, however, there are many thousands of decays or disintegrations per second. The unit curie (Ci), now defined as 3.7×10^{10} decays per second, was originally defined as the number of decays per second in 1 g of radioactive samples have activities that are on the order of microcuries (µCi) or more. Both the becquerel and curie can be used in place of grams to describe quantities of radioactive material. As an example, the amount of americium in an average smoke detector has an activity of 0.9 µCi.

The unit becquerel is named after Henri Becquerel, who discovered radioactivity in 1896. The unit curie is named after Polish scientist Marie Curie, who performed some of the initial investigations into radioactive phenomena and discovered the elements, polonium (Po) and radium (Ra) in the early 1900s.

Example 4.4.1

A sample of radium has an activity of 16.0 mCi (millicuries). If the half-life of radium is 1,600 y, how long before the sample's activity is 1.0 mCi?

SOLUTION

The following table shows the activity of the radium sample over multiple half-lives:

Time in Years	Activity
0	16.0 mCi
1,600	8.0 mCi
3,200	4.0 mCi
4,800	2.0 mCi
6,400	1.0 mCi

Over a period of 4 half-lives, the activity of the radium will be halved four times, at which point its activity will be 1.0 mCi. Thus, it takes 4 half-lives, or $4 \times 1,600$ y = 6,400 y, for the activity to decrease to 1.0 mCi.

Exercise 4.4.1

A sample of radon has an activity of 60,000 Bq. If the half-life of radon is 15 h, how long before the sample's activity is 3,750 Bq?

Other measures of radioactivity are based on the effects it has on living tissue. Radioactivity can transfer energy to tissues in two ways: through the kinetic energy of the particles hitting the tissue and through the electromagnetic energy of the gamma rays being absorbed by the tissue. Either way, the transferred energy—like thermal energy from boiling water—can damage the tissue.

The rad (an acronym for radiation absorbed dose) is a unit equivalent to a gram of tissue absorbing 0.01 J:

1 rad = 0.01 J/g

Another unit of radiation absorption is the gray (Gy):

1 Gy = 100 rad

The rad is more common. To get an idea of the amount of energy this represents, consider that the absorption of 1 rad by 70,000 g of H_2O (approximately the same mass as a 150 lb person) would increase its temperature by only 0.002°C. This may not seem like a lot, but it is enough energy to break about 1 × 10²¹ molecular C–C bonds in a person's body. That amount of damage would not be desirable.

Predicting the effects of radiation is complicated by the fact that various tissues are affected differently by different types of emissions. To quantify these effects, the unit **rem** (an acronym for roentgen equivalent, man) is defined as



$rem = rad \times factor$

where *factor* is a number greater than or equal to 1 that takes into account the type of radioactive emission and sometimes the type of tissue being exposed. For beta particles, the factor equals 1. For alpha particles striking most tissues, the factor is 10, but for eye tissue, the factor is 30. Most radioactive emissions that people are exposed to are on the order of a few dozen millirems (mrem) or less; a medical X ray is about 20 mrem. A sievert (Sv) is a related unit and is defined as 100 rem.

What is a person's annual exposure to radioactivity and radiation? Table 4.4.1 lists the sources and annual amounts of radiation exposure. It may surprise you to learn that fully 82% of the radioactivity and radiation exposure we receive is from natural sources—sources we cannot avoid. Fully 10% of the exposure comes from our own bodies—largely from ¹⁴C and ⁴⁰K.



Table 4.4.1: Average Annual Radiatio	on Exposure (Approximate)
Source	Amount (mrem)
radon gas	200
medical sources	53
radioactive atoms in the body naturally	39
terrestrial sources	28
cosmic sources	28
consumer products	10
nuclear energy	0.05
Total	358

Flying from New York City to San Francisco adds 5 mrem to your overall radiation exposure because the plane flies above much of the atmosphere, which protects us from most cosmic radiation.

The actual effects of radioactivity and radiation exposure on a person's health depend on the type of radioactivity, the length of exposure, and the tissues exposed. Table 4.4.2 lists the potential threats to health at various amounts of exposure over short periods of time (hours or days).

Exposure (rem)	Effect
1 (over a full year)	no detectable effect
~20	increased risk of some cancers
~100	damage to bone marrow and other tissues; possible internal bleeding; decrease in white blood cell count
200–300	visible "burns" on skin, nausea, vomiting, and fatigue
>300	loss of white blood cells; hair loss
~600	death

One of the simplest ways of detecting radioactivity is by using a piece of photographic film embedded in a badge or a pen. On a regular basis, the film is developed and checked for exposure. A comparison of the exposure level of the film with a set of standard exposures indicates the amount of radiation a person was exposed to.





Figure 4.4.1: Detecting Radioactivity. A Geiger counter is a common instrument used to detect radioactivity.

Another means of detecting radioactivity is an electrical device called a Geiger counter (Figure 4.4.1). It contains a gas-filled chamber with a thin membrane on one end that allows radiation emitted from radioactive nuclei to enter the chamber and knock electrons off atoms of gas (usually argon). The presence of electrons and positively charged ions causes a small current, which is detected by the Geiger counter and converted to a signal on a meter or, commonly, an audio circuit to produce an audible "click."

KEY TAKEAWAY

• Radioactivity can be expressed in a variety of units, including rems, rads, and curies.

4.5: USES OF RADIOACTIVE ISOTOPES

LEARNING OBJECTIVES

• To learn some applications of radioactivity.

Radioactive isotopes have a variety of applications. Generally, however, they are useful either because we can detect their radioactivity or we can use the energy they release.

Radioactive isotopes are effective tracers because their radioactivity is easy to detect. A tracer is a substance that can be used to follow the pathway of that substance through some structure. For instance, leaks in underground water pipes can be discovered by running some tritium-containing water through the pipes and then using a Geiger counter to locate any radioactive tritium subsequently present in the ground around the pipes. (Recall that tritium, ³H, is a radioactive isotope of hydrogen.)

Tracers can also be used to follow the steps of a complex chemical reaction. After incorporating radioactive atoms into reactant molecules, scientists can track where the atoms go by following their radioactivity. One excellent example of this is the use of radioactive carbon-14 to determine the steps involved in the photosynthesis in plants. We know these steps because researchers followed the progress of the radioactive carbon-14 throughout the process.

Radioactive isotopes are useful for establishing the ages of various objects. The half-life of radioactive isotopes is unaffected by any environmental factors, so the isotope acts like an internal clock. For example, if a rock is analyzed and is found to contain a certain amount of uranium-235 and a certain amount of its daughter isotope, we can conclude that a certain fraction of the original uranium-235 has radioactively decayed. If half of the uranium has decayed, then the rock has an age of one half-life of uranium-235, or about 4.5×10^9 y. Many analyses like this, using a wide variety of isotopes, have indicated that the age of Earth itself is over 4×10^9 y. In another interesting example of radioactive dating, ³H dating has been used to verify the stated vintages of some old fine wines.

Carbon-14 (half-life is 5,370 y) is particularly useful in determining the age of once-living artifacts (e.g., animal or plant matter). A tiny amount of carbon-14 is produced naturally in the upper reaches of the atmosphere, and living things incorporate some of it into their tissues, building up to a constant, although very low, level. Once a living thing dies, however, it no longer acquires carbon-14, and as time passes, the carbon-14 that was in the tissues decays. If a once-living artifact is discovered and analyzed many years after its death, with the remaining carbon-14 compared to the known constant level, an approximate age of the artifact can be determined. Using such methods, scientists determined that the age of the Shroud of Turin (made of linen, which comes from the flax plant, and purported by some to be the burial cloth of Jesus Christ; Figure 4.5.1) is about 600–700 y, not 2,000 y as claimed by some. Scientists were also able to use radiocarbon dating to show that the age of a mummified body found in the ice of the Alps was 5,300 y.



Figure 4.5.1: Shroud of Turin. In 1989, several groups of scientists used carbon-14 dating to demonstrate that the age of the Shroud of Turin was only 600–700 y. Many people still cling to a different notion, despite the scientific evidence.

The radiation emitted by some radioactive substances can be used to kill microorganisms on a variety of foodstuffs, which extends the shelf life of these products. Produce such as tomatoes, mushrooms, sprouts, and berries are irradiated with the emissions from cobalt-60 or cesium-137. This exposure kills a lot of the bacteria that cause spoilage, so the produce stays fresh longer. Eggs and some meat, such as beef, pork, and poultry, can also be irradiated. Contrary to the belief of some people, irradiation of food *does not* make the food itself radioactive.

Radioactive isotopes have numerous medical applications—diagnosing and treating illnesses and diseases. One example of a diagnostic application is using radioactive iodine-131 to test for thyroid activity (Figure 4.5.2). The thyroid gland in the neck is one of the few places in the body with a significant concentration of iodine. To evaluate thyroid activity, a measured dose of iodine-131 is administered to a patient, and the next day a scanner is used to measure the amount of radioactivity in the thyroid gland. The amount of radioactive iodine that collects there is directly related to the activity of the thyroid, allowing trained physicians to diagnose both



hyperthyroidism and hypothyroidism. Iodine-131 has a half-life of only 8 d, so the potential for damage due to exposure is minimal. Technetium-99 can also be used to test thyroid function. Bones, the heart, the brain, the liver, the lungs, and many other organs can be imaged in similar ways by using the appropriate radioactive isotope.



Figure 4.5.2: Medical Diagnostics. Radioactive iodine can be used to image the thyroid gland for diagnostic purposes. Source: Scan courtesy of Myo Han, http://en.wikipedia.org/wiki/File:Thyroid_scan.jpg.

Very little radioactive material is needed in these diagnostic techniques because the radiation emitted is so easy to detect. However, therapeutic applications usually require much larger doses because their purpose is to preferentially kill diseased tissues. For example, if a thyroid tumor is detected, a much larger infusion (thousands of rem, as opposed to a diagnostic dose of less then 40 rem) of iodine-131 could help destroy the tumor cells. Similarly, radioactive strontium is used to not only detect but also ease the pain of bone cancers. Table 4.5.1 lists several radioactive isotopes and their medical uses.

	Table 4.5.1: Some Radioactive Isotopes That Have Medical Applications
Isotope	Use
³² P	cancer detection and treatment, especially in eyes and skin
⁵⁹ Fe	anemia diagnosis
⁶⁰ Co	gamma ray irradiation of tumors
^{99m} Tc	brain, thyroid, liver, bone marrow, lung, heart, and intestinal scanning; blood volume determination
¹³¹ I	diagnosis and treatment of thyroid function
¹³³ Xe	lung imaging
¹⁹⁸ Au	liver disease diagnosis

In addition to the direct application of radioactive isotopes to diseased tissue, the gamma ray emissions of some isotopes can be directed toward the tissue to be destroyed. Cobalt-60 is a useful isotope for this kind of procedure.

TO YOUR HEALTH: POSITRON EMISSION TOMOGRAPHY SCANS

One relatively rare form of radioactivity is called *positron emission*. It is similar to beta particle emission, except that instead of emitting an electron, a nucleus emits a positively charged electron, called a *positron*. A positron is actually a piece of antimatter; therefore, when a positron encounters an electron, both particles are converted into high-energy gamma radiation.



CHEMISTRY 🏓

Isotopes that emit positrons can be employed in a medical imaging technique called *positron emission tomography (PET)*. A patient receives a compound containing a positron-emitting isotope, either intravenously or by ingestion. The radioactive compound travels throughout the body, and the patient is then pushed slowly through a ring of sensors that detect the gamma radiation given off by the annihilation of positrons and electrons. A computer connected to the sensors constructs a three-dimensional image of the interior of part or all of the patient's body, allowing doctors to see organs or tumors or regulate the function of various organs (such as the brain or the heart) to diagnose the medical condition of the patient.



Figure **4.5.3**: (left) Combined apparatus for positron emission tomography (PET) and X-ray computer tomography (CT), Siemens Biograph (right) Whole-body PET scan using ¹⁸F-FDG. Images used with permission from Wikipedia.

Two isotopes that undergo positron emission are carbon-11 and fluorine-18, with half-lives of 20.4 and 110 min, respectively. Both isotopes can be incorporated into sugar molecules and introduced into the body. Doctors can use the intensity of gamma ray emission to find tissues that metabolize the sugar faster than other tissues; fast-metabolizing tissue is one sign of a malignant (i.e., cancerous) tumor. Researchers use similar techniques to map areas of the brain that are most active during specific tasks, such as reading or speaking.

PET is one of many diagnostic and treatment methods that physicians use to improve the quality of our lives. It is one of the many positive uses of radioactivity in society.

KEY TAKEAWAY

• Radioactivity has several practical applications, including tracers, medical applications, dating once-living objects, and the preservation of food.



4.6: NUCLEAR ENERGY

LEARNING OBJECTIVES

- Explain where nuclear energy comes from.
- Describe the difference between fission and fusion.

Nuclear changes occur with a simultaneous release of energy. Where does this energy come from? If we could precisely measure the masses of the reactants and the products of a nuclear reaction, we would notice that the amount of mass drops slightly in the conversion from reactants to products. Consider the following nuclear reaction, in which the molar mass of each species is indicated to four decimal places:

$$\underbrace{\overset{235}{\underset{0439}{\longrightarrow}}}_{235,0439} \to \underbrace{\overset{139}{\underset{138}{\longrightarrow}}}_{138,9088} + \underbrace{\overset{94}{\underset{03,9343}{\longrightarrow}}}_{23,9343} + \underbrace{\overset{1}{\underset{043}{\xrightarrow}}}_{2\times1,0087} 10087$$
(4.6.1)

If we compare the mass of the reactant (235.0439) to the masses of the products (sum = 234.8605), we notice a mass difference of -0.1834 g, or -0.0001834 kg. Where did this mass go?

According to Albert Einstein's theory of relativity, energy (*E*) and mass (*m*) are related by the following equation:

$$E = mc^2 \tag{4.6.2}$$

where *c* is the speed of light, or 3.00×10^8 m/s. In the course of the uranium nuclear chemical reaction, the mass difference is converted to energy, which is given off by the reaction:

$$egin{aligned} E &= (-0.0001834 \; kg)(3.00 imes 10^8 \; m/s)^2 \ &= -1.65 imes 10^{13} \; J \ &= -1.65 imes 10^{10} \; kJ \end{aligned}$$

That is, 16.5 billion kJ of energy are given off every time 1 mol of uranium-235 undergoes this nuclear reaction. This is an extraordinary amount of energy. Compare it to combustion reactions of hydrocarbons, which give off about 650 kJ/mol of energy for every CH_2 unit in the hydrocarbon—on the order of *hundreds* of kilojoules per mole. Nuclear reactions give off *billions* of kilojoules per mole.

If this energy could be properly harvested, it would be a significant source of energy for our society. Nuclear energy involves the controlled harvesting of energy from fission reactions. The reaction can be controlled because the fission of uranium-235 (and a few other isotopes, such as plutonium-239) can be artificially initiated by injecting a neutron into a uranium nucleus. The overall nuclear equation, with energy included as a product, is then as follows:

 $^{235}\text{U} + {}^{1}\text{n} \rightarrow {}^{139}\text{Ba} + {}^{94}\text{Kr} + 3{}^{1}\text{n} + \text{energy}$

Thus, by the careful addition of extra neutrons into a sample of uranium, we can control the fission process and obtain energy that can be used for other purposes.

THE CURIE FAMILY

Artificial or induced radioactivity was first demonstrated in 1934 by Irène Joliot-Curie and Frédéric Joliot, the daughter and son-inlaw of Marie Curie.

Example 4.6.1: Plutonium-239

Plutonium-239 can absorb a neutron and undergo a fission reaction to produce an atom of gold-204 and an atom of phosphorus-31. Write the balanced nuclear equation for the process and determine the number of neutrons given off as part of the reaction.

SOLUTION

Using the data given, we can write the following initial equation:

$$^{1}_{0}\mathrm{n}+ ^{239}_{94}\mathrm{Pu}
ightarrow ^{204}_{79}\mathrm{Au} + ^{31}_{15}\mathrm{P} + ?^{1}_{0}\mathrm{n}$$

In balanced nuclear equations, the sums of the subscripts on each sides of the equation are the same, as are the sums of the superscripts. The subscripts are already balanced: 0 + 94 = 94 and 79 + 15 = 94. The superscripts on the left equal 240 (1 + 239) but equal 235 (204 + 31) on the right. We need five more mass number units on the right. Five neutrons should be the products of the process for the mass numbers to balance. (Because the atomic number of a neutron is zero, including five neutrons on the right does not change the overall sum of the subscripts.) Thus, the balanced nuclear equation is as follows:



$$^{1}_{0}\mathrm{n} + ^{239}_{94}\mathrm{Pu}
ightarrow ^{204}_{79}\mathrm{Au} + ^{31}_{15}\mathrm{P} + 5^{1}_{0}\mathrm{n}$$

We predict that the overall process will give off five neutrons.

Exercise 4.6.1

Uranium-238 can absorb a neutron and undergo a fission reaction to produce an atom of cesium-135 and an atom of rubidium-96. Write the balanced nuclear equation for the process and determine the number of neutrons given off as part of the reaction.

A nuclear reactor is an apparatus designed to carefully control the progress of a nuclear reaction and extract the resulting energy for useful purposes. Figure 4.6.1 shows a simplified diagram of a nuclear reactor. The energy from the controlled nuclear reaction converts liquid water into high-pressure steam, which is used to run turbines that generate electricity.



Figure 4.6.1: A Diagram of a Nuclear Power Plant for Generating Electricity. The two main components of the power plant are the nuclear reactor itself and the steam-driven turbine and electricity generator.

Notice that the fission of uranium produces two more free neutrons than were present to begin with. These neutrons can themselves stimulate other uranium nuclei to undergo fission, releasing yet more energy and even more neutrons, which can in turn induce even more uranium fission. A single neutron can thus begin a process that grows exponentially in a phenomenon called a chain reaction:

 $1 \rightarrow 2 \rightarrow 4 \rightarrow 8 \rightarrow 16 \rightarrow 32 \rightarrow 64 \rightarrow 128 \rightarrow 256 \rightarrow 512 \rightarrow 1,024 \rightarrow 2,048 \rightarrow 4,096 \rightarrow 8,192 \rightarrow 16,384 \rightarrow \dots$

Because energy is produced with each fission event, energy is also produced exponentially and in an uncontrolled fashion. The quick production of energy creates an explosion. This is the mechanism behind the atomic bomb.

The first controlled chain reaction was achieved on December 2, 1942, in an experiment supervised by Enrico Fermi in a laboratory underneath the football stadium at the University of Chicago.

Although fairly simple in theory, an atomic bomb is difficult to produce, in part because uranium-235, the isotope that undergoes fission, makes up only 0.7% of natural uranium; the rest is mostly uranium-238, which does not undergo fission. (Remember that the radioactive process that a nucleus undergoes is characteristic of the isotope.) To make uranium useful for nuclear reactors, the uranium in uranium-235 must be *enriched* to about 3%. Enrichment of uranium is a laborious and costly series of physical and chemical separations. To be useful in an atomic bomb, the uranium in uranium-235 must be enriched to 70% or more. At lesser concentrations, the chain reaction cannot sustain itself, so no explosion is produced.

Fusion is another nuclear process that can be used to produce energy. In this process, smaller nuclei are combined to make larger nuclei, with an accompanying release of energy. One example is the hydrogen fusion, which makes helium. While the steps of the process are complicated, the net reaction is:

$$4 \,{}^{1}\text{H} \rightarrow {}^{4}\text{He} + 2.58 \times 10^{12} J$$
 (4.6.3)

Notice that the amount of energy given off per mole of reactant is only a fraction of the amount given off by the fission of 1 mol of uranium-235. On a mass (per gram) basis, however, the hydrogen fusion emits many times more energy than fission does. In addition, the product of fission is helium gas, not a wide range of isotopes (some of which are also radioactive) produced by fission.

The practical problem is that to perform fusion, extremely high pressures and temperatures are necessary. Currently, the only known stable systems undergoing fusion are the interiors of stars. The conditions necessary for fusion can be created using an atomic bomb,



but the resulting fusion is uncontrollable (and the basis for another type of bomb, a hydrogen bomb). Currently, researchers are looking for safe, controlled ways of producing useful energy using fusion.

CAREER FOCUS: NUCLEAR MEDICINE TECHNOLOGIST

Generally speaking, a radiological technician deals with X ray equipment and procedures. A *nuclear medicine technologist* has similar responsibilities, using compounds containing radioactive isotopes to help diagnose and treat disease.

Nuclear medicine technologists administer the substances containing the radioactive isotope and subsequently operate the apparatus that detects the radiation produced by radioactive decay. The apparatus may be as simple as a piece of photographic film or as complex as a series of computer-controlled electronic detectors. The images obtained by the technologist are interpreted by a specially trained physician.

One of the chief responsibilities of a nuclear medicine technologist is safety. Improper exposure to radioactivity can be harmful to both patient and technologist alike. Therefore, the technologist must adhere to strict safety standards to keep unnecessary exposure as low as possible. The technologist must also know how to dispose of waste materials safely and appropriately.

KEY TAKEAWAYS

- Nuclear energy comes from tiny mass changes in nuclei as radioactive processes occur.
- In fission, large nuclei break apart and release energy; in fusion, small nuclei merge together and release energy.



4.7: NUCLEAR CHEMISTRY (EXERCISES)

11.1 RADIOACTIVITY

CONCEPT REVIEW EXERCISE

1. What are the major types of radioactivity? Write chemical equations demonstrating each type.

ANSWER

1. The major types of radioactivity are alpha decay, beta decay, and gamma ray emission; alpha decay with gamma emission: ${}^{222}_{86}$ Rn $\rightarrow {}^{218}_{84}$ Po $+ {}^{4}_{2}$ He $+ \gamma$; beta decay: ${}^{14}_{6}$ C $\rightarrow {}^{14}_{7}$ N $+ {}^{0}_{-1}$ e (answers will vary)

EXERCISES

- 1. Define *radioactivity*.
- 2. Give an example of a radioactive isotope.
- 3. How many protons and neutrons are in each isotope?
 - a. ${}^{11}_5\mathrm{B}$ b. ${}^{27}_{13}\mathrm{Al}$
 - c. ⁵⁶Fe
 - d. 224Rn

4. How many protons and neutrons are in each isotope?

a. ${}^{2}_{1}H$ b. ${}^{112}_{48}Cd$ c. ${}^{252}Es$ d. ${}^{40}K$

- 5. Describe an alpha particle. What nucleus is it equivalent to?
- 6. Describe a beta particle. What subatomic particle is it equivalent to?
- 7. Explain what gamma rays are.
- 8. Explain why it is inappropriate to refer to gamma rays as gamma "particles."
- 9. Plutonium has an atomic number of 94. Write the chemical equation for the alpha particle emission of ²⁴⁴Pu. What is the daughter isotope?
- 10. Francium has an atomic number of 87. Write the chemical equation for the alpha particle emission of ²¹²Fr. What is the daughter isotope?
- 11. Tin has an atomic number of 50. Write the chemical equation for the beta particle emission of ¹²¹Sn. What is the daughter isotope?
- 12. Technetium has an atomic number of 43. Write the chemical equation for the beta particle emission of ⁹⁹Tc. What is the daughter isotope?
- 13. Energies of gamma rays are typically expressed in units of megaelectron volts (MeV), where 1 MeV = 1.602×10^{-13} J. Using data provided in the text, calculate the energy, in megaelectron volts, of the gamma ray emitted when radon-222 decays.
- 14. The gamma ray emitted when oxygen-19 gives off a beta particle is 0.197 MeV. What is its energy in joules? (See Exercise 13 for the definition of a megaelectron volt.)
- 15. Which penetrates matter more deeply—alpha particles or beta particles? Suggest ways to protect yourself against both particles.
- 16. Which penetrates matter more deeply—alpha particles or gamma rays? Suggest ways to protect yourself against both emissions.
- 17. Define nuclear fission.
- 18. What general characteristic is typically necessary for a nucleus to undergo spontaneous fission?

ANSWERS

- 1. Radioactivity is the spontaneous emission of particles and radiation from atomic nuclei.
- 3. a. 5 protons; 6 neutrons
 - b. 13 protons; 14 neutrons
 - c. 26 protons; 30 neutrons
 - d. 86 protons; 138 neutrons



- 5. An alpha particle is a combination of two protons and two neutrons and is equivalent to a helium nucleus.
- 7. Gamma rays are high-energy electromagnetic radiation given off in radioactive decay.
- 9. ${}^{244}_{94}Pu \rightarrow {}^{4}_{2}He + {}^{240}_{92}U$; the daughter isotope is ${}^{240}_{92}U$, an atom of uranium.
- $11. {}^{121}_{50}Sn \rightarrow {}^0_{-1}e + {}^{121}_{51}Sb$; the daughter isotope is ${}^{121}_{51}Sb$, an atom of antimony.
- 13. 0.512 MeV
- 15. Beta particles; shielding of the appropriate thickness can protect against both alpha and beta particles.
- 17. Nuclear fission is when large nuclei break down into smaller nuclei.

11.2 HALF-LIFE

CONCEPT REVIEW EXERCISES

- 1. Define half-life.
- 2. Describe a way to determine the amount of radioactive isotope remaining after a given number of half-lives.

ANSWERS

- 1. Half-life is the amount of time needed for half of a radioactive material to decay.
- 2. take half of the initial amount for each half-life of time elapsed

EXERCISES

- 1. Do all isotopes have a half-life? Explain.
- 2. Which is more radioactive—an isotope with a long half-life or an isotope with a short half-life?
- 3. How long does it take for 1.00 g of ¹⁰³Pd to decay to 0.125 g if its half-life is 17.0 d?
- 4. How long does it take for 2.00 g of ⁹⁴Nb to decay to 0.0625 g if its half-life is 20,000 y?
- 5. It took 75 y for 10.0 g of a radioactive isotope to decay to 1.25 g. What is the half-life of this isotope?
- 6. It took 49.2 s for 3.000 g of a radioactive isotope to decay to 0.1875 g. What is the half-life of this isotope?

ANSWERS

- 1. Only radioactive isotopes have half-lives.
- 3. 51.0 d

5.25

11.3 UNITS OF RADIOACTIVITY

CONCEPT REVIEW EXERCISE

1. What units are used to quantify radioactivity?

ANSWER

1. the curie, the becquerel, the rad, the gray, the sievert, and the rem

EXERCISES

- 1. Define rad.
- 2. Define rem.
- 3. How does a becquerel differ from a curie?
- 4. How is the curie defined?
- 5. A sample of radon gas has an activity of 140.0 mCi. If the half-life of radon is 1,500 y, how long before the activity of the sample is 8.75 mCi?
- 6. A sample of curium has an activity of 1,600 Bq. If the half-life of curium is 24.0 s, how long before its activity is 25.0 Bq?
- 7. If a radioactive sample has an activity of 65 µCi, how many disintegrations per second are occurring?
- 8. If a radioactive sample has an activity of 7.55×10^5 Bq, how many disintegrations per second are occurring?
- 9. Describe how a radiation exposure in rems is determined.
- 10. Which contributes more to the rems of exposure—alpha or beta particles? Why?



- 11. Use Table 11.3.2 to determine which sources of radiation exposure are inescapable and which can be avoided. What percentage of radiation is unavoidable?
- 12. What percentage of the approximate annual radiation exposure comes from radioactive atoms that are in the body naturally?
- 13. Explain how a film badge works to detect radiation.
- 14. Explain how a Geiger counter works to detect radiation.

ANSWERS

- 1. Known as the radiation absorbed dose, a rad is the absorption of 0.01 J/g of tissue.
- 3. A becquerel is smaller and equals 1 decay per second. A curie is 3.7×10^{10} Bq.

5. 6000 y

- 7. 2.41×10^6 disintegrations per second
- 9. The radiation exposure is determined by the number of rads times the quality factor of the radiation.
- 11. At least 16% (terrestrial and cosmic sources) of radioactivity is unavoidable; the rest depends on what else a person is exposed to.
- 13. A film badge uses film, which is exposed as it is subjected to radiation.

11.4 USES OF RADIOACTIVE ISOTOPES

CONCEPT REVIEW EXERCISE

1. Describe some of the different ways that amounts of radioactivity are applied in society.

ANSWER

1. Radioactive isotopes are used in dating, as tracers, and in medicine as diagnostic and treatment tools.

EXERCISES

- 1. Define *tracer* is and give an example of how tracers work.
- 2. Name two isotopes that have been used as tracers.
- 3. Explain how radioactive dating works.
- 4. Name an isotope that has been used in radioactive dating.
- 5. The current disintegration rate for carbon-14 is 14.0 Bq. A sample of burnt wood discovered in an archaeological excavation is found to have a carbon-14 decay rate of 3.5 Bq. If the half-life of carbon-14 is 5,700 y, approximately how old is the wood sample?
- 6. A small asteroid crashes to Earth. After chemical analysis, it is found to contain 1 g of technetium-99 to every 3 g of ruthenium-99, its daughter isotope. If the half-life of technetium-99 is 210,000 y, approximately how old is the asteroid?
- 7. What do you think are some of the positive aspects of irradiation of food?
- 8. What do you think are some of the negative aspects of irradiation of food?
- 9. Describe how iodine-131 is used to both diagnose and treat thyroid problems.
- 10. List at least five organs that can be imaged using radioactive isotopes.
- 11. Which radioactive emissions can be used therapeutically?
- 12. Which isotope is used in therapeutics primarily for its gamma ray emissions?

ANSWERS

- 1. A tracer follows the path of a chemical or a physical process. One of the uses of a tracer is following the path of water underground (answers will vary).
- 3. Radioactive dating works by comparing the amounts of parent and daughter isotopes and calculating back to how long ago all of the material was just the parent isotope.
- 5. about 11,400 y
- 7. increased shelf life (answers will vary)
- 9. Iodine-131 is preferentially absorbed by the thyroid gland and can be used to measure the gland's activity or destroy bad cells in the gland.
- 11. gamma rays, beta particles, or alpha particles


11.5 NUCLEAR ENERGY

- CONCEPT REVIEW EXERCISES
- 1. How is nuclear energy produced?
- 2. What is the difference between fission and fusion?

ANSWERS

- 1. Nuclear energy is produced by carefully controlling the speed of a fission reaction.
- 2. In fission, large nuclei break down into small ones; in fusion, small nuclei combine to make larger ones. In both cases, a lot of energy is emitted.

EXERCISES

1. In the spontaneous fission of uranium-233, the following reaction occurs:

 $^{233}U + {}^{1}n \rightarrow {}^{142}Ce + {}^{82}Se + 10^{1}n$

For every mole of ²³³U that decays, 0.1355 g of mass is lost. How much energy is given off per mole of ²³³U reacted?

2. In the spontaneous fission of plutonium-241, the following reaction occurs:

 $^{241}\mathrm{Pu} + {}^{1}\mathrm{n} \rightarrow {}^{104}\mathrm{Ru} + {}^{124}\mathrm{Sn} + 14{}^{1}\mathrm{n}$

For every mole of ²⁴¹Pu that decays, 0.1326 g of mass is lost. How much energy is given off per mole of ²⁴¹Pu reacted?

3. The two rarer isotopes of hydrogen—deuterium and tritium—can also be fused to make helium by the following reaction:

 $^{2}\text{H} + {}^{3}\text{H} \rightarrow {}^{4}\text{He} + {}^{1}\text{n}$

In the course of this reaction, 0.01888 g of mass is lost. How much energy is emitted in the reaction of 1 mol of deuterium and tritium?

4. A process called *helium burning* is thought to occur inside older stars, forming carbon:

 3^4 He $\rightarrow {}^{12}$ C

If the reaction proceeds with 0.00781 g of mass lost on a molar basis, how much energy is given off?

- 5. Briefly describe how a nuclear reactor generates electricity.
- 6. Briefly describe the difference between how a nuclear reactor works and how a nuclear bomb works.
- 7. What is a chain reaction?
- 8. Why must uranium be enriched to supply nuclear energy?

ANSWERS

1. 1.22 $\times \, 10^{13} \, J$

- 3. $1.70 \times 10^{12} \text{ J}$
- 5. A nuclear reactor generates heat, which is used to generate steam that turns a turbine to generate electricity.
- 7. A chain reaction is an ever-expanding series of processes that, if left unchecked, can cause a runaway reaction and possibly an explosion.

11.6: CHAPTER SUMMARY

ADDITIONAL EXERCISES

- 1. Given that many elements are metals, suggest why it would be unsafe to have radioactive materials in contact with acids.
- 2. Many alpha-emitting radioactive substances are relatively safe to handle, but inhaling radioactive dust can be very dangerous. Why?
- 3. Uranium can be separated from its daughter isotope thorium by dissolving a sample in acid and adding sodium iodide, which precipitates thorium(III) iodide:

 $Th^{3+}(aq) + 3I^{-}(aq) \rightarrow ThI_{3}(s)$

If 0.567 g of Th³⁺ were dissolved in solution, how many milliliters of 0.500 M NaI(aq) would have to be added to precipitate all the thorium?

4. Thorium oxide can be dissolved in an acidic solution:

 $ThO_2(s) + 4H^+ \rightarrow Th^{4+}(aq) + 2H_2O(\ell)$



How many milliliters of 1.55 M HCl(aq) are needed to dissolve 10.65 g of ThO₂?

- 5. Radioactive strontium is dangerous because it can chemically replace calcium in the human body. The bones are particularly susceptible to radiation damage. Write the nuclear equation for the beta emission of strontium-90.
- 6. Write the nuclear equation for the beta emission of iodine-131, the isotope used to diagnose and treat thyroid problems.
- 7. A common uranium compound is uranyl nitrate hexahydrate [UO₂(NO₃)₂_6H₂O]. What is the formula mass of this compound?
- 8. Plutonium forms three oxides: PuO, PuO₂, and Pu₂O₃. What are the formula masses of these three compounds?
- 9. A banana contains 600 mg of potassium, 0.0117% of which is radioactive potassium-40. If 1 g of potassium-40 has an activity of 2.626 × 10^5 Bq, what is the activity of a banana?
- 10. Smoke detectors typically contain about 0.25 mg of americium-241 as part of the smoke detection mechanism. If the activity of 1 g of americium-241 is 1.26×10^{11} Bq, what is the activity of americium-241 in the smoke detector?
- 11. Uranium hexafluoride (UF₆) reacts with water to make uranyl fluoride (UO₂F₂) and hydrogen fluoride (HF). Balance the following chemical equation:

 $UF_6 + H_2O \rightarrow UO_2F_2 + HF$

12. The cyclopentadienyl anion (C₅H₅⁻) is an organic ion that can make ionic compounds with positive ions of radioactive elements, such as Np³⁺. Balance the following chemical equation:

 $NpCl_3 + Be(C_5H_5)_2 \rightarrow Np(C_5H_5)_3 + BeCl_2$

ANSWERS

- 1. Acids can dissolve metals, making aqueous solutions.
- 3. 14.7 mL

5. ${}^{90}_{38}{
m Sr} \rightarrow {}^{0}_{-1}{
m e} + {}^{90}_{39}{
m Y}$

- 7. 502 g/mol
- 9. about 18 Bq
- 11. UF₆ + 2H₂O \rightarrow UO₂F₂ + 4HF



4.8: NUCLEAR CHEMISTRY (SUMMARY)

To ensure that you understand the material in this chapter, you should review the meanings of the bold terms in the following summary and ask yourself how they relate to the topics in the chapter.

Some atoms have unstable nuclei that emit particles and high-energy electromagnetic radiation to form new elements that are more stable. This emission of particles and electromagnetic radiation is called **radioactivity**. There are three main types of spontaneous radioactive emission: **alpha particles**, which are equivalent to helium nuclei; **beta particles**, which are electrons; and **gamma radiation**, which is high-energy electromagnetic radiation. Another type of radioactive process is **spontaneous fission**, in which large nuclei spontaneously break apart into smaller nuclei and, often, neutrons. In all forms of radioactivity, new elements are formed from the radioactive reactants.

Radioactive isotopes decay at different rates. The rate of an isotope's decay is expressed as a **half-life**, which is the amount of time required for half of the original material to decay. The length of its half-life is a characteristic of the particular isotope and can range from less than microseconds to billions of years.

Amounts of radioactivity are measured in several different ways. A **becquerel** is equal to one radioactive decay per second. A **curie** represents 3.7×10^{10} decays per second. Other units describe the amount of energy absorbed by body tissues. One **rad** is equivalent to 0.01 joule of energy absorbed per gram of tissue. Different tissues react differently to different types of radioactivity. The **rem** unit takes into account not only the energy absorbed by the tissues, but also includes a numerical multiplication factor to account for the type of radioactivity and the type of tissue. The average annual radiation exposure of a person is less than 360 millirem, over 80% of which is from natural sources. Radioactivity can be detected using photographic film or other devices such as **Geiger counters**.

Radioactive isotopes have many useful applications. They can be used as **tracers** to follow the journey of a substance through a system, like an underground waterway or a metabolic pathway. Radioactive isotopes can be used to date objects, since the amount of parent and daughter isotopes can sometimes be measured very accurately. Radioactive emission can be used to sterilize food for a longer edible lifetime. There are also a number of diagnostic and therapeutic medical applications for radioactive isotopes.

Radioactive processes occur with simultaneous changes in energy. This **nuclear energy** can be used to generate power for human use. **Nuclear reactors** use the energy released by fission of large isotopes to generate electricity. When carefully controlled, fission can produce a **chain reaction** that facilitates the continuous production of energy. If not carefully controlled, a very quick production of energy can result, as in an **atomic bomb**. Natural uranium does not contain enough of the proper isotope of uranium to work in a nuclear reactor, so it must first be **enriched** in uranium-235. Forcing small nuclei together to make larger nuclei, a process called **fusion**, also gives off energy; however, scientists have yet to achieve a controlled fusion process.



5: IONIC BONDING AND SIMPLE IONIC COMPOUNDS

There are only 118 known chemical elements but tens of millions of known chemical compounds. Compounds can be very complex combinations of atoms, but many important compounds are fairly simple. Table salt, as we have seen, consists of only two elements: sodium and chlorine. Nevertheless, the compound has properties completely different from either elemental sodium (a chemically reactive metal) or elemental chlorine (a poisonous, green gas).

5.1: PRELUDE TO IONIC BONDING AND SIMPLE IONIC COMPOUNDS

We will see that the word salt has a specific meaning in chemistry, but to most people, this word refers to table salt. This kind of salt is used as a condiment throughout the world, but it was not always so abundant. Two thousand years ago, Roman soldiers received part of their pay as salt, which explains why the words salt and salary come from the same Latin root (salarium). Today, table salt is either mined or obtained from the evaporation of saltwater.

5.2: TWO TYPES OF BONDING

Atoms have a tendency to have eight electrons in their valence shell. The attraction of oppositely charged ions is what makes ionic bonds.

5.3: IONS

Ions can be positively charged or negatively charged. A Lewis diagram is used to show how electrons are transferred to make ions and ionic compounds.

5.4: FORMULAS FOR IONIC COMPOUNDS

Proper chemical formulas for ionic compounds balance the total positive charge with the total negative charge. Groups of atoms with an overall charge, called polyatomic ions, also exist.

5.5: IONIC NOMENCLATURE

Each ionic compound has its own unique name that comes from the names of the ions. After learning a few more details about the names of individual ions, you will be a step away from knowing how to name ionic compounds. This section begins the formal study of nomenclature, the systematic naming of chemical compounds.

5.6: FORMULA MASS

Formula masses of ionic compounds can be determined from the masses of the atoms in their formulas.

5.7: IONIC BONDING AND SIMPLE IONIC COMPOUNDS (EXERCISES)

These are homework exercises to accompany Chapter 3 of the Ball et al. "The Basics of GOB Chemistry" Textmap.

5.8: IONIC BONDING AND SIMPLE IONIC COMPOUNDS (SUMMARY)

To ensure that you understand the material in this chapter, you should review the meanings of the following bold terms and ask yourself how they relate to the topics in the chapter.



5.1: PRELUDE TO IONIC BONDING AND SIMPLE IONIC COMPOUNDS

We will see that the word salt has a specific meaning in chemistry, but to most people, this word refers to table salt. This kind of salt is used as a condiment throughout the world, but it was not always so abundant. Two thousand years ago, Roman soldiers received part of their pay as salt, which explains why the words salt and salary come from the same Latin root (salarium). Today, table salt is either mined or obtained from the evaporation of saltwater.

Table salt is sodium chloride (NaCl), which is a simple compound of two elements that are necessary for the human body to function properly. Sodium, for example, is important for nerve conduction and fluid balance. In fact, human blood is about a 0.9% sodium chloride solution, and a solution called normal saline is commonly administered intravenously in hospitals.

Although some salt in our diets is necessary to replenish the sodium and chloride ions that we excrete in urine and sweat, too much is unhealthy, and many people may be ingesting more salt than their bodies need. The RDI of sodium is 2,400 mg—the amount in about 1 teaspoon of salt—but the average intake of sodium in the United States is between 4,000 mg and 5,000 mg, partly because salt is a common additive in many prepared foods. Previously, the high ingestion of salt was thought to be associated with high blood pressure, but current research does not support this link. Even so, some doctors still recommend a low-salt diet (never a "no-salt" diet) for patients with high blood pressure, which may include using a salt substitute. Most salt substitutes use potassium instead of sodium, but some people complain that the potassium imparts a slightly bitter taste.



5.2: TWO TYPES OF BONDING

LEARNING OBJECTIVES

- Define the octet rule.
- Describe how ionic bonds are formed.

Atoms can join together by forming a chemical bond, which is a very strong attraction between two atoms. Chemical bonds are formed when electrons in different atoms interact with each other to make an arrangement that is more stable than when the atoms are apart.

What causes atoms to make a chemical bond with other atoms, rather than remaining as individual atoms? A clue comes by considering the noble gas elements, the rightmost column of the periodic table. These elements—helium, neon, argon, krypton, xenon, and radon—do not form compounds very easily, which suggests that they are especially stable as lone atoms. What else do the noble gas elements have in common? Except for helium, they all have eight valence electrons. Chemists have concluded that atoms are especially stable if they have eight electrons in their outermost shell. This useful rule of thumb is called the **octet rule**, and it is a key to understanding why compounds form.

Of the noble gases, only krypton, xenon, and radon have been found to make compounds.

There are two ways for an atom that does not have an octet of valence electrons to obtain an octet in its outer shell. One way is the transfer of electrons between two atoms until all atoms have octets. Because some atoms will lose electrons and some atoms will gain electrons, there is no overall change in the number of electrons, but individual atoms acquire a nonzero electric charge. Those that lose electrons become positively charged, and those that gain electrons become negatively charged. Charged atoms are called ions. Because opposite charges attract (while like charges repel), these oppositely charged ions attract each other, forming **ionic bonds**. The resulting compounds are called **ionic compounds** and are the primary subject of this chapter.

The second way for an atom to obtain an octet of electrons is by sharing electrons with another atom. These shared electrons simultaneously occupy the outermost shell of more than one atom. The bond made by electron sharing is called a **covalent bond**.

Despite our focus on the octet rule, we must remember that for small atoms, such as hydrogen, helium, and lithium, the first shell is, or becomes, the outermost shell and hold only two electrons. Therefore, these atoms satisfy a "**duet rule**" rather than the octet rule.

Example 5.2.1

A sodium atom has one valence electron. Do you think it is more likely for a sodium atom to lose one electron or gain seven electrons to obtain an octet?

SOLUTION

Although either event is possible, a sodium atom is more likely to lose its single valence electron. When that happens, it becomes an ion with a net positive charge. This can be illustrated as follows:

Sodiu	m atom	Sodium ion		
11 protons	11+	11 protons	11+	
11 electrons	11-	10 electrons	10-	
	0 overall charge		+1 overall charge	



$\mathsf{Exercise} \ 5.2.1$

A fluorine atom has seven valence electrons. Do you think it is more likely for a fluorine atom to lose seven electrons or gain one electron to obtain an octet?

KEY TAKEAWAYS

- Atoms have a tendency to have eight electrons in their valence shell.
- The attraction of oppositely charged ions is what makes ionic bonds.



5.3: IONS

LEARNING OBJECTIVES

- Define the two types of ions.
- Use Lewis diagrams to illustrate ion formation.

Most atoms do not have eight electrons in their valence electron shell. Some atoms have only a few electrons in their outer shell, while some atoms lack only one or two electrons to have an octet. In cases where an atom has three or fewer valence electrons, the atom may lose those valence electrons quite easily until what remains is a lower shell that contains an octet. Atoms that lose electrons acquire a positive charge as a result because they are left with fewer negatively charged electrons to balance the positive charges of the protons in the nucleus. Positively charged ions are called cations. Most metals become cations when they make ionic compounds.

Some atoms have nearly eight electrons in their valence shell and can gain additional valence electrons until they have an octet. When these atoms gain electrons, they acquire a negative charge because they now possess more electrons than protons. Negatively charged ions are called anions. Most nonmetals become anions when they make ionic compounds.

The names for positive and negative ions are pronounced CAT-eye-ons (cations) and ANN-eye-ons (anions), respectively.

ELECTRON TRANSFER

We can use electron configurations to illustrate the electron transfer process between sodium atoms and chlorine atoms.

Na

Na:
$$1s^2 2s^2 2p^6 3s^1$$

As demonstrated in Example 1, sodium is likely to achieve an octet in its outermost shell by losing its one valence electron. The remaining species has the following electron configuration:

$$\rightarrow$$
 Na⁺ + e⁻
1s² 2s² 2p⁶

The cation produced in this way, Na^+ , is called the sodium ion to distinguish it from the element. The outermost shell of the sodium ion is the second electron shell, which has eight electrons in it. The octet rule has been satisfied. Figure 5.3.1 is a graphical depiction of this process.



Figure 5.3.1: The Formation of a Sodium Ion. On the left, a sodium atom has 11 electrons. On the right, the sodium ion only has 10 electrons and a 1 + charge.

A chlorine atom has the following electron configuration:

Cl:
$$1s^2 2s^2 2p^6 3s^2 3p^5$$

Only one more electron is needed to achieve an octet in chlorine's valence shell. (In table salt, this electron comes from the sodium atom.) The electron configuration of the new species that results is as follows:

$$:Br + Mg + Br : \longrightarrow Mg^{2+} + 2:Br : \longrightarrow MgBr_2$$

Figure 5.3.2 is a graphical depiction of this process.



Figure **5.3.2***: The Formation of a Chlorine Ion. On the left, the chlorine atom has* 17 *electrons. On the right, the chloride ion has* 18 *electrons and has a* 1- *charge.*

With two oppositely charged ions, there is an electrostatic attraction between them because opposite charges attract. The resulting combination is the compound sodium chloride. Notice that there are no leftover electrons. The number of electrons lost by the sodium atom (one) equals the number of electrons gained by the chlorine atom (one), so the compound is electrically neutral. In macroscopic samples of sodium chloride, there are billions and billions of sodium and chloride ions, although there is always the same number of cations and anions.

In many cases, elements that belong to the same group (vertical column) on the periodic table form ions with the same charge because they have the same number of valence electrons. Thus, the periodic table becomes a tool for remembering the charges on many ions. For example, all ions made from alkali metals, the first column on the periodic table, have a 1+ charge. Ions made from alkaline earth metals, the second group on the periodic table, have a 2+ charge. On the other side of the periodic table, the next-to-last column, the halogens, form ions having a 1- charge. Figure 5.3.3 shows how the charge on many ions can be predicted by the location of an element on the periodic table. Note the convention of first writing the number and then the sign on a multiply charged ion. The barium cation is written Ba^{2+} , not Ba^{+2} .



Figure 5.3.3: Predicting Ionic Charges. The charge that an atom acquires when it becomes an ion is related to the structure of the periodic table. Within a group (family) of elements, atoms form ions of a certain charge.

LEWIS DIAGRAMS

Chemists use simple diagrams to show an atom's valence electrons and how they transfer. These diagrams have two advantages over the electron shell diagrams. First, they show only valence electrons. Second, instead of having a circle around the chemical symbol to represent the electron shell, they have up to eight dots around the symbol; each dot represents a valence electron. These dots are arranged to the right and left and above and below the symbol, with no more than two dots on a side. For example, the representation for sodium is as follows:

Na.

and the representation for chlorine is as follows:

CI



It does not matter what sides the dots are placed on in Lewis diagrams as long as each side has a maximum of two dots.

These diagrams are called **Lewis electron dot diagrams**, or simply Lewis diagrams, after Gilbert N. Lewis, the American chemist who introduced them. Figure 5.3.4 shows the electron configurations and Lewis diagrams of the elements lithium through neon, which is the entire second period of the periodic table. For the main group elements, the number of valence electrons is the same as the group number listed at the top of the periodic table.

Figure 5.3.4: Lewis Electron Dot Diagrams of the Elements Lithium through Neon

The transfer of electrons can be illustrated easily with Lewis diagrams:

$$Na. + CI: \longrightarrow Na^{+} + CI: \longrightarrow NaC$$

In representing the final formula, the dots are omitted.

Example 5.3.1

Starting with lithium and bromine atoms, use Lewis diagrams to show the formation of the ionic compound LiBr.

SOLUTION

From the periodic table, we see that lithium is in the same column as sodium, so it will have the same valence shell electron configuration. That means that the neutral lithium atom will have the same Lewis diagram that the sodium atom has. Similarly, bromine is in the same column as chlorine, so it will have the same Lewis diagram that chlorine has. Therefore,

$$Li \cdot + \dot{Br} : \longrightarrow Li^{+} + \dot{Br} : \longrightarrow LiBr$$

Exercise 5.3.1

Starting with magnesium and oxygen atoms, use Lewis diagrams to show the formation of the ionic compound MgO.

Some ionic compounds have different numbers of cations and anions. In those cases, electron transfer occurs between more than one atom. For example, here is the formation of MgBr₂:

$$: Br' + Mg' + Br' : \longrightarrow Mg^{2+} + 2: Br' : \longrightarrow MgBr_2$$

Notice that in this example there are two bromide ions (1– charge) needed for every one magnesium ion (2+ charge) in order for the overall charge of the compound to equal zero. This is called **charge balance**. The number of each type of ion is indicated in the formula by the subscript.

Most of the elements that make ionic compounds form an ion that has a characteristic charge. For example, sodium makes ionic compounds in which the sodium ion always has a 1+ charge. Chlorine makes ionic compounds in which the chloride ion always has a 1- charge. Some elements, especially transition metals, can form ions of multiple charges. Figure 5.3.5 shows the characteristic charges for some of these ions. As we saw in Figure 5.3.1, there is a pattern to the charges on many of the main group ions, but there is no simple pattern for transition metal ions (or for the larger main group elements).

1A																	8A
H+	2A	2										ЗA	4A	5A	6A	7A	
Li+								0.0						N ³	O ²⁻	F	
Na+	Mg ²⁺	3B	4B	5B	6B	7B	\subset	3B		1B	2B	Al ³⁺		P ³⁻	S ²⁻	CI	
K+	Ca ²⁺	Sc ³⁺	Ti ²⁺ Ti ⁴⁺	V ²⁺ V ³⁺	Cr ²⁺ Cr ³⁺	Mn ²⁺ Mn ⁴⁺	Fe ²⁺ Fe ³⁺	Co ²⁺ Co ³⁺	Ni+	Cu ⁺ Cu ²⁺	Zn ²⁺				Se ²⁻	Br	
Rb+	Sr ²⁺									Ag+	Cd ²⁺		Sn ²⁺			Ŀ	
Cs+	Ba ²⁺									Au ⁺ Au ³⁺			Pb ²⁺				

Figure 5.3.5: Charges of the Monatomic Ions. Note that some atoms commonly form ions of variable charges.



5.4: FORMULAS FOR IONIC COMPOUNDS

LEARNING OBJECTIVES

- Write the chemical formula for a simple ionic compound.
- Recognize polyatomic ions in chemical formulas.

We have already encountered some chemical formulas for simple ionic compounds. A chemical formula is a concise list of the elements in a compound and the ratios of these elements. To better understand what a chemical formula means, we must consider how an ionic compound is constructed from its ions.

Ionic compounds exist as alternating positive and negative ions in regular, three-dimensional arrays called crystals (Figure 5.4.1). As you can see, there are no individual NaCl "particles" in the array; instead, there is a continuous lattice of alternating sodium and chloride ions. However, we can use the ratio of sodium ions to chloride ions, expressed in the lowest possible whole numbers, as a way of describing the compound. In the case of sodium chloride, the ratio of sodium ions to chloride ions, expressed in lowest whole numbers, is 1:1, so we use NaCl (one Na symbol and one Cl symbol) to represent the compound. Thus, NaCl is the chemical formula for sodium chloride, which is a concise way of describing the relative number of different ions in the compound. A macroscopic sample is composed of myriads of NaCl pairs; each individual pair called a **formula unit**. Although it is convenient to think that NaCl crystals are composed of individual NaCl units, Figure 5.4.1 shows that no single ion is exclusively associated with any other single ion. Each ion is surrounded by ions of opposite charge.



Figure 5.4.1: A Sodium Chloride Crystal. A crystal contains a three-dimensional array of alternating positive and negative ions. The precise pattern depends on the compound. A crystal of sodium chloride, shown here, is a collection of alternating sodium and chlorine ions.

The formula for an ionic compound follows several conventions. First, the cation is written before the anion. Because most metals form cations and most nonmetals form anions, formulas typically list the metal first and then the nonmetal. Second, charges are not written in a formula. Remember that in an ionic compound, the component species are ions, not neutral atoms, even though the formula does not contain charges. Finally, the proper formula for an ionic compound always has *and discovered the elements, polonium (Po) and radium (Ra)*. meaning the total positive charge must equal the total negative charge. To determine the proper formula of any combination of ions, determine how many of each ion is needed to balance the total positive and negative charges in the compound.

This rule is ultimately based on the fact that matter is, overall, electrically neutral.

By convention, assume that there is only one atom if a subscript is not present. We do not use 1 as a subscript.

If we look at the ionic compound consisting of lithium ions and bromide ions, we see that the lithium ion has a 1+ charge and the bromide ion has a 1- charge. Only one ion of each is needed to balance these charges. The formula for lithium bromide is LiBr.

When an ionic compound is formed from magnesium and oxygen, the magnesium ion has a 2^+ charge, and the oxygen atom has a 2^- charge. Although both of these ions have higher charges than the ions in lithium bromide, they still balance each other in a one-to-one ratio. Therefore, the proper formula for this ionic compound is MgO.

Now consider the ionic compound formed by magnesium and chlorine. A magnesium ion has a 2+ charge, while a chlorine ion has a 1- charge:

$$Mg^{2+}Cl^{-}$$
 (5.4.1)

Combining one ion of each does not completely balance the positive and negative charges. The easiest way to balance these charges is to assume the presence of *two* chloride ions for each magnesium ion:



$\mathrm{Mg}^{2\,+}\mathrm{Cl}^{-}\mathrm{Cl}^{-}$

(5.4.2)

Now the positive and negative charges are balanced. We could write the chemical formula for this ionic compound as MgClCl but the convention is to use a numerical subscript when there is more than one ion of a given type— $MgCl_2$. This chemical formula says that there are one magnesium ion and *two* chloride ions in this formula. (Do not read the " Cl_2 " part of the formula as a molecule of the diatomic elemental chlorine. Chlorine does not exist as a diatomic element in this compound. Rather, it exists as two individual chloride ions.) By convention, the lowest whole number ratio is used in the formulas of ionic compounds. The formula Mg_2Cl_4 has balanced charges with the ions in a 1:2 ratio, but it is not the lowest whole number ratio.

By convention, the lowest whole-number ratio of the ions is used in ionic formulas. There are exceptions for certain ions, such as Hg_2^{2+} .

Example 5.4.1

Write the chemical formula for an ionic compound composed of each pair of ions.

- a. the sodium ion and the sulfur ion
- b. the aluminum ion and the fluoride ion
- c. the 3+ iron ion and the oxygen ion

SOLUTION

- a. To obtain a valence shell octet, sodium forms an ion with a 1+ charge, while the sulfur ion has a 2- charge. Two sodium 1+ ions are needed to balance the 2- charge on the sulfur ion. Rather than writing the formula as NaNaS, we shorten it by convention to Na_2S .
- b. The aluminum ion has a 3+ charge, while the fluoride ion formed by fluorine has a 1– charge. Three fluorine 1– ions are needed to balance the 3+ charge on the aluminum ion. This combination is written as AlF_3 .
- c. Iron can form two possible ions, but the ion with a 3+ charge is specified here. The oxygen atom has a 2- charge as an ion. To balance the positive and negative charges, we look to the least common multiple—6: two iron 3+ ions will give 6+, while three 2- oxygen ions will give 6-, thereby balancing the overall positive and negative charges. Thus, the formula for this ionic compound is Fe_2O_3 .

Exercise 5.4.1

Write the chemical formula for an ionic compound composed of each pair of ions.

- a. the calcium ion and the oxygen ion
- b. the 2+ copper ion and the sulfur ion
- c. the 1+ copper ion and the sulfur ion

POLYATOMIC IONS

Some ions consist of groups of atoms *covalently* bonded together and have an overall electric charge. Because these ions contain more than one atom, they are called polyatomic ions. Polyatomic ions have characteristic formulas, names, and charges that should be memorized. For example, NO_3^- is the nitrate ion; it has one nitrogen atom and three oxygen atoms and an overall 1– charge. Figure 5.4.2lists the most common polyatomic ions.





Table 5.4.2: Some Polyatomic Ions

The rule for constructing formulas for ionic compounds containing polyatomic ions is the same as for formulas containing monatomic (single-atom) ions: the positive and negative charges must balance. If more than one of a particular polyatomic ion is needed to balance the charge, the *entire formula* for the polyatomic ion must be enclosed in parentheses, and the numerical subscript is placed *outside* the parentheses. This is to show that the subscript applies to the entire polyatomic ion. An example is $Ba(NO_3)_2$.



Example 5.4.2

Write the chemical formula for an ionic compound composed of each pair of ions.

- a. the potassium ion and the sulfate ion
- b. the calcium ion and the nitrate ion

SOLUTION

- a. Potassium ions have a charge of 1+, while sulfate ions have a charge of 2–. We will need two potassium ions to balance the charge on the sulfate ion, so the proper chemical formula is K_2SO_4 .
- b. Calcium ions have a charge of 2+, while nitrate ions have a charge of 1–. We will need two nitrate ions to balance the charge on each calcium ion. The formula for nitrate must be enclosed in parentheses. Thus, we write $Ca(NO_3)_2$ as the formula for this ionic compound.

Exercise 5.4.2

Write the chemical formula for an ionic compound composed of each pair of ions.

a. the magnesium ion and the carbonate ion

b. the aluminum ion and the acetate ion

RECOGNIZING IONIC COMPOUNDS

There are two ways to recognize ionic compounds. First, compounds between metal and nonmetal elements are usually ionic. For example, CaBr₂ contains a metallic element (calcium, a group 2A metal) and a nonmetallic element (bromine, a group 7A nonmetal). Therefore, it is most likely an ionic compound. (In fact, it *is* ionic.) In contrast, the compound NO₂ contains two elements that are both nonmetals (nitrogen, from group 5A, and oxygen, from group 6A). It is not an ionic compound; it belongs to the category of covalent compounds discuss elsewhere. Also note that this combination of nitrogen and oxygen has no electric charge specified, so it is *not* the nitrite ion.

Second, if you recognize the formula of a polyatomic ion in a compound, the compound is ionic. For example, if you see the formula $Ba(NO_3)_2$, you may recognize the "NO₃" part as the nitrate ion, NO_3^- . (Remember that the convention for writing formulas for ionic compounds is not to include the ionic charge.) This is a clue that the other part of the formula, Ba, is actually the Ba^{2+} ion, with the 2+ charge balancing the overall 2– charge from the two nitrate ions. Thus, this compound is also ionic.

Example 5.4.3

Identify each compound as ionic or not ionic.

a. Na₂O

b. PCl₃

c. NH_4Cl

d. OF_2

SOLUTION

a. Sodium is a metal, and oxygen is a nonmetal; therefore, Na₂O is expected to be ionic.

b. Both phosphorus and chlorine are nonmetals. Therefore, PCl_3 is not ionic.

c. The NH_4 in the formula represents the ammonium ion, NH_4^+ , which indicates that this compound is ionic.

d. Both oxygen and fluorine are nonmetals. Therefore, OF_2 is not ionic.



Exercise 5.4.3

Identify each compound as ionic or not ionic.

a. N_2O b. $FeCl_3$ c. $(NH_4)_3PO_4$ d. $SOCl_2$

LOOKING CLOSER: BLOOD AND SEAWATER

Science has long recognized that blood and seawater have similar compositions. After all, both liquids have ionic compounds dissolved in them. The similarity may be more than mere coincidence; many scientists think that the first forms of life on Earth arose in the oceans. A closer look, however, shows that blood and seawater are quite different. A 0.9% solution of sodium chloride approximates the salt concentration found in blood. In contrast, seawater is principally a 3% sodium chloride solution, over three times the concentration in blood. Here is a comparison of the amounts of ions in blood and seawater:

Ion	Percent in Seawater	Percent in Blood
Na ⁺	2.36	0.322
Cl ⁻	1.94	0.366
Mg^{2+}	0.13	0.002
SO4 ²⁻	0.09	—
K^+	0.04	0.016
Ca ²⁺	0.04	0.0096
HCO ₃ ⁻	0.002	0.165
HPO4 ²⁻ , H ₂ PO4 ⁻	_	0.01

Most ions are more abundant in seawater than they are in blood, with some important exceptions. There are far more hydrogen carbonate ions (HCO_3^-) in blood than in seawater. This difference is significant because the hydrogen carbonate ion and some related ions have a crucial role in controlling the acid-base properties of blood. The amount of hydrogen phosphate ions— $HPO_4^2^-$ and $H_2PO_4^-$ —in seawater is very low, but they are present in higher amounts in blood, where they also affect acid-base properties. Another notable difference is that blood does not have significant amounts of the sulfate ion $(SO_4^2^-)$, but this ion is present in seawater.

KEY TAKEAWAYS

- Proper chemical formulas for ionic compounds balance the total positive charge with the total negative charge.
- Groups of atoms with an overall charge, called polyatomic ions, also exist.



5.5: IONIC NOMENCLATURE

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LEARNING OBJECTIVES
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• To use the rules for naming ionic compounds

After learning a few more details about the names of individual ions, you will be a step away from knowing how to name ionic compounds. This section begins the formal study of nomenclature, the systematic naming of chemical compounds.

NAMING IONS

The name of a monatomic cation is simply the name of the element followed by the word *ion*. Thus, Na^+ is the sodium ion, Al^{3+} is the aluminum ion, Ca^{2+} is the calcium ion, and so forth.

We have seen that some elements lose different numbers of electrons, producing ions of different charges. Iron, for example, can form two cations, each of which, when combined with the same anion, makes a different compound with unique physical and chemical properties. Thus, we need a different name for each iron ion to distinguish Fe^{2+} from Fe^{3+} . The same issue arises for other ions with more than one possible charge.

There are two ways to make this distinction. In the simpler, more modern approach, called the *Stock system*, an ion's positive charge is indicated by a roman numeral in parentheses after the element name, followed by the word *ion*. Thus, Fe^{2+} is called the iron(II) ion, while Fe^{3+} is called the iron(III) ion. This system is used only for elements that form more than one common positive ion. We do not call the Na⁺ ion the sodium(I) ion because (I) is unnecessary. Sodium forms only a 1+ ion, so there is no ambiguity about the name *sodium ion*.

Element	Stem	Charge	Name
	form	2+	ferrous ion
поп	1011-	3+	ferric ion
coppor	CUDE	1+	cuprous ion
copper	cupi-	2+	cupric ion
tip	stann	2+	stannous ion
tiii	Stalli-	4+	stannic ion
load	nlumh	2+	plumbous ion
leau	piumb-	4+	plumbic ion
chromium	chrom	2+	chromous ion
chiointuin	chiom-	3+	chromic ion
aold	2117	1+	aurous ion
gola	aul-	3+	auric ion

The second system, called the **common system**, is not conventional but is still prevalent and used in the health sciences. This system recognizes that many metals have two common cations. The common system uses two suffixes (*-ic* and *-ous*) that are appended to the stem of the element name. The *-ic* suffix represents the greater of the two cation charges, and the *-ous* suffix represents the lower one. In many cases, the stem of the element name comes from the Latin name of the element. Table 5.5.1 lists the elements that use the common system, along with their respective cation names.

The name of a monatomic anion consists of the stem of the element name, the suffix *-ide*, and then the word *ion*. Thus, as we have already seen, Cl^- is "chlor-" + "-ide ion," or the chloride ion. Similarly, O^{2^-} is the oxide ion, Se^{2^-} is the selenide ion, and so forth. Table 5.5.2lists the names of some common monatomic ions.

Ion	Name
\mathbf{F}^{-}	fluoride ion
Cl ⁻	chloride ion
Br^-	bromide ion
I_	iodide ion
O ²⁻	oxide ion
S ²⁻	sulfide ion
P ³⁻	phosphide ion
N^{3-}	nitride ion

The polyatomic ions have their own characteristic names, as discussed earlier.

Example 5.5.1



Name each ion.

- a. Ca²⁺
- b. S^{2–}
- c. SO3²⁻
- d. NH4⁺
- e. Cu⁺

Answer a

the calcium ion

Answer b

the sulfide ion (from Table 5.5.2)

Answer c

the sulfite ion

Answer d

the ammonium ion

Answer e

the copper(I) ion or the cuprous ion (copper can form cations with either a 1+ or 2+ charge, so we have to specify which charge this ion has

Exercise 5.5.1

Name each ion. a. Fe^{2+} b. Fe^{3+} c. SO_4^{2-}

d. Ba²⁺

e. HCO₃-

$\mathsf{Example} \ 5.5.2$

Write the formula for each ion.

- a. the bromide ion
- b. the phosphate ion
- c. the cupric ion
- d. the magnesium ion

Answer a

 Br^- Answer b $\mathrm{PO_4^{3^-}}$ Answer c $\mathrm{Cu^{2^+}}$

Answer d Mg²⁺

Ivig-

$\mathsf{Exercise}\;5.5.2$

Write the formula for each ion.

- a. the fluoride ion
- b. the carbonate ion
- c. the stannous ion
- d. the potassium ion



NAMING COMPOUNDS

Now that we know how to name ions, we are ready to name ionic compounds. We do so by placing the name of the cation first, followed by the name of the anion, and dropping the word *ion* from both parts. For example, what is the name of the compound whose formula is $Ba(NO_3)_2$?



barium nitrate

The compound's name does not indicate that there are two nitrate ions for every barium ion. You must determine the relative numbers of ions by balancing the positive and negative charges.

If you are given a formula for an ionic compound whose cation can have more than one possible charge, you must first determine the charge on the cation before identifying its correct name. For example, consider $FeCl_2$ and $FeCl_3$. In the first compound, the iron ion has a 2+ charge because there are two Cl^- ions in the formula (1– charge on each chloride ion). In the second compound, the iron ion has a 3+ charge, as indicated by the three Cl^- ions in the formula. These are two different compounds that need two different names. By the Stock system, the names are iron(II) chloride and iron(III) chloride. If we were to use the stems and suffixes of the common system, the names would be ferrous chloride and ferric chloride, respectively.

Example 5.5.3

Name each ionic compound, using both Stock and common systems if necessary.
a. Ca ₃ (PO ₄) ₂
b. (NH ₄) ₂ Cr ₂ O ₇
c. KCl
d. CuCl
e. SnF ₂
Answer a
calcium phosphate
Answer b
ammonium dichromate (the prefix <i>di</i> - is part of the name of the anion)
Answer c
potassium chloride
Answer d
copper(I) chloride or cuprous chloride
Answer e
tin(II) fluoride or stannous fluoride
Exercise 5.5.3
Name each ionic compound, using both Stock and common systems if necessary.
a. ZnBr ₂
b. $Fe(NO_3)_3$

c. Al_2O_3

d. AuF_3

e. AgF

Figure 5.5.1 is a synopsis of how to name simple ionic compounds.





Figure 5.5.1: A Guide to Naming Simple Ionic Compounds. Follow these steps to name a simple ionic compound.

KEY TAKEAWAY

• Each ionic compound has its own unique name that comes from the names of the ions.



5.6: FORMULA MASS

LEARINING	ODJECTIVES

• To determine the formula mass of an ionic compound.

One skill needed in future chapters is the ability to determine the mass of the formula of an ionic compound. This quantity is called the formula mass. The formula mass is obtained by adding the masses of each individual atom in the formula of the compound. Because a proper formula is electrically neutral (with no net electrons gained or lost), the ions can be considered atoms for the purpose of calculating the formula mass.

Let us start by calculating the formula mass of sodium chloride (NaCl). This formula mass is the sum of the atomic masses of one sodium atom and one chlorine atom, which we find from the periodic table; here, we use the masses to two decimal places:

Na:	22.99 amu
Cl:	+ 35.45 amu
Total:	58.44 amu

To two decimal places, the formula mass of NaCl is 58.44 amu.

When an ionic compound has more than one anion or cation, you must remember to use the proper multiple of the atomic mass for the element in question. For the formula mass of calcium fluoride (CaF₂), we must multiply the mass of the fluorine atom by 2 to account for the two fluorine atoms in the chemical formula:

Ca:	1×40.08	40.08 amu
F:	2 × 19.00 =	+ 38.00 amu
Total:		78.08 amu

The formula mass of CaF_2 is 78.08 amu.

For ionic compounds with polyatomic ions, the sum must include the number and mass of each atom in the formula for the polyatomic ion. For example, potassium nitrate (KNO₃) has one potassium atom, one nitrogen atom, and three oxygen atoms:

К:	1 × 39.10	39.10 amu			
N:	1 × 14.00	+ 14.00 amu			
O:	3 × 16.00 =	+ 48.00 amu			
Total:		101.10 amu			

The formula mass of KNO₃ is 101.10 amu.

Potassium nitrate is a key ingredient in gunpowder and has been used clinically as a diuretic.



When a formula contains more than one polyatomic unit in the chemical formula, as in $Ca(NO_3)_2$, do not forget to multiply the atomic mass of every atom inside the parentheses by the subscript outside the parentheses. This is necessary because the subscript refers to the *entire polyatomic ion*. Thus, for $Ca(NO_3)_2$, the subscript 2 implies two complete nitrate ions, so we must sum the masses of two (1×2) nitrogen atoms and six (3×2) oxygen atoms, along with the mass of a single calcium atom:

Ca:	1×40.08	40.08 amu
N:	2 × 14.00 =	+ 28.00 amu
O:	6 × 16.00 =	+ 96.00 amu
Total:		164.08 amu

The key to calculating the formula mass of an ionic compound is to correctly count each atom in the formula and multiply the atomic masses of its atoms accordingly.

Example 5.6.1						
Use the atomic masses (rounder ionic compound.	Use the atomic masses (rounded to two decimal places) from the inside cover of this book to determine the formula mass for each ionic compound.					
a. FeCl ₃ b. (NH ₄) ₃ PO ₄						
SOLUTION						
a.						
Fe:		55.85 amu				
Cl:	3 × 35.45 =	+ 106.35 amu				
Total:		162.20 amu				
The formula mass of FeCl ₃ is 10	52.20 amu.					
a. When we distribute the subs	cript 3 through the parentheses containing	ng the formula for the ammonium ion, we see that we have 3				
nitrogen atoms and 12 hydro	ogen atoms. Thus, we set up the sum as	follows:				
N:	3 × 14.00 =	42.00 amu				
H:	12 × 1.00 =	+ 12.00 amu				
Р:		+ 30.97 amu				
O:	4 × 16.00 =	+ 64.00 amu				
Total:		148.97 amu				
The formula mass for $(NH_4)_2PC$	0₄ is 148.97 amu.					



Exercise 5.6.1

Use the atomic masses (rounded to two decimal places) from the inside cover of this book to determine the formula mass for each ionic compound.

- a. TiO₂
- b. AgBr
- c. Au(NO₃)₃
- d. Fe₃(PO₄)₂

TO YOUR HEALTH: HYDRATES

Some ionic compounds have water (H_2O) incorporated within their formula unit. These compounds, called *hydrates*, have a characteristic number of water units associated with each formula unit of the compound. Hydrates are solids, not liquids or solutions, despite the water they contain.

To write the chemical formula of a hydrate, write the number of water units per formula unit of compound after its chemical formula. The two chemical formulas are separated by a vertically centered dot. The hydrate of copper(II) sulfate has five water units associated with each formula unit, so it is written as $CuSO_4 \bullet 5 H_2O$. The name of this compound is copper(II) sulfate pentahydrate, with the *penta*- prefix indicating the presence of five water units per formula unit of copper(II) sulfate.



Magnesium sulfate heptahydrate. Image used with permission (Public Domain; Chemicalinterest).

Hydrates have various uses in the health industry. Calcium sulfate hemihydrate ($CaSO_4 \bullet \frac{1}{2}H_2O$), known as plaster of Paris, is used to make casts for broken bones. Epsom salt ($MgSO_4 \bullet 7 H_2O$) is used as a bathing salt and a laxative. Aluminum chloride hexahydrate is an active ingredient in antiperspirants. The accompanying table lists some useful hydrates.

Formula	Name	Uses
AlCl ₃ •6H ₂ O	aluminum chloride hexahydrate	antiperspirant
CaSO ₄ •½H ₂ O	calcium sulfate hemihydrate (plaster of Paris)	casts (for broken bones and castings)
CaSO ₄ •2H ₂ O	calcium sulfate dihydrate (gypsum)	drywall component
CoCl ₂ •6H ₂ O	cobalt(II) chloride hexahydrate	drying agent, humidity indicator
CuSO ₄ •5H ₂ O	copper(II) sulfate pentahydrate	fungicide, algicide, herbicide
MgSO ₄ •7H ₂ O	magnesium sulfate heptahydrate (Epsom salts)	laxative, bathing salt
Na ₂ CO ₃ •10H ₂ O	sodium carbonate decahydrate (washing soda)	laundry additive/cleaneKEY TAKEAWAY

KEY TAKEAWAY

• Formula masses of ionic compounds can be determined from the masses of the atoms in their formulas.



5.7: IONIC BONDING AND SIMPLE IONIC COMPOUNDS (EXERCISES)

ADDITIONAL EXERCISES

- 1. What number shell is the valence electron shell of a sodium atom? What number shell is the valence shell of a sodium ion? Explain the difference.
- 2. What number shell is the valence electron shell of a bromine atom? What number shell is the valence shell of a bromide ion? Explain the difference between these answers and the answers to Exercise 1.
- 3. What is the electron configuration of each ion?

a. K⁺ b. Mg²⁺ c. F⁻

- d. S²⁻
- 4. What is the electron configuration of each ion?
 - a. Li⁺
 - b. Ca²⁺
 - c. Cl⁻
 - d. O²⁻
- 5. a. If a sodium atom were to lose two electrons, what would be the electron configuration of the resulting cation?
- b. Considering that electron shells are typically separated by large amounts of energy, use your answer to Exercise 5a to suggest why sodium atoms do not form a 2+ cation.
- 6. a. If a chlorine atom were to gain two electrons, what would be the electron configuration of the resulting anion?
 - b. Considering that electron shells are typically separated by large amounts of energy, use your answer to Exercise 6a to suggest why chlorine atoms do not form a 2– anion.
- 7. Use Lewis diagrams and arrows to show the electron transfer that occurs during the formation of an ionic compound among Mg atoms and F atoms. (Hint: how many atoms of each will you need?)
- 8. Use Lewis diagrams and arrows to show the electron transfer that occurs during the formation of an ionic compound among K atoms and O atoms. (Hint: how many atoms of each will you need?)
- 9. Mercury forms two possible cations— Hg^{2+} and Hg_{2}^{2+} , the second of which is actually a two-atom cation with a 2+ charge.

a. Using common names, give the probable names of these ions.

b. What are the chemical formulas of the ionic compounds these ions make with the oxide ion, O^{2-} ?

- 10. The uranyl ion $(UO_2^{2^+})$ is a common water-soluble form of uranium. What is the chemical formula of the ionic compound uranyl nitrate? What is the chemical formula of the ionic compound uranyl phosphate?
- 11. The formal chemical name of the mineral *strengite* is iron(III) phosphate dihydrate. What is the chemical formula of strengite? What is the formula mass of strengite?
- 12. What is the formula mass of $MgSO_4 \cdot 7H_2O$?
- 13. What is the formula mass of $CaSO_4 \cdot \frac{1}{2}H_2O$?
- 14. What mass does 20 formula units of NaCl have?
- 15. What mass does 75 formula units of K₂SO₄ have?
- 16. If an atomic mass unit equals 1.66×10^{-24} g, what is the mass in grams of one formula unit of NaCl?
- 17. If an atomic mass unit equals 1.66×10^{-24} g, what is the mass in grams of 5.00×10^{22} formula units of NaOH?
- 18. If an atomic mass unit equals 1.66×10^{-24} g, what is the mass in grams of 3.96×10^{23} formula units of (NH₄)₂SO₄?
- 19. Both tin and lead acquire 2+ or 4+ charges when they become ions. Use the periodic table to explain why this should not surprise you.
- 20. Which ion would you expect to be larger in size—In³⁺ or Tl³⁺? Explain.
- 21. Which ion would you expect to be smaller in size—I⁻ or Br⁻? Explain.
- 22. Which ion with a 2+ charge has the following electron configuration? $1s^22s^22p^6$
- 23. Which ion with a 3– charge has the following electron configuration? $1s^22s^22p^6$

ANSWERS



- 1. For sodium, the valence shell is the third shell; for the sodium ion, the valence shell is the second shell because it has lost all its third shell electrons.
- 3. a. $1s^22s^22p^63s^23p^6$
 - b. $1s^2 2s^2 2p^6$
 - c. $1s^2 2s^2 2p^6$
 - d. $1s^2 2s^2 2p^6 3s^2 3p^6$
- 5. a. $1s^2 2s^2 2p^5$
 - b. It probably requires too much energy to form.

$$:F: + Mg: + F: \longrightarrow Mg^{2+} + 2:F: \longrightarrow MgF_2$$

- 9. a. mercuric and mercurous, respectively b. HgO and Hg₂O, respectively
- 11. FePO₄·2H₂O; 186.86 u
- 13. 145.16 u
- 15. 13,070.25 u
- 17. 3.32 g
- 19. Both tin and lead have two p electrons and two s electrons in their valence shells.
- 21. Br⁻ because it is higher up on the periodic table

23. N³⁻



5.8: IONIC BONDING AND SIMPLE IONIC COMPOUNDS (SUMMARY)

To ensure that you understand the material in this chapter, you should review the meanings of the following bold terms and ask yourself how they relate to the topics in the chapter.

Atoms combine into compounds by forming **chemical bonds**. A survey of stable atoms and molecules leads to the **octet rule**, which says that stable atoms tend to have eight electrons in their outermost, or valence, shell. One way atoms obtain eight electrons in the valence shell is for some atoms to lose electrons while other atoms gain them. When this happens, the atoms take on an electrical charge. Charged atoms are called **ions**. Ions having opposite charges attract each other. This attraction is called **ionic bonding**, and the compounds formed are called **ionic compounds**.

Positively charged ions are called **cations**, while negatively charged ions are called **anions**. The formation of both cations and anions can be illustrated using electron configurations. Because elements in a column of the periodic table have the same valence shell electron configuration, atoms in the same column of the periodic table tend to form ions having the same charge. **Electron dot diagrams**, or **Lewis diagrams**, can also be used to illustrate the formation of cations and anions.

Ionic compounds are represented in writing by a **chemical formula**, which gives the lowest ratio of cations and anions present in the compound. In a formula, the symbol of the cation is written first, followed by the symbol of the anion. **Formula unit** is considered the basic unit of an ionic compound because ionic compounds do not exist as discrete units. Instead, they exist as **crystals**, three-dimensional arrays of ions, with cations surrounded by anions and anions surrounded by cations. Chemical formulas for ionic compounds are determined by balancing the positive charge from the cation(s) with the negative charge from the anion(s). A subscript to the right of the ion indicates that more than one of that ion is present in the chemical formula.

Some ions are groups of atoms bonded together and having an overall electrical charge. These are called **polyatomic ions**. Writing formulas with polyatomic ions follows the same rules as with monatomic ions, except that when more than one polyatomic ion is present in a chemical formula, the polyatomic ion is enclosed in parentheses and the subscript is outside the right parenthesis. Ionic compounds typically form between metals and nonmetals or between polyatomic ions.

Names of ionic compounds are derived from the names of the ions, with the name of the cation coming first, followed by the name of the anion. If an element can form cations of different charges, there are two alternate systems for indicating the compound's name. In the **Stock system**, a roman numeral in parentheses indicates the charge on the cation. An example is the name for FeCl₂, which is iron(II) chloride. In the common system, the suffixes *-ous* and *-ic* are used to stand for the lower and higher possible charge of the cation, respectively. These suffixes are attached to a stem representing the element (which frequently comes from the Latin form of the element name). An example is the common name for FeCl₂, which is ferrous chloride.

The **formula mass** of an ionic compound is the sum of the masses of each individual atom in the formula. Care must be taken when calculating formula masses for formulas containing multiple polyatomic ions because the subscript outside the parentheses refers to all the atoms in the polyatomic ion.



6: COVALENT BONDING AND SIMPLE MOLECULAR COMPOUNDS

Ionic bonding results from the transfer of electrons among atoms or groups of atoms. In this chapter, we will consider another type of bonding—covalent bonding. We will examine how atoms share electrons to form these bonds, and we will begin to explore how the resulting compounds, such as cholesterol, are different from ionic compounds.

6.1: PRELUDE TO COVALENT BONDING AND SIMPLE MOLECULAR COMPOUNDS

Cholesterol, a compound that is sometimes in the news, is a white, waxy solid produced in the liver of every animal, including humans. It is important for building cell membranes and in producing certain hormones (chemicals that regulate cellular activity in the body). As such, it is necessary for life, but why is cholesterol the object of attention? Most medical professionals recommend diets that minimize the amount of ingested cholesterol as a way of preventing heart attacks and strokes.

6.2: COVALENT BONDS

You have already seen examples of substances that contain covalent bonds. One substance mentioned previously was water (H₂O). You can tell from its formula that it is not an ionic compound; it is not composed of a metal and a nonmetal. Consequently, its properties are different from those of ionic compounds. A covalent bond is formed between two atoms by sharing electrons.

6.3: COVALENT COMPOUNDS - FORMULAS AND NAMES

The chemical formula of a simple covalent compound can be determined from its name. The name of a simple covalent compound can be determined from its chemical formula.

6.4: MULTIPLE COVALENT BONDS

Some molecules must have multiple covalent bonds between atoms to satisfy the octet rule.

6.5: CHARACTERISTICS OF COVALENT BONDS

Covalent bonds between different atoms have different bond lengths. Covalent bonds can be polar or nonpolar, depending on the electronegativity difference between the atoms involved.

6.6: CHARACTERISTICS OF MOLECULES

A molecule has a certain mass, called the molecular mass. Simple molecules have geometries that can be determined from VSEPR theory.

6.7: INTERMOLECULAR INTERACTIONS

A phase is a form of matter that has the same physical properties throughout. Molecules interact with each other through various forces: ionic and covalent bonds, dipole-dipole interactions, hydrogen bonding, and dispersion forces.

6.8: ORGANIC CHEMISTRY

Organic chemistry is the study of the chemistry of carbon compounds. Organic molecules can be classified according to the types of elements and bonds in the molecules.

6.9: COVALENT BONDING AND SIMPLE MOLECULAR COMPOUNDS (EXERCISES)

These are homework exercises to accompany Chapter 4 of the Ball et al. "The Basics of GOB Chemistry" Textmap.

6.10: COVALENT BONDING AND SIMPLE MOLECULAR COMPOUNDS (SUMMARY)

To ensure that you understand the material in this chapter, you should review the meanings of the following bold terms in the following summary and ask yourself how they relate to the topics in the chapter.



6.1: PRELUDE TO COVALENT BONDING AND SIMPLE MOLECULAR COMPOUNDS

Cholesterol ($C_{27}H_{46}O$), a compound that is sometimes in the news, is a white, waxy solid produced in the liver of every animal, including humans. It is important for building cell membranes and in producing certain hormones (chemicals that regulate cellular activity in the body). As such, it is necessary for life, but why is cholesterol the object of attention?

Besides producing cholesterol, we also ingest some whenever we eat meat or other animal-based food products. People who eat such products in large quantities, or whose metabolisms are unable to handle excess amounts, may experience an unhealthy buildup of cholesterol in their blood. Deposits of cholesterol, called plaque, may form on blood vessel walls, eventually blocking the arteries and preventing the delivery of oxygen to body tissues. Heart attacks, strokes, and other circulatory problems can result.

Most medical professionals recommend diets that minimize the amount of ingested cholesterol as a way of preventing heart attacks and strokes. Tests are available to measure cholesterol in the blood, and there are several drugs capable of lowering cholesterol levels.



Figure 6.1.1: A Molecular Model of Cholesterol



6.2: COVALENT BONDS

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FARMING	() BIECTIVES

• To describe how a covalent bond forms.

You have already seen examples of substances that contain covalent bonds. One substance mentioned previously was water (H_2O) . You can tell from its formula that it is not an ionic compound; it is not composed of a metal and a nonmetal. Consequently, its properties are different from those of ionic compounds.

ELECTRON SHARING

Previously, we discussed ionic bonding where electrons can be transferred from one atom to another so that both atoms have an energy-stable outer electron shell. Because most filled electron shells have eight electrons in them, chemists called this tendency the octet rule. However, there is another way an atom can achieve a full valence shell: atoms can *share* electrons.

This concept can be illustrated by using two hydrogen atoms, each of which has a single electron in its valence shell. (For small atoms such as hydrogen atoms, the valence shell will be the first shell, which holds only two electrons.) We can represent the two individual hydrogen atoms as follows:



In contrast, when two hydrogen atoms get close enough together to share their electrons, they can be represented as follows:



By sharing their valence electrons, both hydrogen atoms now have two electrons in their respective valence shells. Because each valence shell is now filled, this arrangement is more stable than when the two atoms are separate. The sharing of electrons between atoms is called a covalent bond, and the two electrons that join atoms in a covalent bond are called a bonding pair of electrons. A discrete group of atoms connected by covalent bonds is called a molecule—the smallest part of a compound that retains the chemical identity of that compound.

Chemists frequently use Lewis diagrams to represent covalent bonding in molecular substances. For example, the Lewis diagrams of two separate hydrogen atoms are as follows:

The Lewis diagram of two hydrogen atoms sharing electrons looks like this:

н:н

This depiction of molecules is simplified further by using a dash to represent a covalent bond. The hydrogen molecule is then represented as follows:

$$H - H$$

Remember that the dash, also referred to as a single bond, represents a *pair* of electrons.

The bond in a hydrogen molecule, measured as the distance between the two nuclei, is about 7.4×10^{-11} m, or 74 picometers (pm; 1 pm = 1×10^{-12} m). This particular bond length represents a balance between several forces: the attractions between oppositely charged



electrons and nuclei, the repulsion between two negatively charged electrons, and the repulsion between two positively charged nuclei. If the nuclei were closer together, they would repel each other more strongly; if the nuclei were farther apart, there would be less attraction between the positive and negative particles.

Fluorine is another element whose atoms bond together in pairs to form *diatomic* (two-atom) molecules. Two separate fluorine atoms have the following electron dot diagrams:

Each fluorine atom contributes one valence electron, making a single bond and giving each atom a complete valence shell, which fulfills the octet rule:

:F:F:

The circles show that each fluorine atom has eight electrons around it. As with hydrogen, we can represent the fluorine molecule with a dash in place of the bonding electrons:

Each fluorine atom has six electrons, or three pairs of electrons, that are not participating in the covalent bond. Rather than being shared, they are considered to belong to a single atom. These are called nonbonding pairs (or lone pairs) of electrons.

COVALENT BONDS BETWEEN DIFFERENT ATOMS

Now that we have looked at electron sharing between atoms of the same element, let us look at covalent bond formation between atoms of different elements. Consider a molecule composed of one hydrogen atom and one fluorine atom:

Each atom needs one additional electron to complete its valence shell. By each contributing one electron, they make the following molecule:



In this molecule, the hydrogen atom does not have nonbonding electrons, while the fluorine atom has six nonbonding electrons (three lone electron pairs). The circles show how the valence electron shells are filled for both atoms.

Example 6.2.1

Draw the Lewis diagram for each compound.

a. a molecule composed of two chlorine atoms

b. a molecule composed of a hydrogen atom and a bromine atom

SOLUTION

a. Chlorine has the same valence shell electron configuration as fluorine, so the Lewis diagram for a molecule composed of two chlorine atoms is similar to the one for fluorine:

b. Bromine has the same valence shell electron configuration as fluorine, so the Lewis diagram for a molecule composed of a hydrogen atom and a bromine atom is similar to that for hydrogen and fluorine:



Exercise 6.2.1

Draw the Lewis diagram for each compound.

a. a molecule composed of one chlorine atom and one fluorine atom

b. a molecule composed of one hydrogen atom and one iodine atom



Larger molecules are constructed in a similar fashion, with some atoms participating in more than one covalent bond. For example, water, with two hydrogen atoms and one oxygen atom (H_2O) and methane (CH_4), with one carbon atom and four hydrogen atoms, can be represented as follows:



 Figure 6.2.1 shows the number of covalent bonds various atoms typically form.

 1
 4
 3
 2
 1

 4
 3,5
 2,6
 1

 4
 3,5
 2,6
 1

 2
 1
 1
 1
 1

 1
 2
 1
 1

 1
 1
 1
 2
 1

Figure 6.2.1: How Many Covalent Bonds Are Formed? In molecules, there is a pattern to the number of covalent bonds that different atoms can form. Each block with a number indicates the number of covalent bonds formed by that atom in neutral compounds.

CONCEPT REVIEW EXERCISES

- 1. How is a covalent bond formed between two atoms?
- 2. How does covalent bonding allow atoms in group 6A to satisfy the octet rule?

ANSWERS

- 1. Covalent bonds are formed by two atoms sharing electrons.
- 2. The atoms in group 6A make two covalent bonds.

KEY TAKEAWAY

• A covalent bond is formed between two atoms by sharing electrons.

EXERCISES

- 1. Define *covalent bond*.
- 2. What is electron sharing?
- 3. Draw the Lewis diagram for the covalent bond in the Br₂ molecule.
- 4. Draw the Lewis diagram for the covalent bond in the I₂ molecule.
- 5. Draw the Lewis diagram for the covalent bond in the HCl molecule.
- 6. Draw the Lewis diagram for the covalent bond in the HI molecule.
- 7. What is the difference between a molecule and a formula unit?
- 8. Why do hydrogen atoms not follow the octet rule when they form covalent bonds?
- 9. Draw the Lewis diagram for the covalent bonding in H₂S. How many bonding electrons and nonbonding electrons are in the molecule?
- 10. Draw the Lewis diagram for the covalent bonding in NI₃. How many bonding electrons and nonbonding electrons are in the molecule?
- 11. Draw the Lewis diagram for the covalent bonding in CF₄. How many bonding electrons and nonbonding electrons are in the molecule?
- 12. Draw the Lewis diagram for the covalent bonding in PCl₃. How many bonding electrons and nonbonding electrons are in the molecule?



- 13. How many covalent bonds does a hydrogen atom typically form? Why?
- 14. How many covalent bonds does an oxygen atom typically form? Why?
- 15. Tellurium atoms make covalent bonds. How many covalent bonds would a tellurium atom make? Predict the formula of a compound between tellurium and hydrogen.
- 16. Tin atoms make covalent bonds. How many covalent bonds would a tin atom make? Predict the formula of a compound between tin and hydrogen.
- 17. Astatine is a synthetic element, made one atom at a time in huge "atom-smasher" machines. It is in the halogen group on the periodic table. How many covalent bonds would an atom of this element form?
- 18. There have been reports that atoms of element 116 were made by smashing smaller atoms together. Using the periodic table, determine what column element 116 would be in and suggest how many covalent bonds an atom of this element would form.

ANSWERS

1. A covalent bond is formed when two atoms share electrons.

7. A molecule is a discrete combination of atoms; a formula unit is the lowest ratio of ions in a crystal.

9.

bonding electrons: 4; nonbonding electrons: 4

11.

bonding electrons: 8; nonbonding electrons: 24

13. Hydrogen atoms form only one covalent bond because they have only one valence electron to pair.

15. two; H₂Te

17. one



6.3: COVALENT COMPOUNDS - FORMULAS AND NAMES

LEARNING OBJECTIVES

- Determine the chemical formula of a simple covalent compound from its name.
- Determine the name of a simple covalent compound from its chemical formula.

What elements make covalent bonds? Covalent bonds form when two or more nonmetals combine. For example, both hydrogen and oxygen are nonmetals, and when they combine to make water, they do so by forming covalent bonds. Nonmetal atoms in polyatomic ions are joined by covalent bonds, but the ion as a whole participates in ionic bonding. For example, ammonium chloride has ionic bonds between a polyatomic ion, NH_4^+ , and Cl^- ions, but within the ammonium ion, the nitrogen and hydrogen atoms are connected by covalent bonds:



Example 6.3.1

Is each compound formed from ionic bonds, covalent bonds, or both?

a.
$$Na_2O$$

c. N_2O_4

Answer a

The elements in Na₂O are a metal and a nonmetal, which form ionic bonds.

Answer b

Because sodium is a metal and we recognize the formula for the phosphate ion, we know that this compound is ionic. However, polyatomic ions are held together by covalent bonds, so this compound contains both ionic and covalent bonds.

Answer c

The elements in N_2O_4 are both nonmetals, rather than a metal and a nonmetal. Therefore, the atoms form covalent bonds.

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Is each compound are formed from ionic bonds, covalent bonds, or both?

a. $Ba(OH)_2$ b. F_2

c. PCl_3

The chemical formulas for covalent compounds are referred to as **molecular formulas** because these compounds exist as separate, discrete molecules. Typically, a molecular formula begins with the nonmetal that is closest to the lower left corner of the periodic table, except that hydrogen is almost never written first (H_2O is the prominent exception). Then the other nonmetal symbols are listed. Numerical subscripts are used if there is more than one of a particular atom. For example, we have already seen CH_4 , the molecular formula for methane.

Naming *binary* (two-element) covalent compounds is similar to naming simple ionic compounds. The first element in the formula is simply listed using the name of the element. The second element is named by taking the stem of the element name and adding the suffix *-ide*. A system of numerical prefixes is used to specify the number of atoms in a molecule. Table 6.3.1 lists these numerical prefixes. Normally, no prefix is added to the first element's name if there is only one atom of the first element in a molecule. If the second element is oxygen, the trailing vowel is usually omitted from the end of a polysyllabic prefix but not a monosyllabic one (that is, we would say "monoxide" rather than "troxide").



Table 6.3.1: Numerical Prefixes for Naming Binary Covalent Compounds

Number of Atoms in Compound	Prefix on the Name of the Element
1	mono-*
2	di-
3	tri-
4	tetra-
5	penta-
6	hexa-
7	hepta-
8	octa-
9	nona-
10	deca-

*This prefix is not used for the first element's name.

Let us practice by naming the compound whose molecular formula is CCl₄. The name begins with the name of the first element carbon. The second element, chlor*ine*, becomes chlor*ide*, and we attach the correct numerical prefix ("tetra-") to indicate that the molecule contains four chlor*ine* atoms. Putting these pieces together gives the name *carbon tetrachloride* for this compound.

Example 6.3.2

Write the molecular formula for each compound.

- a. chlorine trifluoride
- b. phosphorus pentachloride
- c. sulfur dioxide
- d. dinitrogen pentoxide

SOLUTION

If there is no numerical prefix on the first element's name, we can assume that there is only one atom of that element in a molecule.

- a. ClF₃
- b. PCl₅
- $c.\ SO_2$

d. N₂O₅ (The *di*- prefix on nitrogen indicates that two nitrogen atoms are present.)

Exercise 6.3.2

Write the molecular formula for each compound.

- a. nitrogen dioxide
- b. dioxygen difluoride
- c. sulfur hexafluoride
- d. selenium monoxide

Because it is so unreactive, sulfur hexafluoride is used as a spark suppressant in electrical devices such as transformers.

Example 6.3.3

Write the name for each compound.

a. BrF₅

b. S_2F_2



c. CO

SOLUTION

- a. bromine pentafluoride
- b. disulfur difluoride
- c. carbon monoxide

EXERCISE 6.3.3Write the name for each compound. a. CF_4

b. SeCl₂

c. SO₃

For some simple covalent compounds, we use common names rather than systematic names. We have already encountered these compounds, but we list them here explicitly:

- H₂O: water
- NH₃: ammonia
- CH₄: methane

Methane is the simplest organic compound. Organic compounds are compounds with carbon atoms and are named by a separate nomenclature system that we will introduce in Section 4.6 "Introduction to Organic Chemistry".

CONCEPT REVIEW EXERCISES

- 1. How do you recognize a covalent compound?
- 2. What are the rules for writing the molecular formula of a simple covalent compound?
- 3. What are the rules for naming a simple covalent compound?

ANSWERS

- 1. A covalent compound is usually composed of two or more nonmetal elements.
- 2. It is just like an ionic compound except that the element further down and to the left on the periodic table is listed first and is named with the element name.
- 3. Name the first element first and then the second element by using the stem of the element name plus the suffix -ide. Use numerical prefixes if there is more than one atom of the first element; always use numerical prefixes for the number of atoms of the second element.

KEY TAKEAWAYS

- The chemical formula of a simple covalent compound can be determined from its name.
- The name of a simple covalent compound can be determined from its chemical formula.

EXERCISES

- 1. Identify whether each compound has covalent bonds.
 - a. NaI
 - b. Na₂CO₃
 - c. N₂O
 - d. SiO₂

2. Identify whether each compound has covalent bonds.

a. C_2H_6

- b. C_6H_5Cl
- c. KC₂H₃O₂
- d. Ca(OH)₂

3. Identify whether each compound has ionic bonds, covalent bonds, or both.

- a. Na_3PO_4
- b. K_2O
- c. COCl₂
- d. CoCl₂



- 4. Identify whether each compound has ionic bonds, covalent bonds, or both.
 - a. FeCl₃
 - b. Fe(NO₃)₃
 - c. (NH₂)₂CO
 - d. SO₃
- 5. Which is the correct molecular formula—H₄Si or SiH₄? Explain.
- 6. Which is the correct molecular formula—SF₆ or F₆S? Explain.
- 7. Write the name for each covalent compound.
 - a. SiF₄
 - b. NO₂
 - c. CS_2
 - d. P₂O₅
- 8. Write the name for each covalent compound.
 - a. CO
 - b. S₂O₃
 - c. BF₃
 - d. GeS₂
- 9. Write the formula for each covalent compound.
 - a. iodine trichloride
 - b. disulfur dibromide
 - c. arsenic trioxide
 - d. xenon hexafluoride
- 10. Write the formula for each covalent compound.
 - a. boron trichloride
 - b. carbon dioxide
 - c. tetraphosphorus decoxide
 - d. germanium dichloride
- 11. Write two covalent compounds that have common rather than systematic names.
- 12. What is the name of the simplest organic compound? What would its name be if it followed the nomenclature for binary covalent compounds?

ANSWERS

- 1. a. no
 - b. yes
 - c. yes
 - d. yes
- 3. a. both
 - b. ionic
 - c. covalent
 - d. ionic

5. SiH₄; except for water, hydrogen is almost never listed first in a covalent compound.

- 7. a. silicon tetrafluoride
 - b. nitrogen dioxide
 - c. carbon disulfide
 - d. diphosphorus pentoxide
- 9. a. ICl₃
 - b. S₂Br₂
 - c. AsO₃
 - d. XeF₆
- 11. H₂O and NH₃ (water and ammonia) (answers will vary)



6.4: MULTIPLE COVALENT BONDS

LEARNING OBJECTIVES

• To recognize molecules that are likely to have multiple covalent bonds.

In many molecules, the octet rule would not be satisfied if each pair of bonded atoms shares two electrons. Consider carbon dioxide (CO_2) . If each oxygen atom shares one electron with the carbon atom, we get the following:



This does not give the carbon atom a complete octet; you will find only six electrons in its valence shell. In addition, each oxygen atom has only seven electrons in its valence shell. Finally, no atom makes the number of bonds it typically forms. This arrangement of shared electrons is far from satisfactory.

Sometimes more than one pair of electrons must be shared between two atoms for both atoms to have an octet. In carbon dioxide, a second electron from each oxygen atom is also shared with the central carbon atom, and the carbon atom shares one more electron with each oxygen atom:



In this arrangement, the carbon atom shares four electrons (two pairs) with the oxygen atom on the left and four electrons with the oxygen atom on the right. There are now eight electrons around each atom. Two pairs of electrons shared between two atoms make a double bond between the atoms, which is represented by a double dash:

Some molecules contain triple bonds, covalent bonds in which *three* pairs of electrons are shared by two atoms. A simple compound that has a triple bond is acetylene (C_2H_2), whose Lewis diagram is as follows:




or

Exercise 6.4.1

Draw the Lewis diagram for each molecule.

a. O_2 b. C_2H_4

FORMALDEHYDE AND FORMALIN

One application of CH₂O, also called formaldehyde, is the preservation of biological specimens. Aqueous solutions of CH₂O are called formalin and have a sharp, characteristic (pungent) odor.

KEY TAKEAWAY

• Some molecules must have multiple covalent bonds between atoms to satisfy the octet rule.

EXERCISES

1. What is one clue that a molecule has a multiple bond?

2. Each molecule contains multiple bonds. Draw the Lewis diagram for each. The first element is the central atom.

- a. CS_2
- b. C₂F₄
- c. COCl₂
- 3. Each molecule contains double bonds. Draw the Lewis diagram for each. Assume that the first element is the central atom, unless otherwise noted.

a. N_2

- b. HCN (The carbon atom is the central atom.)
- c. POCl (The phosphorus atom is the central atom.)
- 4. Explain why hydrogen atoms do not form double bonds.
- 5. Why is it incorrect to draw a double bond in the Lewis diagram for MgO?

ANSWERS

1. If single bonds between all atoms do not give all atoms (except hydrogen) an octet, multiple covalent bonds may be present.

2. a.

:s=c=s:

c.

b.

4. Hydrogen can accept only one more electron; multiple bonds require more than one electron pair to be shared.



6.5: CHARACTERISTICS OF COVALENT BONDS

LEARNING OBJECTIVES

• Covalent bonds have certain characteristics that depend on the identities of the atoms participating in the bond. Two characteristics are bond length and bond polarity.

BOND LENGTH

We previously stated that the covalent bond in the hydrogen molecule (H₂) has a certain length (about 7.4×10^{-11} m). Other covalent bonds also have known bond lengths, which are dependent on both the identities of the atoms in the bond and whether the bonds are single, double, or triple bonds. Table 6.5.1 lists the approximate bond lengths for some single covalent bonds. The exact bond length may vary depending on the identity of the molecule but will be close to the value given in the table.

Table $6.5.1$: Approximate Bond Lengths of Some Single Bonds				
Bond	Length (× $10^{-12} m$)			
H–H	74			
H–C	110			
H–N	100			
H–O	97			
H–I	161			
C–C	154			
C–N	147			
C-0	143			
N–N	145			
0–0	145			

Table 6.5.2 compares the lengths of single covalent bonds with those of double and triple bonds between the same atoms. Without exception, as the number of covalent bonds between two atoms increases, the bond length decreases. With more electrons between the two nuclei, the nuclei can get closer together before the internuclear repulsion is strong enough to balance the attraction.

Bond	Length (× $10^{-12} m$)
C–C	154
C=C	134
C≡C	120
C–N	147
C=N	128
C≡N	116
С-О	143
C=O	120
C≡O	113
N–N	145
N=N	123
N≡N	110
0–0	145
O=O	121

ELECTRONEGATIVITY AND BOND POLARITY



Although we defined covalent bonding as electron sharing, the electrons in a covalent bond are not always shared equally by the two bonded atoms. Unless the bond connects two atoms of the same element, there will always be one atom that attracts the electrons in the bond more strongly than the other atom does, as shown in Figure 6.5.1. When such an imbalance occurs, there is a resulting buildup of some negative charge (called a partial negative charge and designated δ -) on one side of the bond and some positive charge (designated δ +) on the other side of the bond. A covalent bond that has an unequal sharing of electrons, as in Figure 6.5.1*b* is called a **polar covalent bond**. A covalent bond that has an equal sharing of electrons (Figure 6.5.1*a*) is called a **nonpolar covalent bond**.



Figure 6.5.1 Polar versus Nonpolar Covalent Bonds. (a) The electrons in the covalent bond are equally shared by both hydrogen atoms. This is a nonpolar covalent bond. (b) The fluorine atom attracts the electrons in the bond more than the hydrogen atom does, leading to an imbalance in the electron distribution. This is a polar covalent bond.

Any covalent bond between atoms of different elements is a polar bond, but the degree of polarity varies widely. Some bonds between different elements are only minimally polar, while others are strongly polar. Ionic bonds can be considered the ultimate in polarity, with electrons being transferred rather than shared. To judge the relative polarity of a covalent bond, chemists use **electronegativity**, which is a relative measure of how strongly an atom attracts electrons when it forms a covalent bond. There are various numerical scales for rating electronegativity. Figure 6.5.2 shows one of the most popular—the Pauling scale. The polarity of a covalent bond can be judged by determining the difference in the electronegativities of the two atoms making the bond. The greater the difference in electronegativities is less than about 0.4, the bond is considered nonpolar; if the difference is greater than 0.4, the bond is considered polar. If the difference in electronegativities is large enough (generally greater than about 1.8), the resulting compound is considered ionic rather than covalent. An electronegativity difference of zero, of course, indicates a nonpolar covalent bond.



Figure 6.5.2 Electronegativities of Various Elements. A popular scale for electronegativities has the value for fluorine atoms set at 4.0, the highest value.

LOOKING CLOSER: LINUS PAULING

Arguably the most influential chemist of the 20th century, Linus Pauling (1901–94) is the only person to have won two individual (that is, unshared) Nobel Prizes. In the 1930s, Pauling used new mathematical theories to enunciate some fundamental principles of the chemical bond. His 1939 book *The Nature of the Chemical Bond* is one of the most significant books ever published in chemistry.

By 1935, Pauling's interest turned to biological molecules, and he was awarded the 1954 Nobel Prize in Chemistry for his work on protein structure. (He was very close to discovering the double helix structure of DNA when James Watson and James Crick announced their own discovery of its structure in 1953.) He was later awarded the 1962 Nobel Peace Prize for his efforts to ban the testing of nuclear weapons.





Linus Pauling was one of the most influential chemists of the 20th century.

In his later years, Pauling became convinced that large doses of vitamin C would prevent disease, including the common cold. Most clinical research failed to show a connection, but Pauling continued to take large doses daily. He died in 1994, having spent a lifetime establishing a scientific legacy that few will ever equal.

Example 6.5.1

Describe the electronegativity difference between each pair of atoms and the resulting polarity (or bond type).

- a. C and H
- b. H and H
- c. Na and Cl
- d. O and H

SOLUTION

- a. Carbon has an electronegativity of 2.5, while the value for hydrogen is 2.1. The difference is 0.3, which is rather small. The C–H bond is therefore considered nonpolar.
- b. Both hydrogen atoms have the same electronegativity value—2.1. The difference is zero, so the bond is nonpolar.
- c. Sodium's electronegativity is 0.9, while chlorine's is 3.0. The difference is 2.1, which is rather high, and so sodium and chlorine form an ionic compound.
- d. With 2.1 for hydrogen and 3.5 for oxygen, the electronegativity difference is 1.4. We would expect a very polar bond, but not so polar that the O–H bond is considered ionic.

Exercise 6.5.1

Describe the electronegativity difference between each pair of atoms and the resulting polarity (or bond type).

- a. C and O
- b. K and Br
- c. N and N
- d. Cs and F

When a molecule's bonds are polar, the molecule as a whole can display an uneven distribution of charge, depending on how the individual bonds are oriented. For example, the orientation of the two O–H bonds in a water molecule (Figure 6.5.3) is bent: one end of the molecule has a partial positive charge, and the other end has a partial negative charge. In short, the molecule itself is polar. The polarity of water has an enormous impact on its physical and chemical properties. (For example, the boiling point of water [100°C] is high for such a small molecule and is due to the fact that polar molecules attract each other strongly.) In contrast, while the two C=O bonds in carbon dioxide are polar, they lie directly opposite each other and so cancel each other's effects. Thus, carbon dioxide molecules are nonpolar overall. This lack of polarity influences some of carbon dioxide's properties. (For example, carbon dioxide becomes a gas at -77° C, almost 200° lower than the temperature at which water boils.)





Figure 6.5.3 Physical Properties and Polarity. The physical properties of water and carbon dioxide are affected by their polarities.

CONCEPT REVIEW EXERCISES

- 1. What is the name for the distance between two atoms in a covalent bond?
- 2. What does the electronegativity of an atom indicate?
- 3. What type of bond is formed between two atoms if the difference in electronegativities is small? Medium? Large?

ANSWERS

- 1. bond length
- 2. Electronegativity is a qualitative measure of how much an atom attracts electrons in a covalent bond.
- 3. nonpolar; polar; ionic

KEY TAKEAWAYS

- Covalent bonds between different atoms have different bond lengths.
- Covalent bonds can be polar or nonpolar, depending on the electronegativity difference between the atoms involved.

EXERCISES

- 1. Which is longer—a C–H bond or a C–O bond? (Refer to Table 6.5.1)
- 2. Which is shorter—an N–H bond or a C–H bond? (Refer to Table 6.5.1)
- 3. A nanometer is 10^{-9} m. Using the data in Table 6.5.1 and Table 6.5.2 determine the length of each bond in nanometers.
 - a. a C–O bond
 - b. a C=O bond
 - c. an H–N bond
 - d. a C=N bond
- 4. An angstrom (Å) is defined as 10^{-10} m. Using Table 6.5.1 and Table 6.5.2 determine the length of each bond in angstroms.
 - a. a C–C bond
 - b. a C=C bond
 - c. an N≡N bond
 - d. an H–O bond
- 5. Refer to Exercise 3. Why is the nanometer unit useful as a unit for expressing bond lengths?
- 6. Refer to Exercise 4. Why is the angstrom unit useful as a unit for expressing bond lengths?
- 7. Using Figure 6.5.2 determine which atom in each pair has the higher electronegativity.
 - a. H or C
 - b. O or Br
 - c. Na or Rb
 - d. I or Cl

8. Using Figure 6.5.2 determine which atom in each pair has the lower electronegativity.

- a. Mg or O
- b. S or F
- c. Al or Ga
- d. O or I
- 9. Will the electrons be shared equally or unequally across each covalent bond? If unequally, to which atom are the electrons more strongly drawn?

a. a C–O bond b. an F–F bond

c. an S–N bond



d. an I–Cl bond

- 10. Will the electrons be shared equally or unequally across each covalent bond? If unequally, to which atom are the electrons more strongly drawn?
 - a. a C–C bond
 - b. a S–Cl bond
 - c. an O–H bond
 - d. an H–H bond

ANSWERS

- 1. A C–O bond is longer.
- 3. a. 0.143 nm
 - b. 0.120 nm
 - c. 0.100 nm
 - d. 0.116 nm

5. Actual bond lengths are very small, so the nanometer unit makes the expression of length easier to understand.

- 7. a. C
 - b. O
 - c. Na
 - d. Cl
- 9. a. unequally toward the O
 - b. equally
 - c. unequally toward the N
 - d. unequally toward the Cl



6.6: CHARACTERISTICS OF MOLECULES

LEARNING OBJECTIVES

- Determine the molecular mass of a molecule.
- Predict the general shape of a simple covalent molecule.

Unlike the ions in ionic compounds, which are arranged in lattices called crystals, molecules of covalent compounds exist as discrete units with a characteristic mass and a certain three-dimensional shape.

MOLECULAR MASS

The mass of a molecule—the molecular mass (sometimes called the molecular weight)—is simply the sum of the masses of its atoms. As with formula masses, it is important that you keep track of the number of atoms of each element in the molecular formula to obtain the correct molecular mass.

Example 6.6.1						
What is the molecular mass of each covalent compound?						
a. H ₂ O b. C ₆ H ₆ c. NO ₂ d. N ₂ O ₅						
SOLUTION						
Use the masses of the atoms from the Table	A4.					
The molecular formula H_2O indicates that masses of these atoms,	there are two hydrogen atoms and one ox	gen atom in each molecule. Summing the				
2 H:	2 × 1.01 =	2.02 amu				
1 0:		+ 16.00 amu				
Total:		18.02 amu				
The molecular mass of H_2O is 18.02 amu.						
6 C:	6 × 12.01 =	72.06 amu				
6 H:	6 × 1.01 =	+ 6.06 amu				
Total:		78.12 amu				
The molecular mass of $\rm C_6H_6$ is 78.12 amu.						
1 N:		14.01 amu				
2 O:	2 × 16.00 =	+ 32.00 amu				
Total:		46.01 amu				
The molecular mass of NO_2 is 46.01 amu.						
2 N:	2 × 14.01 =	28.02 amu				
5 O:	5 × 16.00 =	+ 80.00 amu				
Total:		108.02 amu				

The molecular mass of N_2O_5 is 108.02 amu.

Note that the two different nitrogen and oxygen compounds in these examples have different molecular masses.

Exercise 6.6.1

What is the molecular mass of each covalent compound?

a. C_2H_2

b. CO

 $c. \ CO_2$

 $d. \; BF_3$

MOLECULAR SHAPE: VSEPR THEORY



Unlike ionic compounds, with their extended crystal lattices, covalent molecules are discrete units with specific three-dimensional shapes. The shape of a molecule is determined by the fact that covalent bonds, which are composed of negatively charged electrons, tend to repel one another. This concept is called the **valence shell electron pair repulsion (VSEPR) theory**. For example, the two covalent bonds in $BeCl_2$ stay as far from each other as possible, ending up 180° apart from each other. The result is a linear molecule:



The three covalent bonds in BF₃ repel each other to form 120° angles in a plane, in a shape called *trigonal planar*:



The molecules BeCl₂ and BF₃ actually violate the octet rule; however, such exceptions are rare and will not be discussed in this text.

Try sticking three toothpicks into a marshmallow or a gumdrop and see if you can find different positions where your "bonds" are farther apart than the planar 120° orientation.

The four covalent bonds in CCl_4 arrange themselves three dimensionally, pointing toward the corner of a tetrahedron and making bond angles of 109.5°. CCl_4 is said to have a tetrahedral shape:



Molecules with lone electron pairs around the central atom have a shape based on the position of the atoms, not the electron pairs. For example, NH₃ has one lone electron pair and three bonded electron pairs. These four electron pairs repel each other and adopt a tetrahedral arrangement:



However, the shape of the molecule is described in terms of the positions of the atoms, not the lone electron pairs. Thus, NH₃ is said to have a **trigonal pyramidal shape**, not a tetrahedral one. Similarly, H₂O has two lone pairs of electrons around the central oxygen atom, in addition to the two bonded pairs:



Although the four electron pairs adopt a tetrahedral arrangement due to repulsion, the shape of the molecule is described by the positions of the atoms only. The shape of H_2O is bent with an approximate 109.5° angle.

In determining the shapes of molecules, it is useful to first determine the Lewis diagram for a molecule. The shapes of molecules with multiple bonds are determined by treating the multiple bonds as one bond. Thus, CH_2O has a shape similar to that of BF₃:



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Example 6.6.2

Describe the shape of each molecule.

a. PCl₃

b. CO₂

SOLUTION

a. The Lewis diagram for $\ensuremath{\mathsf{PCl}}_3$ is as follows:



The four electron pairs arrange themselves tetrahedrally, but the lone electron pair is not considered in describing the molecular shape. Like NH₃, this molecule is pyramidal.

b. The Lewis diagram for CO₂ is as follows:



The multiple bonds are treated as one group. Thus, CO_2 has only two groups of electrons that repel each other. They will direct themselves 180° apart from each other, so CO_2 molecules are linear.

Exercise 6.6.2

Describe the shape of each molecule.

a. CBr₄

b. BCl₃

CONCEPT REVIEW EXERCISES

- 1. How do you determine the molecular mass of a covalent compound?
- 2. How do you determine the shape of a molecule?

ANSWERS

- 1. The molecular mass is the sum of the masses of the atoms in the formula.
- 2. The shape of a molecule is determined by the position of the atoms, which in turn is determined by the repulsion of the bonded and lone electron pairs around the central atom.

KEY TAKEAWAYS

- A molecule has a certain mass, called the molecular mass.
- Simple molecules have geometries that can be determined from VSEPR theory.

EXERCISES

- 1. What is the molecular mass of each compound?
 - a. H₂S

b. N₂O₄

c. ICl₃

d. HCl

- 2. What is the molecular mass of each compound?
 - a. O_2F_2
 - b. CCl₄
 - c. C_6H_6
 - d. SO $_3$
- 3. Aspirin $(C_9H_8O_4)$ is a covalent compound. What is its molecular mass?
- 4. Cholesterol (C₂₇H₄₆O) is a biologically important compound. What is its molecular mass?



5. What is the shape of each molecule?

a. H_2S

b. COCl₂

c. SO_2

6. What is the shape of each molecule?

a. NBr₃

- b. SF₂
- c. SiH₄
- 7. Predict the shape of nitrous oxide (N₂O), which is used as an anesthetic. A nitrogen atom is in the center of this three-atom molecule.
- 8. Predict the shape of acetylene (C_2H_2), which has the two carbon atoms in the middle of the molecule with a triple bond. What generalization can you make about the shapes of molecules that have more than one central atom?

ANSWERS

- 1. a. 34.62 amu
 - b. 92.02 amu
 - c. 233.25 amu
 - d. 36.46 amu
- 3. 180.17 amu
- 5. a. bent
 - b. trigonal planar c. bent

7. bent



6.7: INTERMOLECULAR INTERACTIONS

LEARNING OBJECTIVES

- Define *phase*.
- Identify the types of interactions between molecules.

A phase is a certain form of matter that includes a specific set of physical properties. That is, the atoms, the molecules, or the ions that make up the phase do so in a consistent manner throughout the phase. Science recognizes three stable phases: the *solid phase*, in which individual particles can be thought of as in contact and held in place; the *liquid phase*, in which individual particles are in contact but moving with respect to each other; and the *gas phase*, in which individual particles are separated from each other by relatively large distances. Not all substances will readily exhibit all phases. For example, carbon dioxide does not exhibit a liquid phase unless the pressure is greater than about six times normal atmospheric pressure. Other substances, especially complex organic molecules, may decompose at higher temperatures, rather than becoming a liquid or a gas.

For many substances, there are different arrangements the particles can take in the solid phase, depending on temperature and pressure.

Which phase a substance adopts depends on the pressure and the temperature it experiences. Of these two conditions, temperature variations are more obviously related to the phase of a substance. When it is very cold, H_2O exists in the solid form as ice. When it is warmer, the liquid phase of H_2O is present. At even higher temperatures, H_2O boils and becomes steam.

Pressure changes can also affect the presence of a particular phase (as we indicated for carbon dioxide), but its effects are less obvious most of the time. We will mostly focus on the temperature effects on phases, mentioning pressure effects only when they are important. Most chemical substances follow the same pattern of phases when going from a low temperature to a high temperature: the solid phase, then the liquid phase, and then the gas phase. However, the temperatures at which these phases are present differ for all substances and can be rather extreme. Table 6.7.1 shows the temperature ranges for solid, liquid, and gas phases for three substances. As you can see, there is extreme variability in the temperature ranges.

Table 6.7.1: Temperature Ranges for the Three Phases of Various Substances						
Substance	Solid Phase Below	Liquid Phase Above	Gas Phase Above			
hydrogen (H ₂)	−259°C	−259°C	−253°C			
water (H ₂ O)	0°C	0°C	100°C			
sodium chloride (NaCl)	801°C	801°C	1413°C			

The *melting point* of a substance is the temperature that separates a solid and a liquid. The *boiling point* of a substance is the temperature that separates a liquid and a gas.

What accounts for this variability? Why do some substances become liquids at very low temperatures, while others require very high temperatures before they become liquids? It all depends on the strength of the intermolecular interactions between the particles of substances. (Although ionic compounds are not composed of discrete molecules, we will still use the term *intermolecular* to include interactions between the ions in such compounds.) Substances that experience strong intermolecular interactions require higher temperatures to become liquids and, finally, gases. Substances that experience weak intermolecular interactions do not need much energy (as measured by temperature) to become liquids and gases and will exhibit these phases at lower temperatures.

Substances with the highest melting and boiling points have covalent network bonding. This type of intermolecular interaction is actually a covalent bond. In these substances, all the atoms in a sample are covalently bonded to other atoms; in effect, the entire sample is essentially one large molecule. Many of these substances are solid over a large temperature range because it takes a lot of energy to disrupt all the covalent bonds at once. One example of a substance that shows covalent network bonding is diamond (Figure 6.7.1), which is a form of pure carbon. At temperatures over 3,500°C, diamond finally vaporizes into gas-phase atoms.





Figure 6.7.1: Diamond. Diamond, a form of pure carbon, has covalent network bonding. It takes a very high temperature—over $3,500^{\circ}C$ —for diamond to leave the solid state. Source: Photo © Thinkstock

The strongest force between any two particles is the ionic bond, in which two ions of opposing charge are attracted to each other. Thus, ionic interactions between particles are another type of intermolecular interaction. Substances that contain ionic interactions are relatively strongly held together, so these substances typically have high melting and boiling points. Sodium chloride (Figure 6.7.2) is an example of a substance whose particles experience ionic interactions (Table 6.7.1).



Figure 6.7.2: Sodium Chloride. Solid NaCl is held together by ionic interactions. Source: Photo © Thinkstock

Many substances that experience covalent bonding exist as discrete molecules. In many molecules, the electrons that are shared in a covalent bond are not shared equally between the two atoms in the bond. Typically, one of the atoms attracts the electrons more strongly than the other, leading to an unequal sharing of electrons in the bond. This idea is illustrated in Figure 6.7.3 which shows a diagram of the covalent bond in hydrogen fluoride (HF). The fluorine atom attracts the electrons in the bond more than the hydrogen atom does. The result is an unequal distribution of electrons in the bond, favoring the fluorine side of the covalent bond. Because of this unequal distribution, the fluorine side of the covalent bond actually takes on a partial negative charge (indicated by the δ^- in Figure 6.7.3), while the hydrogen side of the bond, being electrons is called a polar covalent bond. (A covalent bond that has an equal sharing of electrons is called a nonpolar covalent bond.) A molecule with a net unequal distribution of electrons in a polar molecule. HF is an example of a polar molecule.

δ+ δ-Η **→** F

Figure 6.7.3: Polar Covalent Bonds. The electrons in the HF molecule are not equally shared by the two atoms in the bond. Because the fluorine atom has nine protons in its nucleus, it attracts the negatively charged electrons in the bond more than the hydrogen atom does with its one proton in its nucleus. Thus, electrons are more strongly attracted to the fluorine atom, leading to an imbalance in the electron distribution between the atoms. The fluorine side of the bond picks up a partial overall negative charge (represented by the δ - in the diagram), while the hydrogen side of the bond has an overall partial positive charge (represented by the δ + in the diagram). Such a bond is called a *polar covalent bond*.

The charge separation in a polar covalent bond is not as extreme as is found in ionic compounds, but there is a related result: oppositely charged ends of different molecules will attract each other. This type of intermolecular interaction is called a dipole-dipole interaction. Many molecules with polar covalent bonds experience dipole-dipole interactions. The covalent bonds in some molecules are oriented in space in such a way that the bonds in the molecules cancel each other out. The individual bonds are polar, but the overall molecule is not polar; rather, the molecule is *nonpolar*. Such molecules experience little or no dipole-dipole interactions. Carbon dioxide (CO_2) and carbon tetrachloride (CCl_4) are examples of such molecules (Figure 6.7.4).



Figure 6.7.4: Nonpolar Molecules. Although the individual bonds in both CO_2 and CCl_4 are polar, their effects cancel out because of the spatial orientation of the bonds in each molecule. As a result, such molecules experience little or no dipole-dipole interaction.

The H–F, O–H, and N–H bonds are strongly polar; in molecules that have these bonds, particularly strong dipole-dipole interactions (as strong as 10% of a true covalent bond) can occur. Because of this strong interaction, hydrogen bonding is used to describe this dipole-



dipole interaction. The physical properties of water, which has two O–H bonds, are strongly affected by the presence of hydrogen bonding between water molecules. Figure 6.7.5 shows how molecules experiencing hydrogen bonding can interact.



Figure 6.7.5: Hydrogen Bonding between Water Molecules. The presence of hydrogen bonding in molecules like water can have a large impact on the physical properties of a substance.

Finally, there are forces between all molecules that are caused by electrons being in different places in a molecule at any one time, which sets up a temporary separation of charge that disappears almost as soon as it appears. These are very weak intermolecular interactions and are called dispersion forces (or London forces). (An alternate name is London dispersion forces.) Molecules that experience no other type of intermolecular interaction will at least experience dispersion forces. Substances that experience only dispersion forces are typically soft in the solid phase and have relatively low melting points. Because dispersion forces are caused by the instantaneous distribution of electrons in a molecule, larger molecules with a large number of electrons can experience substantial dispersion forces. Examples include *waxes*, which are long hydrocarbon chains that are solids at room temperature because the molecules have so many electrons. The resulting dispersion forces between these molecules make them assume the solid phase at normal temperatures.

The phase that a substance adopts depends on the type and magnitude of the intermolecular interactions the particles of a substance experience. If the intermolecular interactions are relatively strong, then a large amount of energy—in terms of temperature—is necessary for a substance to change phases. If the intermolecular interactions are weak, a low temperature is all that is necessary to move a substance out of the solid phase.

Example 6.7.1: Intermolecular Forces

What intermolecular forces besides dispersion forces, if any, exist in each substance? Are any of these substances solids at room temperature?

- a. potassium chloride (KCl)
- b. ethanol (C_2H_5OH)
- c. bromine (Br₂)

SOLUTION

- a. Potassium chloride is composed of ions, so the intermolecular interaction in potassium chloride is ionic forces. Because ionic interactions are strong, it might be expected that potassium chloride is a solid at room temperature.
- b. Ethanol has a hydrogen atom attached to an oxygen atom, so it would experience hydrogen bonding. If the hydrogen bonding is strong enough, ethanol might be a solid at room temperature, but it is difficult to know for certain. (Ethanol is actually a liquid at room temperature.)
- c. Elemental bromine has two bromine atoms covalently bonded to each other. Because the atoms on either side of the covalent bond are the same, the electrons in the covalent bond are shared equally, and the bond is a nonpolar covalent bond. Thus, diatomic bromine does not have any intermolecular forces other than dispersion forces. It is unlikely to be a solid at room temperature unless the dispersion forces are strong enough. Bromine is a liquid at room temperature.

Exercise 6.7.1

What intermolecular forces besides dispersion forces, if any, exist in each substance? Are any of these substances solids at room temperature?

a. methylamine (CH₃NH₂)



b. calcium sulfate (CaSO₄)

c. carbon monoxide (CO)

CONCEPT REVIEW EXERCISE

1. What types of intermolecular interactions can exist in compounds?

ANSWER

1. polar and nonpolar covalent bonding, ionic bonding, dispersion forces, dipole-dipole interactions, and hydrogen bonding

KEY TAKEAWAYS

- A phase is a form of matter that has the same physical properties throughout.
- Molecules interact with each other through various forces: ionic and covalent bonds, dipole-dipole interactions, hydrogen bonding, and dispersion forces.

EXERCISES

- 1. List the three common phases in the order you are likely to find them—from lowest temperature to highest temperature.
- 2. List the three common phases in the order they exist from lowest energy to highest energy.
- 3. List these intermolecular interactions from weakest to strongest: London forces, hydrogen bonding, and ionic interactions.
- 4. List these intermolecular interactions from weakest to strongest: covalent network bonding, dipole-dipole interactions, and dispersion forces.
- 5. What type of intermolecular interaction is predominate in each substance?
 - a. water (H_2O)
 - b. sodium sulfate (Na₂SO₄)
 - c. decane ($C_{10}H_{22}$)
- 6. What type of intermolecular interaction is predominate in each substance?
 - a. diamond (C, crystal)
 - b. helium (He)
 - c. ammonia (NH₃)
- 7. Explain how a molecule like carbon dioxide (CO₂) can have polar covalent bonds but be nonpolar overall.
- 8. Sulfur dioxide (SO₂) has a formula similar to that of carbon dioxide (see Exercise 7) but is a polar molecule overall. What can you conclude about the shape of the SO₂ molecule?
- 9. What are some of the physical properties of substances that experience covalent network bonding?
- 10. What are some of the physical properties of substances that experience only dispersion forces?

ANSWERS

- 1. solid, liquid, and gas
- 3. London forces, hydrogen bonding, and ionic interactions
- 5. a. hydrogen bonding
 - b. ionic interactions
 - c. dispersion forces
- 7. The two covalent bonds are oriented in such a way that their dipoles cancel out.
- 9. very hard, high melting point



6.8: ORGANIC CHEMISTRY

LEARNING OBJECTIVES

- Define *organic chemistry*.
- Identify organic molecules as alkanes, alkenes, alkynes, alcohols, or carboxylic acids.

When methane was mentioned previously, we described it as the simplest organic compound. In this section, we introduce organic chemistry more formally. Organic chemistry is the study of the chemistry of carbon compounds. Carbon is singled out because it has a chemical diversity unrivaled by any other chemical element. Its diversity is based on the following:

- Carbon atoms bond reasonably strongly with other carbon atoms.
- Carbon atoms bond reasonably strongly with atoms of other elements.
- Carbon atoms make a large number of covalent bonds (four).

Curiously, elemental carbon is not particularly abundant. It does not even appear in the list of the most common elements in Earth's crust. Nevertheless, all living things consist of organic compounds. Most organic chemicals are covalent compounds, which is why we introduce organic chemistry here. By convention, compounds containing carbonate ions and bicarbonate ions, as well as carbon dioxide and carbon monoxide, are not considered part of organic chemistry, even though they contain carbon.

The simplest organic compounds are the **hydrocarbons**, compounds composed of carbon and hydrogen atoms only. Some hydrocarbons have only single bonds and appear as a chain (which can be a straight chain or can have branches) of carbon atoms also bonded to hydrogen atoms. These hydrocarbons are called **alkanes (saturated hydrocarbons**). Each alkane has a characteristic, systematic name depending on the number of carbon atoms in the molecule. These names consist of a stem that indicates the number of carbon atoms in the chain plus the ending -ane. The stem meth- means one carbon atom, so methane is an alkane with one carbon atom. Similarly, the stem eth- means two carbon atoms; ethane is an alkane with two carbon atoms. Continuing, the stem prop- means three carbon atoms, so propane is an alkane with three carbon atoms. Figure 6.8.1 gives the formulas and the molecular models of the three simplest alkanes.



Figure 6.8.1: Formulas and Molecular Models of the Three Simplest Alkanes. The three smallest alkanes are methane, ethane, and propane.

Some hydrocarbons have one or more carbon–carbon double bonds (denoted C=C). These hydrocarbons are called alkenes. Figure 6.8.2 shows the formulas and the molecular models of the two simplest alkenes. Note that the names of alkenes have the same stem as the alkane with the same number of carbon atoms in its chain but have the ending *-ene*. Thus, ethene is an alkene with two carbon atoms per molecule, and propene is a compound with three carbon atoms and one double bond.





Figure 6.8.2: Formulas and Molecular Models of the Two Simplest Alkenes. Ethene is commonly called ethylene, while propene is commonly called propylene.

Alkynes are hydrocarbons with a carbon–carbon triple bond (denoted C=C) as part of their carbon skeleton. Figure 6.8.3 shows the formulas and the molecular models of the two simplest alkynes and their systematic names. The names for alkynes have the same stems as for alkanes but with the ending *-yne*.



Figure 6.8.3 Formulas and Molecular Models of the Two Simplest Alkynes. Ethyne is more commonly called acetylene.

The compound acetylene, with its carbon–carbon triple bond, was introduced previously and is an alkyne.

To YOUR HEALTH: SATURATED AND UNSATURATED FATS

Hydrocarbons are not the only compounds that can have carbon–carbon double bonds. A group of compounds called fats can have them as well, and their presence or absence in the human diet is becoming increasingly correlated with health issues.

Fats are combinations of long-chain organic compounds (fatty acids) and glycerol ($C_3H_8O_3$). (For more information on fats, see Chapter 17) The long carbon chains can have either all single bonds, in which case the fat is classified as *saturated*, or one or more double bonds, in which case it is a *monounsaturated* or a *polyunsaturated* fat, respectively. Saturated fats are typically solids at room temperature; beef fat (tallow) is one example. Mono- or polyunsaturated fats are likely to be liquids at room temperature and are often called oils. Olive oil, flaxseed oil, and many fish oils are mono- or polyunsaturated fats.

Studies have linked higher amounts of saturated fats in people's diets with a greater likelihood of developing heart disease, high cholesterol, and other diet-related diseases. In contrast, increases in unsaturated fats (either mono- or polyunsaturated) have been linked to a lower incidence of certain diseases. Thus, there have been an increasing number of recommendations by government bodies and health associations to decrease the proportion of saturated fat and increase the proportion of unsaturated fat in the diet. Most of these organizations also recommend decreasing the total amount of fat in the diet.

Recently, certain fats called trans fats have been implicated in the presence of heart disease. These are fats from animal sources and are also produced when liquid oils are exposed to partial hydrogenation, an industrial process that increases their saturation. Trans fats are used in many prepared and fried foods. Because they bring with them the health risks that naturally occurring saturated fats do, there has been some effort to better quantify the presence of trans fats in food products. US law now requires that food labels list the amount of trans fat in each serving.

Since the early 1900's, the US Department of Agriculture has been providing science-based dietary guidelines for the public. The most current version is the MyPlate illustration that gives a simple, visual picture of how much of what kind of foods make up a good, balanced diet. It recommends minimizing daily intake of sugars, the "bad fats", trans and saturated fat, and sodium. "Good fats", unsaturated fats or oils, are not considered a food group but do contain essential nutrients and therefore are included as part of a healthy eating pattern. The difference as simple as the difference between a single and double carbon–carbon bond, good and bad fats, can have a significant impact on health.





The carbon–carbon double and triple bonds are examples of functional groups in organic chemistry. A functional group is a specific structural arrangement of atoms or bonds that imparts a characteristic chemical reactivity to a molecule. Alkanes have no functional group. A carbon–carbon double bond is considered a functional group because carbon–carbon double bonds chemically react in specific ways that differ from reactions of alkanes (for example, under certain circumstances, alkenes react with water); a carbon–carbon triple bond also undergoes certain specific chemical reactions. In the remainder of this section, we introduce two other common functional groups.

If an OH group (also called a hydroxyl group) is substituted for a hydrogen atom in a hydrocarbon molecule, the compound is an alcohol. Alcohols are named using the parent hydrocarbon name but with the final *-e* dropped and the suffix *-ol* attached. The two simplest alcohols are methanol and ethanol. Figure 6.8.4 shows their formulas along with a molecular model of each.



Figure 6.8.4: The Two Simplest Organic Alcohol Compounds. Alcohols have an OH functional group in the molecule.

Cholesterol, described in the chapter-opening essay, has an alcohol functional group, as its name implies.

ALCOHOL

Ethanol (also called ethyl alcohol) is the alcohol in alcoholic beverages. Other alcohols include methanol (or methyl alcohol), which is used as a solvent and a cleaner, and isopropyl alcohol (or rubbing alcohol), which is used as a medicinal disinfectant. Neither methanol nor isopropyl alcohol should be ingested, as they are toxic even in small quantities.

Another important family of organic compounds has a carboxyl group, in which a carbon atom is double-bonded to an oxygen atom and to an OH group. Compounds with a carboxyl functional group are called carboxylic acids, and their names end in *-oic acid*. Figure 6.8.5 shows the formulas and the molecular models of the two simplest carboxylic acids, perhaps best known by the common names formic acid and acetic acid. The carboxyl group is sometimes written in molecules as COOH.





Figure 6.8.5: The Two Smallest Organic Acids. The two smallest carboxylic acids are formic acid (found in the stingers of ants) and acetic acid (found in vinegar).

Many organic compounds are considerably more complex than the examples described here. Many compounds, such as cholesterol discussed in the chapter-opening essay, contain more than one functional group. The formal names can also be quite complex.

Example 6.8.1

Identify the functional group(s) in each molecule as a double bond, a triple bond, an alcohol, or a carboxyl.



d. CH₃CH₂CH₂CH₂OH

Answer a

This molecule has a double bond and a carboxyl functional group.

Answer b

This molecule has an alcohol functional group.

Answer c

This molecule has a double bond and a carboxyl functional group.

Answer d

This molecule has an alcohol functional group.

Exercise 6.8.1

Identify the functional group(s) in each molecule as a double bond, a triple bond, an alcohol, or a carboxyl.





CAREER FOCUS: FORENSIC CHEMIST

The main job of a forensic chemist is to identify unknown materials and their origins. Although forensic chemists are most closely associated in the public mind with crime labs, they are employed in pursuits as diverse as tracing evolutionary patterns in living organisms, identifying environmental contaminants, and determining the origin of manufactured chemicals.

In a crime lab, the forensic chemist has the job of identifying the evidence so that a crime can be solved. The unknown samples may consist of almost anything—for example, paint chips, blood, glass, cloth fibers, drugs, or human remains. The forensic chemist subjects them to a variety of chemical and instrumental tests to discover what the samples are. Sometimes these samples are extremely small, but sophisticated forensic labs have state-of-the-art equipment capable of identifying the smallest amount of unknown sample.

Another aspect of a forensic chemist's job is testifying in court. Judges and juries need to be informed about the results of forensic analyses, and it is the forensic chemist's job to explain those results. Good public-speaking skills, along with a broad background in chemistry, are necessary to be a successful forensic chemist.

CONCEPT REVIEW EXERCISES

- 1. What is organic chemistry?
- 2. What is a functional group? Give at least two examples of functional groups.

ANSWERS

- 1. Organic chemistry is the study of the chemistry of carbon compounds.
- 2. A functional group is a specific structural arrangement of atoms or bonds that imparts a characteristic chemical reactivity to the molecule; alcohol group and carboxylic group (answers will vary).

KEY TAKEAWAYS

- Organic chemistry is the study of the chemistry of carbon compounds.
- Organic molecules can be classified according to the types of elements and bonds in the molecules.

EXERCISES

- 1. Give three reasons why carbon is the central element in organic chemistry.
- 2. Are organic compounds based more on ionic bonding or covalent bonding? Explain.

CH.

3. Identify the type of hydrocarbon in each structure.

a. $CH_{3} CH_{2} CH_{2} CH_{2} CH_{3}$ b. $CH_{3} CH_{2} CH_{2} CH_{3} CH_{3}$ c. $CH_{2} CH_{2} CH_{3} CH_{3}$ c. $CH_{2} CH_{3} CH_{3} CH_{3}$ c. $CH_{2} CH_{3} CH_{3} CH_{3}$ c.



4. Identify the type of hydrocarbon in each structure.

сн≡с-сн,



5. Identify the functional group(s) in each molecule.





6. Identify the functional group(s) in each molecule.



7. How many functional groups described in this section contain carbon and hydrogen atoms only? Name them.

8. What is the difference in the ways the two oxygen atoms in the carboxyl group are bonded to the carbon atom?

ANSWERS

- 1. Carbon atoms bond reasonably strongly with other carbon atoms. Carbon atoms bond reasonably strongly with atoms of other elements. Carbon atoms make a large number of covalent bonds (four).
- 3. a. alkane
 - b. alkene
 - c. alkene
 - d. alkyne
- 5. a. alcohol
 - b. carboxyl
 - c. alcohol
 - d. carbon-carbon double bond and carbon-carbon triple bond
- 7. two; carbon-carbon double bonds and carbon-carbon triple bonds



1. An atomic mass unit equals 1.661×10^{-24} g. What is the mass in grams of each molecule of (a) H₂S (b) N₂O₄ (c) ICl₃ (d) NCl₃?

2. An atomic mass unit equals 1.661×10^{-24} g. What is the mass in grams of (a) O_2F_2 (b) CCl_4 (c) C_6H_6 (d) SO_3 ?

3. An atomic mass unit equals 1.661×10^{-24} g. What is the mass in grams of 5.00×10^{22} molecules of C₉H₈O₄?

4. An atomic mass unit equals 1.661×10^{-24} g. What is the mass in grams of 1.885×10^{20} molecules of C₂₇H₄₆O?

5. Acetic acid has the following structure:



This molecule can lose a hydrogen ion (H⁺) and the resulting anion can combine with other cations, such as Na⁺:



Name this ionic compound.

- 6. Formic acid (HCOOH) loses a hydrogen ion to make the formate ion (HCOO⁻). Write the formula for each ionic compound: potassium formate, calcium formate, and ferric formate.
- 7. Cyanogen has the formula C_2N_2 . Propose a bonding scheme that gives each atom the correct number of covalent bonds. (Hint: the two carbon atoms are in the center of a linear molecule.)
- 8. The molecular formula C_3H_6 represents not only propene, a compound with a carbon–carbon double bond, but also a molecule that has all single bonds. Draw the molecule with formula C_3H_6 that has all single bonds.
- 9. How many carbon-carbon single bonds, linked together, are needed to make a carbon chain that is 1.000 cm long?
- 10. How many carbon-carbon double bonds, linked together, are needed to make a carbon chain that is 1.000 cm long?
- 11. In addition to themselves, what other atoms can carbon atoms bond with and make covalent bonds that are nonpolar (or as nonpolar as possible)?
- 12. What is the greatest possible electronegativity difference between any two atoms? Use Figure 4.4 to find the answer.
- 13. Acetaminophen, a popular painkiller, has the following structure:



Name the recognizable functional groups in this molecule. Do you think there are other groups of atoms in this molecule that might qualify as functional groups?

14. Glutamic acid is the parent compound of monosodium glutamate (known as MSG), which is used as a flavor enhancer. Glutamic acid has the following structure:



Name the functional groups you recognize in this molecule. Do you think there are other groups of atoms in this molecule that might qualify as functional groups?

ANSWERS

1. 1a: 5.75×10^{-23} g; 1b: 1.53×10^{-22} g; 1c: 3.88×10^{-22} g; 1d: 6.06×10^{-23} g

- 3. 14.96 g
- 5. sodium acetate

CHEMIST



- 7. N≡C–C≡N
- 9. 6.49 \times 10^7 bonds
- 11. Hydrogen atoms make relatively nonpolar bonds with carbon atoms.
- 13. alcohol; the N–H group, the ring with double bonds, and the C=O are also likely functional groups.



6.10: COVALENT BONDING AND SIMPLE MOLECULAR COMPOUNDS (SUMMARY)

To ensure that you understand the material in this chapter, you should review the meanings of the following bold terms in the following summary and ask yourself how they relate to the topics in the chapter.

Atoms can share pairs of valence electrons to obtain a valence shell octet. This sharing of electrons is a **covalent bond**. A species formed from covalently bonded atoms is a **molecule** and is represented by a **molecular formula**, which gives the number of atoms of each type in the molecule. The two electrons shared in a covalent bond are called a **bonding pair of electrons**. The electrons that do not participate in covalent bonds are called **nonbonding pairs** (or **lone pairs**) **of electrons**. A covalent bond consisting of one pair of shared electrons is called a **single bond**.

Covalent bonds occur between nonmetal atoms. Naming simple covalent compounds follows simple rules similar to those for ionic compounds. However, for covalent compounds, numerical prefixes are used as necessary to specify the number of atoms of each element in the compound.

In some cases, more than one pair of electrons is shared to satisfy the octet rule. Two pairs of electrons are shared by two atoms to make a **double bond**. Three pairs of atoms are shared to make a **triple bond**. Single, double, and triple covalent bonds may be represented by one, two, or three dashes, respectively, between the symbols of the atoms.

The distance between two covalently bonded atoms is the **bond length**. Bond lengths depend on the types of atoms participating in the bond as well as the number of electron pairs being shared. A covalent bond can be a **polar covalent bond** if the electron sharing between the two atoms is unequal. If the sharing is equal, the bond is a **nonpolar covalent bond**. Because the strength of an atom's attraction for electrons in a bond is rated by the atom's **electronegativity**, the difference in the two atoms' electronegativities indicates how polar a covalent bond between those atoms will be.

The mass of a molecule is called its **molecular mass** and is the sum of the masses of the atoms in the molecule. The shape of a molecule can be predicted using **valence shell electron pair repulsion (VSEPR)**, which uses the fact that the negative electrons in covalent bonds repel each other as much as possible.

Organic chemistry is the chemistry of carbon compounds. Carbon forms covalent bonds with other carbon atoms and with the atoms of many other elements. The simplest organic compounds are **hydrocarbons**, which consist solely of carbon and hydrogen. Hydrocarbons containing only single bonds are called **alkanes (saturated hydrocarbons)**. Hydrocarbons containing carbon–carbon double bonds are **alkenes**, while hydrocarbons with carbon–carbon triple bonds are **alkynes**. Carbon-carbon double and triple bonds are examples of **functional groups**, atoms or bonds that impart a characteristic chemical function to the molecule. Other functional groups include the alcohol functional group (OH) and the **carboxyl functional group** (COOH). They are the characteristic functional group in organic compounds called **alcohols** and **carboxylic acids**.



7: INTRODUCTION TO CHEMICAL REACTIONS

Chemical change is a central concept in chemistry. The goal of chemists is to know how and why a substance changes in the presence of another substance or even by itself. Because there are tens of millions of known substances, there are a huge number of possible chemical reactions. In this chapter, we will find that many of these reactions can be classified into a small number of categories according to certain shared characteristics.

7.1: PRELUDE TO INTRODUCTION TO CHEMICAL REACTIONS

Although yeast has been used for thousands of years, its true nature has been known only for the last two centuries. Yeasts are singlecelled fungi. About 1,000 species are recognized, but the most common species is Saccharomyces cerevisiae, which is used in bread making. Other species are used for the fermentation of alcoholic beverages. Some species can cause infections in humans.

7.2: THE LAW OF CONSERVATION OF MATTER

One scientific law that provides the foundation for understanding in chemistry is the law of conservation of matter. It states that in any given system that is closed to the transfer of matter (in and out), the amount of matter in the system stays constant. A concise way of expressing this law is to say that the amount of matter in a system is conserved. The amount of matter in a closed system is conserved.

7.3: CHEMICAL EQUATIONS

Chemical reactions are represented by chemical equations that list reactants and products. Proper chemical equations are balanced; the same number of each element's atoms appears on each side of the equation.

7.4: QUANTITATIVE RELATIONSHIPS BASED ON CHEMICAL EQUATIONS

A balanced chemical equation not only describes some of the chemical properties of substances—by showing us what substances react with what other substances to make what products—but also shows numerical relationships between the reactants and the products. The study of these numerical relationships is called stoichiometry. A balanced chemical equation gives the ratios in which molecules of substances react and are produced in a chemical relation.

7.5: SOME TYPES OF CHEMICAL REACTIONS

Although there are untold millions of possible chemical reactions, most can be classified into a small number of general reaction types. Classifying reactions has two purposes: it helps us to recognize similarities among them, and it enables us to predict the products of certain reactions. A particular reaction may fall into more than one of the categories that we will define in this book.

7.6: OXIDATION-REDUCTION (REDOX) REACTIONS

Chemical reactions in which electrons are transferred are called oxidation-reduction, or redox, reactions. Oxidation is the loss of electrons. Reduction is the gain of electrons. Oxidation and reduction always occur together, even though they can be written as separate chemical equations.

7.7: REDOX REACTIONS IN ORGANIC CHEMISTRY AND BIOCHEMISTRY

Redox reactions are common in organic and biological chemistry, including the combustion of organic chemicals, respiration, and photosynthesis.

7.8: INTRODUCTION TO CHEMICAL REACTIONS (EXERCISES)

7.9: INTRODUCTION TO CHEMICAL REACTIONS (SUMMARY)

To ensure that you understand the material in this chapter, you should review the meanings of the following bold terms in the following summary and ask yourself how they relate to the topics in the chapter.



7.1: PRELUDE TO INTRODUCTION TO CHEMICAL REACTIONS

Although yeast has been used for thousands of years, its true nature has been known only for the last two centuries. Yeasts are single-celled fungi. About 1,000 species are recognized, but the most common species is *Saccharomyces cerevisiae*, which is used in bread making. Other species are used for the fermentation of alcoholic beverages. Some species can cause infections in humans.

Yeasts live primarily on sugars, such as glucose ($C_6H_{12}O_6$). They convert glucose into carbon dioxide (CO_2) and ethanol (C_2H_5OH) in a chemical transformation that is represented as follows:

$$C_6H_{12}O_6 \rightarrow 2CO_2(g) + 2C_2H_5OH(\ell)$$
 (7.1.1)

Bread making depends on the production of carbon dioxide. The gas, which is produced in tiny pockets in bread dough, acts as a leavening agent: it expands during baking and makes the bread rise. Leavened bread is softer, lighter, and easier to eat and chew than unleavened bread. The other major use of yeast, fermentation, depends on the production of ethanol, which results from the same chemical transformation. Some alcoholic beverages, such as champagne, can also be carbonated using the carbon dioxide produced by the yeast.

Yeast is among the simplest life forms on Earth, yet it is absolutely necessary for at least two major food industries. Without yeast to turn dough into bread and juice into wine, these foods and food industries would not exist today.

7.2: THE LAW OF CONSERVATION OF MATTER

LEARNING OBJECTIVES

- Correctly define a law as it pertains to science.
- State the law of conservation of matter.

In science, a law is a general statement that explains a large number of observations. Before being accepted, a law must be verified many times under many conditions. Laws are therefore considered the highest form of scientific knowledge and are generally thought to be inviolable. Scientific laws form the core of scientific knowledge. One scientific law that provides the foundation for understanding in chemistry is the law of conservation of matter. It states that in any given system that is closed to the transfer of matter (in and out), the amount of matter in the system stays constant. A concise way of expressing this law is to say that the amount of matter in a system is *conserved*.

With the development of more precise ideas on elements, compounds and mixtures, scientists began to investigate how and why substances react. French chemist A. Lavoisier laid the foundation to the scientific investigation of matter by describing that substances react by following certain laws. These laws are called the laws of chemical combination. These eventually formed the basis of Dalton's Atomic Theory of Matter.

LAW OF CONSERVATION OF MASS

According to this law, during any physical or chemical change, the total mass of the products remains equal to the total mass of the reactants.

$$\underbrace{\underbrace{\operatorname{HgO}(s)}_{100 \text{ g}}}_{100 \text{ g}} \xrightarrow{\operatorname{Mercury}}_{92.6 \text{ g}} \underbrace{\underbrace{\underbrace{\operatorname{Hg(l)}}_{92.6 \text{ g}}}_{7.4 \text{ g}}}_{7.4 \text{ g}}$$
(7.2.1)

The law of conservation of mass is also known as the "law of indestructibility of matter."

Example 7.2.1

If heating 10 grams of $CaCO_3$ produces 4.4 g of CO_2 and 5.6 g of CaO, show that these observations are in agreement with the law of conservation of mass.



A sample of calcium carbonate (CaCO3). Image used with permission (Public Domain; Walkerma).

SOLUTION

- Mass of the reactants: 10 *g*
- Mass of the products: 4.4 g + 5.6 g = 10 g.

Because the mass of the reactants is equal to the mass of the products, the observations are in agreement with the law of conservation of mass.

What does this mean for chemistry? In any chemical change, one or more initial substances change into a different substance or substances. Both the initial and final substances are composed of atoms because all matter is composed of atoms. According to the law of conservation of matter, matter is neither created nor destroyed, so we must have the same number and type of atoms after the chemical change as were present before the chemical change.

Before looking at explicit examples of the law of conservation of matter, we need to examine the method chemists use to represent chemical changes.

Exercise 7.2.1



- a. What is the law of conservation of matter?
- b. How does the law of conservation of matter apply to chemistry?

Answer a

The law of conservation of matter states that in any given system that is closed to the transfer of matter, the amount of matter in the system stays constant

Answer b

The law of conservation of matter says that in chemical reactions, the total mass of the products must equal the total mass of the reactants.

SUMMARY

The amount of matter in a closed system is conserved.

CONTRIBUTORS

• Binod Shrestha (University of Lorraine)

EXERCISES

- 1. Express the law of conservation of matter in your own words.
- 2. Explain why the concept of conservation of matter is considered a scientific law.

ANSWER

1. Matter may not be created or destroyed.



7.3: CHEMICAL EQUATIONS

LEARNING OBJECTIVES

- Define chemical reaction.
- Use a balanced chemical equation to represent a chemical reaction.

Water (H_2O) is composed of hydrogen and oxygen. Suppose we imagine a process in which we take some elemental hydrogen (H_2) and elemental oxygen (O_2) and let them react to make water. The statement

"hydrogen and oxygen react to make water"

is one way to represent that process, which is called a chemical reaction. Figure 7.3.1 shows a rather dramatic example of this very reaction.



Figure 7.3.1: The Formation of Water. Hydrogen and oxygen combine to form water. Here, the hydrogen gas in the zeppelin *SS Hindenburg* reacts with oxygen in the air to make water. Source: Photo courtesy of the US Navy. For a video of this see https://www.youtube.com/watch?v=CgWHbpMVQ1U.

To simplify the writing of reactions, we use formulas instead of names when we describe a reaction. We can also use symbols to represent other words in the reaction. A plus sign connects the initial substances (and final substances, if there is more than one), and an arrow (\rightarrow) represents the chemical change:

$$\mathrm{H}_{2} + \mathrm{O}_{2} \to \mathrm{H}_{2}\mathrm{O} \tag{7.3.1}$$

This statement is one example of a chemical equation, an abbreviated way of using symbols to represent a chemical change. The substances on the left side of the arrow are called reactants, and the substances on the right side of the arrow are called products. It is not uncommon to include a phase label with each formula—(s) for solid, (ℓ) for liquid, (g) for gas, and (aq) for a substance dissolved in water, also known as an *aqueous solution*. If we included phase labels for the reactants and products, under normal environmental conditions, the reaction would be as follows:

$$H_2(g) + O_2(g) \to H_2O(\ell)$$
 (7.3.2)

Chemical equations can also be used to describe physical changes. We will see examples of this soon.

This equation is still not complete because *it does not satisfy the law of conservation of matter*. Count the number of atoms of each element on each side of the arrow. On the reactant side, there are two H atoms and two O atoms; on the product side, there are two H atoms and only one oxygen atom. The equation is not balanced because the number of oxygen atoms on each side is not the same (Figure 7.3.2).



Figure 7.3.2: Balanced—Yes or No?. By counting the atoms of each element, we can see that the reaction is not balanced as written.

To make this chemical equation conform to the law of conservation of matter, we must revise the amounts of the reactants and the products as necessary to get the same number of atoms of a given element on each side. Because every substance has a characteristic chemical formula, we cannot change the chemical formulas of the individual substances. For example, we cannot change the formula for elemental oxygen to O. However, we can assume that different numbers of reactant molecules or product molecules may be involved. For instance, perhaps two water molecules are produced, not just one:

$$H_2(g) + O_2(g) \to 2 H_2O(\ell)$$
 (7.3.3)



The 2 preceding the formula for water is called a coefficient. It implies that two water molecules are formed. There are now two oxygen atoms on each side of the equation.

This point is so important that we should repeat it. You **cannot** change the formula of a chemical substance to balance a chemical reaction! You **must** use the proper chemical formula of the substance.

Unfortunately, by inserting the coefficient 2 in front of the formula for water, we have also changed the number of hydrogen atoms on the product side as well. As a result, we no longer have the same number of hydrogen atoms on each side. This can be easily fixed, however, by putting a coefficient of 2 in front of the diatomic hydrogen reactant:

$$2 H_2(g) + O_2(g) \rightarrow 2 H_2O(\ell)$$
 (7.3.4)

Now we have four hydrogen atoms and two oxygen atoms on each side of the equation. The law of conservation of matter is satisfied because we now have the same number of atoms of each element in the reactants and in the products. We say that the reaction is balanced (Figure 7.3.3). The diatomic oxygen has a coefficient of 1, which typically is not written but assumed in balanced chemical equations.



Figure 7.3.3: Balanced—Yes or No?. By counting the atoms of each element, we can see that the reaction is now balanced.

Proper chemical equations should be balanced. Writing balanced reactions is a chemist's way of acknowledging the law of conservation of matter.

Example 7.3.1

Is each chemical equation balanced?

a. $2Na(s) + O_2(g) \rightarrow 2Na_2O(s)$

b. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell)$

c. $AgNO_3(aq) + 2KCl(aq) \rightarrow AgCl(s) + KNO_3(aq)$

SOLUTION

- a. By counting, we find two sodium atoms and two oxygen atoms in the reactants and four sodium atoms and two oxygen atoms in the products. This equation is not balanced.
- b. The reactants have one carbon atom, four hydrogen atoms, and four oxygen atoms. The products have one carbon atom, four hydrogen atoms, and four oxygen atoms. This equation is balanced.
- c. The reactants have one silver atom, one nitrogen atom, three oxygen atoms, two potassium atoms, and two chlorine atoms. The products have one silver atom, one chlorine atom, one potassium atom, one nitrogen atom, and three oxygen atoms. Because there are different numbers of chlorine and potassium atoms, this equation is not balanced.



Exercise 7.3.1

Is each chemical equation balanced?

$$\begin{array}{l} \text{a. } 2Hg_{(\ell)} + O_{2(g)} \rightarrow Hg_2O_{2(s)} \\ \text{b. } C_2H_{4(g)} + 2O_{2(g)} \rightarrow 2CO_{2(g)} + 2H2O_{(\ell)} \\ \text{c. } Mg(NO_3)_{2(s)} + 2Li_{(s)} \rightarrow Mg_{(s)} + 2LiNO_{3(s)} \end{array}$$

How does one balance a chemical equation, starting with the correct formulas of the reactants and products? Basically, a back-andforth approach is adopted, counting the number of atoms of one element on one side, checking the number of atoms of that element on the other side, and changing a coefficient if necessary. Then check another element, going back and forth from one side of the equation to another, until each element has the same number of atoms on both sides of the arrow. In many cases, it does not matter which element is balanced first and which is balanced last, as long as all elements have the same number of atoms on each side of the equation.

For example, to balance the equation

$$\operatorname{CH}_{4} + \operatorname{Cl}_{2} \to \operatorname{CCl}_{4} + \operatorname{HCl}$$
 (7.3.5)

we might choose to count the carbon atoms first, finding that both sides are balanced with one carbon atom. The reactant side has four hydrogen atoms, so the product side must also have four hydrogen atoms. We fix this by putting a 4 in front of the HCl:

$$\operatorname{CH}_4 + \operatorname{Cl}_2 \to \operatorname{CCl}_4 + 4\operatorname{HCl}$$
 (7.3.6)

Now each side has four hydrogen atoms. The product side has a total of eight chlorine atoms (four from the CCl_4 and four from the four molecules of HCl), so we need eight chlorine atoms as reactants. Because elemental chlorine is a diatomic molecule, we need four chlorine molecules to get a total of eight chlorine atoms. We add another 4 in front of the Cl_2 reactant:

$$\mathrm{CH}_4 + 4\,\mathrm{Cl}_2 \to \mathrm{CCl}_4 + 4\,\mathrm{HCl} \tag{7.3.7}$$

Now we check: each side has one carbon atom, four hydrogen atoms, and eight chlorine atoms. The chemical equation is balanced.

Exercise 7.3.2

a. What are the parts of a chemical equation?

b. Explain why chemical equations need to be balanced.

Answer a

reactants and products

Answer b

Chemical equations need to be balanced to satisfy the law of conservation of matter.

SUMMARY

Chemical reactions are represented by chemical equations that list reactants and products. Proper chemical equations are balanced; the same number of each element's atoms appears on each side of the equation.

EXERCISES

- 1. Write a chemical equation to express the fact that hydrogen gas and solid iodine react to make gaseous hydrogen iodide. Make sure the equation satisfies the law of conservation of matter.
- 2. Write a chemical equation to express the fact that sodium metal and chlorine gas react to make solid sodium chloride. Make sure the equation satisfies the law of conservation of matter.
- 3. Write an equation expressing the fact that hydrogen gas and fluorine gas react to make gaseous hydrogen fluoride. Make sure the equation satisfies the law of conservation of matter.
- 4. Write an equation expressing the fact that solid potassium and fluorine gas react to make solid potassium fluoride. Make sure the equation satisfies the law of conservation of matter.
- 5. Mercury reacts with oxygen to make mercury(II) oxide. Write a balanced chemical equation that summarizes this reaction.
- 6. Octane (C₈H₁₈) reacts with oxygen to make carbon dioxide and water. Write a balanced chemical equation that summarizes this reaction.



- 7. Propyl alcohol (C₃H₇OH) reacts with oxygen to make carbon dioxide and water. Write a balanced chemical equation that summarizes this reaction.
- 8. Sulfuric acid reacts with iron metal to make iron(III) sulfate and hydrogen gas. Write a balanced chemical equation that summarizes this reaction.
- 9. Balance each equation.

a. $MgCl_2 + K \rightarrow KCl + Mg$ b. $C_6H_{12}O_6 + O_2 \rightarrow CO_2 + H_2O$ c. $NaN_3 \rightarrow Na + N_2$ (This is the reaction used to inflate airbags in cars.)

10. Balance each equation.

a. $NH_4NO_3 \rightarrow N_2O + H_2O$ b. $TiBr_4 + H_2O \rightarrow TiO_2 + HBr$ c. $C_3H_5N_3O_9 \rightarrow CO_2 + N_2 + O_2 + H_2O$ (This reaction represents the decomposition of nitroglycerine.)

11. Balance each equation.

a. $NH_3 + O_2 \rightarrow NO + H_2O$ b. $Li + N_2 \rightarrow Li_3N$ c. $AuCl \rightarrow Au + AuCl_3$

12. Balance each equation.

a. NaOH + H₃PO₄ \rightarrow Na₃PO₄ + H₂O b. N₂H₄ + Cl₂ \rightarrow N₂ + HCl c. Na₂S + H₂S \rightarrow NaSH

- 13. Chromium(III) oxide reacts with carbon tetrachloride to make chromium(III) chloride and phosgene (COCl₂). Write the balanced chemical equation for this reaction.
- 14. The reaction that occurs when an Alka-Seltzer tablet is dropped into a glass of water has sodium bicarbonate reacting with citric acid (H₃C₆H₅O₇) to make carbon dioxide, water, and sodium citrate (Na₃C₆H₅O₇). Write the balanced chemical equation for this reaction.
- 15. When sodium hydrogen carbonate is used to extinguish a kitchen fire, it decomposes into sodium carbonate, water, and carbon dioxide. Write a balanced chemical equation for this reaction.
- 16. Elemental bromine gas can be generated by reacting sodium bromide with elemental chlorine. The other product is sodium chloride. Write a balanced chemical equation for this reaction.

ANSWERS

- $1. \text{ H}_2(g) + I_2(s) \rightarrow 2\text{HI}(g)$
- 3. $H_2(g) + F_2(g) \rightarrow 2HF(g)$
- 5. 2Hg + O₂ \rightarrow 2HgO
- 7. $2C_3H_7OH + 9O_2 \rightarrow 6CO_2 + 8H_2O$
- 9. a. $MgCl_2 + 2K \rightarrow 2KCl + Mg$ b. $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$ c. $2NaN_3 \rightarrow 2Na + 3N_2$
- 11. a. $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$ b. $6Li + N_2 \rightarrow 2Li_3N$ c. $3AuCl \rightarrow 2Au + AuCl_3$
- 13. $Cr_2O_3 + 3CCl_4 \rightarrow 2CrCl_3 + 3COCl_2$
- 15. $2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O)$



7.4: QUANTITATIVE RELATIONSHIPS BASED ON CHEMICAL EQUATIONS

LEARNING OBJECTIVES

• To calculate the amount of one substance that will react with or be produced from a given amount of another substance.

A balanced chemical equation not only describes some of the chemical properties of substances—by showing us what substances react with what other substances to make what products—but also shows numerical relationships between the reactants and the products. The study of these numerical relationships is called stoichiometry. The stoichiometry of chemical equations revolves around the coefficients in the balanced chemical equation because these coefficients determine the molecular ratio in which reactants react and products are made.

The word stoichiometry is pronounced "stow-eh-key-OM-et-tree." It is of mixed Greek and English origins, meaning roughly "measure of an element."

LOOKING CLOSER: STOICHIOMETRY IN COOKING

Let us consider a stoichiometry analogy from the kitchen. A recipe that makes 1 dozen biscuits needs 2 cups of flour, 1 egg, 4 tablespoons of shortening, 1 teaspoon of salt, 1 teaspoon of baking soda, and 1 cup of milk. If we were to write this as a chemical equation, we would write

2 c flour + 1 egg + 4 tbsp shortening + 1 tsp salt + 1 tsp baking soda + 1 c milk \rightarrow 12 biscuits

(Unlike true chemical reactions, this one has all 1 coefficients written explicitly—partly because of the many different units here.) This equation gives us ratios of how much of what reactants are needed to make how much of what product. Two cups of flour, when combined with the proper amounts of the other ingredients, will yield 12 biscuits. One teaspoon of baking soda (when also combined with the right amounts of the other ingredients) will make 12 biscuits. One egg must be combined with 1 cup of milk to yield the product food. Other relationships can also be expressed.

We can use the ratios we derive from the equation for predictive purposes. For instance, if we have 4 cups of flour, how many biscuits can we make if we have enough of the other ingredients? It should be apparent that we can make a double recipe of 24 biscuits.

But how would we find this answer formally, that is, mathematically? We would set up a conversion factor, much like we did in Chapter 1 "Chemistry, Matter, and Measurement". Because 2 cups of flour make 12 biscuits, we can set up an equivalency ratio:

$$\frac{12 \text{ biscuits}}{2 \text{ c flour}} \tag{7.4.1}$$

We then can use this ratio in a formal conversion of flour to biscuits:

$$4 \text{ c flour} \times \frac{12 \text{ biscuits}}{2 \text{ c flour}} = 24 \text{ biscuits}$$
(7.4.2)

Similarly, by constructing similar ratios, we can determine how many biscuits we can make from any amount of ingredient. When you are doubling or halving a recipe, you are doing a type of stoichiometry. Applying these ideas to chemical reactions should not be difficult if you use recipes when you cook.





A recipe shows how much of each ingredient is needed for the proper reaction to take place. Image used with permission from Wikipedia.

Consider the following balanced chemical equation:

$$2C_2H_2 + 5O_2 \to 4CO_2 + 2H_2O$$
 (7.4.3)

The coefficients on the chemical formulas give the ratios in which the reactants combine and the products form. Thus, we can make the following statements and construct the following ratios:

Statement from the Balanced Chemical Reaction	Ratio	Inverse Ratio
two C_2H_2 molecules react with five O_2 molecules	$\frac{2\mathrm{C}_{2}\mathrm{H}_{2}}{5\mathrm{O}_{2}}$	$\frac{5\mathrm{O}_2}{2\mathrm{C}_2\mathrm{H}_2}$
two C_2H_2 molecules react to make four CO_2 molecules	$\frac{2C_2H_2}{4CO_2}$	$\frac{4\mathrm{CO}_2}{2\mathrm{C}_2\mathrm{H}_2}$
five O_2 molecules react to make two H_2O molecules	$\frac{5\mathrm{O}_2}{2\mathrm{H}_2\mathrm{O}}$	$\frac{2H_2O}{5O_2}$
four CO_2 molecules are made at the same time as two H_2O molecules	$\frac{2\mathrm{H}_{2}\mathrm{O}}{4\mathrm{CO}_{2}}$	$\frac{4\mathrm{CO}_2}{2\mathrm{H}_2\mathrm{O}}$

Other relationships are possible; in fact, 12 different conversion factors can be constructed from this balanced chemical equation. In each ratio, the unit is assumed to be molecules because that is how we are interpreting the chemical equation.

Any of these fractions can be used as a conversion factor to relate an amount of one substance to an amount of another substance. For example, suppose we want to know how many CO₂ molecules are formed when 26 molecules of C₂H₂ are reacted. As usual with a conversion problem, we start with the amount we are given—26C₂H₂—and multiply it by a conversion factor that cancels out our original unit and introduces the unit we are converting to—in this case, CO₂. That conversion factor is $\frac{4CO_2}{2C_2H_2}$, which is composed of terms that come directly from the balanced chemical equation. Thus, we have

$$26C_2H_2 imes rac{4CO_2}{2C_2H_2}$$
 (7.4.4)

The molecules of C₂H₂ cancel, and we are left with molecules of CO₂. Multiplying through, we get

$$26C_2H_2 \times \frac{4CO_2}{2C_2H_2} = 52CO_2 \tag{7.4.5}$$

Thus, 52 molecules of CO₂ are formed.

This application of stoichiometry is extremely powerful in its predictive ability, as long as we begin with a balanced chemical equation. Without a balanced chemical equation, the predictions made by simple stoichiometric calculations will be incorrect.



Example 7.4.1

Start with this balanced chemical equation.

 $KMnO_4 + 8HCl + 5FeCl_2 \rightarrow 5 FeCl_3 + MnCl_2 + 4H_2O + KCl$

- 1. Verify that the equation is indeed balanced.
- 2. Give 2 ratios that give the relationship between HCl and FeCl₃.

SOLUTION

- 1. Each side has 1 K atom and 1 Mn atom. The 8 molecules of HCl yield 8 H atoms, and the 4 molecules of H₂O also yield 8 H atoms, so the H atoms are balanced. The Fe atoms are balanced, as we count 5 Fe atoms from 5 FeCl₂ reactants and 5 FeCl₃ products. As for Cl, on the reactant side, there are 8 Cl atoms from HCl and 10 Cl atoms from the 5 FeCl₂ formula units, for a total of 18 Cl atoms. On the product side, there are 15 Cl atoms from the 5 FeCl₃ formula units, 2 from the MnCl₂ formula unit, and 1 from the KCl formula unit. This is a total of 18 Cl atoms in the products, so the Cl atoms are balanced. All the elements are balanced, so the entire chemical equation is balanced.
- 2. Because the balanced chemical equation tells us that 8 HCl molecules react to make 5 FeCl₃ formula units, we have the following 2 ratios: $\frac{8 \text{HCl}}{5 \text{FeCl}_3}$ and $\frac{5 \text{FeCl}_3}{8 \text{HCl}}$. There are a total of 42 possible ratios. Can you find the other 40 relationships?

Exercise 7.4.1

Start with this balanced chemical equation.

$$2KMnO_4 + 3CH_2 {=} CH_2 + 4H_2O \rightarrow 2MnO_2 + 3HOCH_2CH_2OH + 2KOH$$

- a. Verify that the equation is balanced.
- b. Give 2 ratios that give the relationship between KMnO₄ and CH₂=CH₂. (A total of 30 relationships can be constructed from this chemical equation. Can you find the other 28?)

SUMMARY

A balanced chemical equation gives the ratios in which molecules of substances react and are produced in a chemical reaction.

CONCEPT REVIEW EXERCISES

- 1. Explain how stoichiometric ratios are constructed from a chemical equation.
- 2. Why is it necessary for a chemical equation to be balanced before it can be used to construct conversion factors?

ANSWERS

- 1. Stoichiometric ratios are made using the coefficients of the substances in the balanced chemical equation.
- 2. A balanced chemical equation is necessary so one can construct the proper stoichiometric ratios.

EXERCISES

1. Balance this equation and write every stoichiometric ratio you can from it.

$$NH_4NO_3 \rightarrow N_2O + H_2O$$

2. Balance this equation and write every stoichiometric ratio you can from it.

$$N_2 + H_2 \rightarrow NH_3$$

3. Balance this equation and write every stoichiometric ratio you can from it.

$$Fe_2O_3 + C \rightarrow Fe + CO_2$$

4. Balance this equation and write every stoichiometric ratio you can from it.

$$Fe_2O_3 + CO \rightarrow Fe + CO_2$$

5. Balance this equation and determine how many molecules of CO_2 are formed if 15 molecules of C_6H_6 are reacted.

$$C_6H_6 + O_2 \rightarrow CO_2 + H_2O_2$$

6. Balance this equation and determine how many molecules of Ag₂CO₃(s) are produced if 20 molecules of Na₂CO₃ are reacted.

 $Na_2CO_3(aq) + AgNO_3(aq) \rightarrow NaNO_3(aq) + Ag_2CO_3(s)$

7. Copper metal reacts with nitric acid according to this equation:

 $3Cu(s) + 8HNO_3(aq) \rightarrow 3Cu(NO_3)_2(aq) + 2NO(g) + 4H_2O(\ell)$





a. Verify that this equation is balanced.

- b. How many Cu atoms will react if 488 molecules of aqueous HNO₃ are reacted?
- 8. Gold metal reacts with a combination of nitric acid and hydrochloric acid according to this equation:

$$Au(s) + 3HNO_3(aq) + 4HCl(aq) \rightarrow HAuCl_4(aq) + 3NO_2(g) + 3H_2O(\ell)$$

- a. Verify that this equation is balanced.
- b. How many Au atoms react with 639 molecules of aqueous HNO₃?
- 9. Sulfur can be formed by reacting sulfur dioxide with hydrogen sulfide at high temperatures according to this equation:

$$SO_2(g) + 2H_2S(g) \rightarrow 3S(g) + 2H_2O(g)$$

- a. Verify that this equation is balanced.
- b. How many S atoms will be formed from by reacting 1,078 molecules of H₂S?

10. Nitric acid is made by reacting nitrogen dioxide with water:

$$3NO_2(g) + H_2O(\ell) \rightarrow 2HNO_3(aq) + NO(g)$$

a. Verify that this equation is balanced.

b. How many molecules of NO will be formed by reacting 2,268 molecules of NO₂?

ANSWERS

$$1. \text{ NH}_4\text{NO}_3 \rightarrow \text{N}_2\text{O} + 2\text{H}_2\text{O}; \text{ the stoichiometric ratios are } \frac{1\text{NH}_4\text{NO}_3}{1\text{N}_2\text{O}}, \frac{1\text{NH}_4\text{NO}_3}{2\text{H}_2\text{O}}, \frac{1\text{N}_2\text{O}}{2\text{H}_2\text{O}}, \text{ and their reciprocals.}$$

$$3. 2\text{Fe}_2\text{O}_3 + 3\text{C} \rightarrow 4\text{Fe} + 3\text{CO}_2; \text{ the stoichiometric ratios are } \frac{2\text{Fe}_2\text{O}_3}{3\text{C}}, \frac{2\text{Fe}_2\text{O}_3}{4\text{Fe}}, \frac{2\text{Fe}_2\text{O}_3}{3\text{CO}_2}, \frac{3\text{C}}{4\text{Fe}}, \frac{3\text{C}}{3\text{CO}_2}, \frac{4\text{Fe}}{3\text{CO}_2}, \text{ and their reciprocals.}$$

reciprocals.

- 5. $2C_6H_6$ + 15O₂ → 12CO₂ + 6H₂O; 90 molecules
- 7. a. It is balanced. b. 183 atoms
- 9. a. It is balanced.

b. 1,617 atoms



7.5: SOME TYPES OF CHEMICAL REACTIONS

LEARNING OBJECTIVES

• To classify a given chemical reaction into a variety of types.

Although there are untold millions of possible chemical reactions, most can be classified into a small number of general reaction types. Classifying reactions has two purposes: it helps us to recognize similarities among them, and it enables us to predict the products of certain reactions. A particular reaction may fall into more than one of the categories that we will define in this book.

COMBINATION (COMPOSITION) REACTIONS

A combination (composition) reaction is a chemical reaction that makes a single substance from two or more reactants. There may be more than one molecule of product in the balanced chemical equation, but there is only one substance produced. For example, the equation

$$4 \operatorname{Fe} + 3 \operatorname{O}_2 \to 2 \operatorname{Fe}_2 \operatorname{O}_3 \tag{7.5.1}$$

is a combination reaction that produces Fe_2O_3 from its constituent elements—Fe and O_2 . Combination reactions do not have to combine elements, however. The chemical equation

$$\operatorname{Fe}_2\operatorname{O}_3 + 3\operatorname{SO}_3 \to \operatorname{Fe}_2(\operatorname{SO}_4)_3$$
(7.5.2)

shows a combination reaction in which Fe₂O₃ combines with three molecules of SO₃ to make Fe₂(SO₄)₃.

Example 7.5.1

Which equations are combination reactions?

a. $\operatorname{Co}(s) + \operatorname{Cl}_2(g) \rightarrow \operatorname{Co}\operatorname{Cl}_2(s)$ b. $\operatorname{CO}(g) + \operatorname{Cl}_2(g) \rightarrow \operatorname{CO}\operatorname{Cl}_2(g)$ c. $\operatorname{N}_2\operatorname{H}_4(\ell) + \operatorname{O}_2(g) \rightarrow \operatorname{N}_2(g) + 2\operatorname{H}_2\operatorname{O}(\ell)$

SOLUTION

a. This is a combination reaction.

- b. This is a combination reaction. (The compound COCl₂ is called phosgene and, in the past, was used as a gassing agent in chemical warfare.)
- c. This is not a combination reaction.

Exercise 7.5.1

Which equations are combination reactions?

a. $P_4(s) + 6Cl_2(g) \rightarrow 4PCl_3(g)$

b. $SO_3(\ell) + H_2O(\ell) \rightarrow H_2SO_4(\ell)$

c. NaOH(s) + HCl(g) \rightarrow NaCl(s) + H₂O(ℓ)

DECOMPOSITION REACTIONS

A decomposition reaction is the reverse of a combination reaction. In a decomposition reaction, a single substance is converted into two or more products. There may be more than one molecule of the reactant, but there is only one substance initially. For example, the equation

$$2 \operatorname{NaHCO}_{3}(s) \to \operatorname{Na}_{2} \operatorname{CO}_{3}(s) + \operatorname{CO}_{2}(g) + \operatorname{H}_{2} \operatorname{O}(\ell)$$

$$(7.5.3)$$

is a decomposition reaction that occurs when NaHCO3 is exposed to heat. Another example is the decomposition of KClO3:

$$2 \operatorname{KClO}_3(s) \to 2 \operatorname{KCl}(s) + 3 \operatorname{O}_2(g) \tag{7.5.4}$$

This reaction was once commonly used to generate small amounts of oxygen in the chemistry lab.

The decomposition reaction of $NaHCO_3$ is the reaction that occurs when baking soda is poured on a small kitchen fire. The intent is that the H_2O and CO_2 produced by the decomposition will smother the flames.

COMBUSTION REACTIONS


A combustion reaction occurs when a substance combines with molecular oxygen to make oxygen-containing compounds of other elements in the reaction. One example is the burning of acetylene (C_2H_2) in torches:

$$2 C_2 H_2 + 5 O_2 \rightarrow 4 CO_2 + 2 H_2 O$$
 (7.5.5)

Oxygen (in its elemental form) is a crucial reactant in combustion reactions, and it is also present in the products.

Energy in the form of heat is usually given off as a product in a combustion reaction as well.

Example 7.5.2

Identify each type of reaction.

a. $2K(s) + S(s) + 2O_2(g) \rightarrow K_2SO_4(s)$

b. $(NH_4)_2Cr_2O_7(s) \rightarrow N_2(g) + Cr_2O_3(s) + 4H_2O(\ell)$

c. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell)$

SOLUTION

- a. Multiple reactants are combining to make a single product, so this reaction is a combination reaction.
- b. A single substance reacts to make several products, so we have a decomposition reaction.
- c. Oxygen reacts with a compound to make carbon dioxide (an oxide of carbon) and water (an oxide of hydrogen). This is a combustion reaction.

Exercise 7.5.2

```
Identify each type of reaction.
```

a. $C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$

b. $2Ca(s) + O_2(g) \rightarrow 2CaO(s)$

c. $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

SUMMARY

There are several recognizable types of chemical reactions: combination, decomposition, and combustion reactions are examples.

CONCEPT REVIEW EXERCISES

- 1. What is the difference between a combination reaction and a combustion reaction?
- 2. Give the distinguishing characteristic(s) of a decomposition reaction.
- 3. How do we recognize a combustion reaction?

ANSWERS

- 1. A combination reaction produces a certain substance; a combustion reaction is a vigorous reaction, usually a combination with oxygen, that is accompanied by the production of light and/or heat.
- 2. In a decomposition reaction, a single substance reacts to make multiple substances as products.
- 3. A combustion reaction is typically a vigorous reaction accompanied by light and/or heat, usually because of reaction with oxygen.

EXERCISES

1. Identify each type of reaction.

a.
$$C_6H_5CH_3 + 9O_2 \rightarrow 7CO_2 + 4H_2O$$

b. $2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$
c. $C + 2H_2 \rightarrow CH_4$

2. Identify each type of reaction.

```
a. P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4
b. FeO + SO<sub>3</sub> \rightarrow FeSO<sub>4</sub>
c. CaCO<sub>3</sub>(s) \rightarrow CO<sub>2</sub>(g) + CaO(s)
```

3. Identify each type of reaction.

```
a. 2NH_4NO_3(s) \rightarrow 2N_2(g) + 4H_2O(g) + O_2(g)
```



- b. Hg(ℓ) + ¹/₂O₂ (g) \rightarrow HgO(s) c. CH₂CH₂(g) + Br₂(ℓ) \rightarrow CH₂BrCH₂Br
- 4. Identify each type of reaction.
 - a. Ti(s) + O₂(g) \rightarrow TiO₂(s)
 - b. H₂SO₃(aq) \rightarrow H₂O(ℓ) + SO₂(g)
 - c. $3O_2(g) \rightarrow 2O_3(g)$

- 1. a. combustion
 - b. decomposition
 - c. combination
- 3. a. decomposition
 - b. combustion or combination
 - c. combination



7.6: OXIDATION-REDUCTION (REDOX) REACTIONS

LEARNING OBJECTIVES

• To identify a chemical reaction as an oxidation-reduction reaction.

When zinc metal is submerged into a quantity of aqueous HCl, the following reaction occurs (Figure 7.6.1):

$$\operatorname{Zn}(s) + 2\operatorname{HCl}(\operatorname{aq}) \to \operatorname{H}_{2}(g) + \operatorname{ZnCl2}(\operatorname{aq})$$
 (7.6.1)

This is one example of what is sometimes called a single replacement reaction because Zn replaces H in combination with Cl.



Figure 7.6.1: Zinc Metal plus Hydrochloric Acid. It is fairly obvious that zinc metal reacts with aqueous hydrochloric acid! The bubbles are hydrogen gas.

Because some of the substances in this reaction are aqueous, we can separate them into ions:

$$Zn(s) + 2 H^{+}(aq) + 2 Cl^{-}(aq) \rightarrow H_{2}(g) + Zn^{2+}(aq) + 2 Cl^{-}(aq)$$
 (7.6.2)

Viewed this way, the net reaction seems to be a charge transfer between zinc and hydrogen atoms. (There is no net change experienced by the chloride ion.) In fact, electrons are being transferred from the zinc atoms to the hydrogen atoms (which ultimately make a molecule of diatomic hydrogen), changing the charges on both elements.

To understand electron-transfer reactions like the one between zinc metal and hydrogen ions, chemists separate them into two parts: one part focuses on the loss of electrons, and one part focuses on the gain of electrons. The loss of electrons is called oxidation. The gain of electrons is called reduction. Because any loss of electrons by one substance must be accompanied by a gain in electrons by something else, oxidation and reduction always occur together. As such, electron-transfer reactions are also called oxidation-reduction reactions, or simply **redox reactions**. The atom that loses electrons is **oxidized**, and the atom that gains electrons is **reduced**. Also, because we can think of the species being oxidized as causing the reduction, the species being oxidized is called the reducing agent, and the species being reduced is called the oxidizing agent.

Because batteries are used as sources of electricity (that is, of electrons), all batteries are based on redox reactions.

Although the two reactions occur together, it can be helpful to write the oxidation and reduction reactions separately as half reactions. In half reactions, we include only the reactant being oxidized or reduced, the corresponding product species, any other species needed to balance the half reaction, and the electrons being transferred. Electrons that are lost are written as products; electrons that are gained are written as reactants. For example, in our earlier equation, now written without the chloride ions,

$$Zn(s) + 2 H^{+}(aq) \rightarrow Zn^{2+}(aq) + H_{2}(g)$$
 (7.6.3)

zinc atoms are oxidized to Zn^{2+} . The half reaction for the oxidation reaction, omitting phase labels, is as follows:

$$Zn \to Zn^{2+} + 2e^{-}$$
 (7.6.4)

This half reaction is balanced in terms of the number of zinc atoms, and it also shows the two electrons that are needed as products to account for the zinc atom losing two negative charges to become a 2+ ion. With half reactions, there is one more item to balance: the overall charge on each side of the reaction. If you check each side of this reaction, you will note that both sides have a zero net charge. Hydrogen is reduced in the reaction. The balanced reduction half reaction is as follows:



(7.6.5)

$$2\,\mathrm{H^+} + 2\,\mathrm{e^-} \to \mathrm{H_2}$$

There are two hydrogen atoms on each side, and the two electrons written as reactants serve to neutralize the 2+ charge on the reactant hydrogen ions. Again, the overall charge on both sides is zero.

The overall reaction is simply the combination of the two half reactions and is shown by adding them together.

$$Zn \rightarrow Zn^{2+} + 2e^{2}$$

$$\frac{2H^{+} + 2e^{2} \rightarrow H_{2}}{Zn + 2H^{+} \rightarrow Zn^{2+} + H_{2}}$$

Because we have two electrons on each side of the equation, they can be canceled. This is the key criterion for a balanced redox reaction: the electrons have to cancel exactly. If we check the charge on both sides of the equation, we see they are the same—2+. (In reality, this positive charge is balanced by the negative charges of the chloride ions, which are not included in this reaction because chlorine does not participate in the charge transfer.)

Redox reactions are often balanced by balancing each individual half reaction and then combining the two balanced half reactions. Sometimes a half reaction must have all of its coefficients multiplied by some integer for all the electrons to cancel. The following example demonstrates this process.

Example 7.6.1: Reducing Silver Ions

Write and balance the redox reaction that has silver ions and aluminum metal as reactants and silver metal and aluminum ions as products.

SOLUTION

We start by using symbols of the elements and ions to represent the reaction:

$$Ag^{+} + Al \rightarrow Ag + Al^{3+}$$
(7.6.6)

The equation looks balanced as it is written. However, when we compare the overall charges on each side of the equation, we find a charge of +1 on the left but a charge of +3 on the right. This equation is not properly balanced. To balance it, let us write the two half reactions. Silver ions are reduced, and it takes one electron to change Ag⁺ to Ag:

$$Ag^+ + e^- \rightarrow Ag$$
 (7.6.7)

Aluminum is oxidized, losing three electrons to change from Al to Al³⁺:

$$Al \to Al^{3+} + 3e^{-}$$
 (7.6.8)

To combine these two half reactions and cancel out all the electrons, we need to multiply the silver reduction reaction by 3:

$$3(Ag^{+} + e^{-} \rightarrow Ag)$$

$$Al \rightarrow Al^{3+} + 3e^{-}$$

$$3Ag^{+} + Al \rightarrow 3Ag + Al^{3+}$$

Now the equation is balanced, not only in terms of elements but also in terms of charge.



Exercise 7.6.1

Write and balance the redox reaction that has calcium ions and potassium metal as reactants and calcium metal and potassium ions as products.

Potassium has been used as a reducing agent to obtain various metals in their elemental form.

TO YOUR HEALTH: REDOX REACTIONS AND PACEMAKER BATTERIES

All batteries use redox reactions to supply electricity because electricity is basically a stream of electrons being transferred from one substance to another. Pacemakers—surgically implanted devices for regulating a person's heartbeat—are powered by tiny batteries, so the proper operation of a pacemaker depends on a redox reaction.

Pacemakers used to be powered by NiCad batteries, in which nickel and cadmium (hence the name of the battery) react with water according to this redox reaction:

$$Cd(s) + 2 \operatorname{NiOOH}(s) + 2 \operatorname{H}_2O(\ell) \to Cd(OH)_2(s) + 2 \operatorname{Ni}(OH)2(s)$$
(7.6.9)

The cadmium is oxidized, while the nickel atoms in NiOOH are reduced. Except for the water, all the substances in this reaction are solids, allowing NiCad batteries to be recharged hundreds of times before they stop operating. Unfortunately, NiCad batteries are fairly heavy batteries to be carrying around in a pacemaker. Today, the lighter lithium/iodine battery is used instead. The iodine is dissolved in a solid polymer support, and the overall redox reaction is as follows:

$$2 \operatorname{Li}(s) + I_2(s) \to 2 \operatorname{LiI}(s)$$
 (7.6.10)

Lithium is oxidized, and iodine is reduced. Although the lithium/iodine battery cannot be recharged, one of its advantages is that it lasts up to 10 years. Thus, a person with a pacemaker does not have to worry about periodic recharging; about once per decade a person requires minor surgery to replace the pacemaker/battery unit. Lithium/iodine batteries are also used to power calculators and watches.



Figure 7.6.1: A small button battery like this is used to power a watch, pacemaker, or calculator. Image used with permission from Gerhard H Wrodnigg (via Wikipedia)

Oxidation and reduction can also be defined in terms of changes in composition. The original meaning of oxidation was "adding oxygen," so when oxygen is added to a molecule, the molecule is being oxidized. The reverse is true for reduction: if a molecule loses oxygen atoms, the molecule is being reduced. For example, the acetaldehyde (CH3CHO) molecule takes on an oxygen atom to become acetic acid (CH_3COOH).

$$2 \operatorname{CH}_3 \operatorname{CHO} + \operatorname{O}_2 \rightarrow 2 \operatorname{CH}_3 \operatorname{COOH}$$
 (7.6.11)

Thus, acetaldehyde is being oxidized.

Similarly, oxidation and reduction can be defined in terms of the gain or loss of hydrogen atoms. If a molecule adds hydrogen atoms, it is being reduced. If a molecule loses hydrogen atoms, the molecule is being oxidized. For example, in the conversion of acetaldehyde into ethanol (CH_3CH_2OH), hydrogen atoms are added to acetaldehyde, so the acetaldehyde is being reduced:

$$CH_3CHO + H_2 \rightarrow CH_3CH_2OH$$
 (7.6.12)

Example 7.6.2

In each conversion, indicate whether oxidation or reduction is occurring.



a. $N_2 \rightarrow NH_3$ b. $CH_3CH_2OHCH_3 \rightarrow CH_3COCH_3$ c. $HCHO \rightarrow HCOOH$

SOLUTION

- a. Hydrogen is being added to the original reactant molecule, so reduction is occurring.
- b. Hydrogen is being removed from the original reactant molecule, so oxidation is occurring.
- c. Oxygen is being added to the original reactant molecule, so oxidation is occurring.

Exercise 7.6.2

In each conversion, indicate whether oxidation or reduction is occurring.

a. $CH_4 \rightarrow CO_2 + H_2O$ b. $NO_2 \rightarrow N_2$ c. $CH_2=CH_2 \rightarrow CH_3CH_3$

SUMMARY

Chemical reactions in which electrons are transferred are called oxidation-reduction, or redox, reactions. Oxidation is the loss of electrons. Reduction is the gain of electrons. Oxidation and reduction always occur together, even though they can be written as separate chemical equations.

CONCEPT REVIEW EXERCISES

- 1. Give two different definitions for oxidation and reduction.
- 2. Give an example of each definition of oxidation and reduction.

ANSWERS

1. Oxidation is the loss of electrons or the addition of oxygen; reduction is the gain of electrons or the addition of hydrogen.

2. Zn \rightarrow Zn²⁺ +2e⁻ (oxidation); C₂H₄ + H₂ \rightarrow C₂H₆ (reduction) (answers will vary)

EXERCISES

1. Which reactions are redox reactions? For those that are redox reactions, identify the oxidizing and reducing agents.

a. NaOH + HCl \rightarrow H₂O + NaCl b. 3Mg + 2AlCl₃ \rightarrow 2Al + 3MgCl₂ c. H₂O₂ + H₂ \rightarrow 2H₂O d. KCl + AgNO₃ \rightarrow AgCl + KNO₃

2. Which reactions are redox reactions? For those that are redox reactions, identify the oxidizing and reducing agents.

a. $3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$ b. $2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$ c. $2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$ d. $2K + 2H_2O \rightarrow 2KOH + H_2$

3. Balance each redox reaction by writing appropriate half reactions and combining them to cancel the electrons.

a. $Ca(s) + H^{+}(aq) \rightarrow Ca^{2+}(aq) + H_{2}(g)$ b. $I^{-}(aq) + Br_{2}(\ell) \rightarrow Br^{-}(aq) + I_{2}(s)$

4. Balance each redox reaction by writing appropriate half reactions and combining them to cancel the electrons.

a. Fe(s) + Sn⁴⁺(aq) \rightarrow Fe³⁺(aq) + Sn²⁺(aq)

b. $Pb(s) + Pb^{4+}(aq) \rightarrow Pb^{2+}(aq)$ (Hint: both half reactions will start with the same reactant.)

ANSWERS

1. a. no

- b. yes; oxidizing agent: AlCl₃; reducing agent: Mg
- c. yes; oxidizing agent: $\mathrm{H}_2\mathrm{O}_2$; reducing agent: H_2
- d. no
- 3. a. Ca \rightarrow Ca²⁺ + 2e⁻



 $\begin{array}{l} 2H^++2e^-\rightarrow H_2\\ Combined:\ Ca+2H^+\rightarrow Ca^{2+}+H_2\\ b.\ Br_2+2e^-\rightarrow 2Br^-\\ 2I^-\rightarrow I_2+2e^-\\ Combined:\ Br_2+2I^-\rightarrow 2Br^-+I_2 \end{array}$



7.7: REDOX REACTIONS IN ORGANIC CHEMISTRY AND BIOCHEMISTRY

LEARNING OBJECTIVES

• To identify oxidation-reduction reactions with organic compounds.

Oxidation-reduction reactions are of central importance in organic chemistry and biochemistry. The burning of fuels that provides the energy to maintain our civilization and the metabolism of foods that furnish the energy that keeps us alive both involve redox reactions.



Figure 7.7.1: The Burning of Natural Gas. The burning of natural gas is not only a combustion reaction but also a redox reaction. Similar reactions include the burning of gasoline and coal. These are also redox reactions. Image used with permission from Wikipedia.

All combustion reactions are also redox reactions. A typical combustion reaction is the burning of methane, the principal component of natural gas (Figure 7.7.1).

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \tag{7.7.1}$$

In respiration, the biochemical process by which the oxygen we inhale in air oxidizes foodstuffs to carbon dioxide and water, redox reactions provide energy to living cells. A typical respiratory reaction is the oxidation of glucose ($C_6H_{12}O_6$), the simple sugar we encountered in the chapter-opening essay that makes up the diet of yeast:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$$
 (7.7.2)

Organic chemists use a variety of redox reactions. For example, potassium dichromate $(K_2Cr_2O_7)$ is a common oxidizing agent that can be used to oxidize alcohols (symbolized by the general formula ROH). The product of the reaction depends on the location of the OH functional group in the alcohol molecule, the relative proportions of alcohol and the dichromate ion, and reaction conditions such as temperature. If the OH group is attached to a terminal carbon atom and the product is distilled off as it forms, the product is an aldehyde, which has a terminal *carbonyl group* (C=O) and is often written as RCHO. One example is the reaction used by the Breathalyzer to detect ethyl alcohol (C_2H_5OH) in a person's breath:

$$3 C_{2}H_{5}OH + Cr_{2}O_{7}^{2-} + 8 H^{+} \rightarrow 3 CH_{3}CHO + 2 Cr^{3+} + 7 H_{2}O$$
(7.7.3)

If the product acetaldehyde (CH_3CHO) is not removed as it forms, it is further oxidized to acetic acid (CH_3COOH). In this case, the overall reaction is as follows:

$$3 C_{2}H_{5}OH + 2 Cr_{2}O_{7}^{2-} + 16 H^{+} \rightarrow 3 CH_{3}COOH + 4 Cr^{3+} + 11 H_{2}O$$
(7.7.4)

In this reaction, the chromium atom is reduced from $Cr_2O_7^{2-}$ to Cr^{3+} , and the ethanol is oxidized to acetic acid.

When the OH group of the alcohol is bonded to an interior carbon atom, the oxidation of an alcohol will produce a ketone (the formulas of ketones are often written as RCOR, and the carbon–oxygen bond is a double bond). The simplest ketone is derived from 2-propanol ($CH_3CHOHCH_3$). It is the common solvent acetone [$(CH_3)_2CO$], which is used in varnishes, lacquers, rubber cement, and nail polish remover. Acetone can be formed by the following redox reaction:

$$3 CH_{3}CHOHCH_{3} + Cr_{2}O_{7}^{2-} + 8 H^{+} \rightarrow 3 (CH_{3})_{2}CO + 2 Cr^{3+} + 7 H_{2}O$$
(7.7.5)

As we have just seen, aldehydes and ketones can be formed by the oxidation of alcohols. Conversely, aldehydes and ketones can be reduced to alcohols. Reduction of the carbonyl group is important in living organisms. For example, in anaerobic metabolism, in which biochemical processes take place in the absence of oxygen, pyruvic acid ($CH_3COCOOH$) is reduced to lactic acid ($CH_3CHOHCOOH$) in the muscles.

$$CH_3COCOOH \rightarrow CH_3CHOHCOOH$$
 (7.7.6)



(Pyruvic acid is both a carboxylic acid and a ketone; only the ketone group is reduced.) The buildup of lactic acid during vigorous exercise is responsible in large part for the fatigue that we experience.

In food chemistry, the substances known as antioxidants are reducing agents. Ascorbic acid (vitamin C; $C_6H_8O_6$) is thought to retard potentially damaging oxidation of living cells. In the process, it is oxidized to dehydroascorbic acid ($C_6H_6O_6$). In the stomach, ascorbic acid reduces the nitrite ion (NO_2^-) to nitric oxide (NO):

$$C_6H_8O_6 + 2H^+ + 2NO_2^- \rightarrow C_6H_6O_6 + 2H_2O + 2NO$$
 (7.7.7)

If reaction in Equation 7.7.7 did not occur, nitrite ions from foods would oxidize the iron in hemoglobin, destroying its ability to carry oxygen.

Tocopherol (vitamin E) is also an antioxidant. In the body, vitamin E is thought to act by scavenging harmful by-products of metabolism, such as the highly reactive molecular fragments called free radicals. In foods, vitamin E acts to prevent fats from being oxidized and thus becoming rancid. Vitamin C is also a good antioxidant (Figure 7.7.2).



Figure 7.7.2: Citrus Fruits. Citrus fruits, such as oranges, lemons, and limes, are good sources of vitamin C, which is an antioxidant. Wedges of pink grapefruit, lime, and lemon, and a half orange (clockwise from top). Image used with permission from Wikipedia.

Finally, and of greatest importance, green plants carry out the redox reaction that makes possible almost all life on Earth. They do this through a process called photosynthesis, in which carbon dioxide and water are converted to glucose ($C_6H_{12}O_6$). The synthesis of glucose requires a variety of proteins called enzymes and a green pigment called chlorophyll that converts sunlight into chemical energy (Figure 7.7.3). The overall change that occurs is as follows:

$$6 \operatorname{CO}_2 + 6 \operatorname{H}_2 \operatorname{O} \to \operatorname{C}_6 \operatorname{H}_{12} \operatorname{O}_6 + 6 \operatorname{O}_2$$
 (7.7.8)

In this reaction, carbon dioxide is reduced to glucose, and water is oxidized to oxygen gas. Other reactions convert the glucose to more complex carbohydrates, plant proteins, and oils.



Figure 7.7.3: Life on Earth. Photosynthesis is the fundamental process by which plants use sunlight to convert carbon dioxide and water into glucose and oxygen. Then plants make more complex carbohydrates. It is the ultimate source of all food on Earth, and it is a redox reaction. Image used with permission (Public Domain; Wikipedia).

SUMMARY

Redox reactions are common in organic and biological chemistry, including the combustion of organic chemicals, respiration, and photosynthesis.

CONCEPT REVIEW EXERCISE

1. Give some biochemical examples of oxidation and reduction reactions.



ANSWER

1. photosynthesis and antioxidants in foods (answers will vary)

EXERCISES

1. A typical respiratory reaction discussed in the text is the oxidation of glucose ($C_6H_{12}O_6$):

$$_{6}H_{12}O_{6} + 6O_{2} \rightarrow 6CO_{2} + 6H_{2}O$$

- Is this a redox reaction? If so, what are the oxidizing and reducing agents?
- 2. The major net reaction in photosynthesis is as follows:

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$$

Is this a redox reaction? If so, what are the oxidizing and reducing agents?

3. What would be the ultimate organic product if CH₃CH₂CH₂OH were to react with a solution of K₂Cr₂O₇?

C

- 4. What would be the ultimate organic product if CH₃CH₂CH₂OH were to react with a solution of K₂Cr₂O₇?
- 5. What would be the final organic product if CH₃CH₂CHOHCH₃ were to react with a solution of K₂Cr₂O₇?
- 6. What would be the major organic product if CH₃CH₂CHOHCH₂CH₃ were to react with a solution of K₂Cr₂O₇?
- 7. What alcohol is produced in the reduction of acetone [(CH₃)₂CO]?
- 8. What alcohol is produced in the reduction of propanal (CH₃CH₂CHO)?

- 1. yes; oxidizing agent: O_2 ; reducing agent: $C_6H_{12}O_6$
- 3. CH₃CH₂COOH
- 5. $CH_3CH_2C(O)CH_3$, where the carbon is double bonded to the oxygen
- 7. CH₃CHOHCH₃, or isopropyl alcohol



7.8: INTRODUCTION TO CHEMICAL REACTIONS (EXERCISES)

ADDITIONAL EXERCISES

- 1. Isooctane (C_8H_{18}) is used as a standard for comparing gasoline performance. Write a balanced chemical equation for the combustion of isooctane.
- 2. Heptane (C₇H₁₆), like isooctane (see Exercise 1), is also used as a standard for determining gasoline performance. Write a balanced chemical equation for the combustion of heptane.
- 3. What is the difference between a combination reaction and a redox reaction? Are all combination reactions also redox reactions? Are all redox reactions also combination reactions?
- 4. Are combustion reactions always redox reactions as well? Explain.
- 5. A friend argues that the equation

$Fe^{2+} + Na \rightarrow Fe + Na^+$

is balanced because each side has one iron atom and one sodium atom. Explain why your friend is incorrect.

- 6. Some antacids contain aluminum hydroxide [Al(OH)₃]. This compound reacts with excess hydrochloric acid (HCl) in the stomach to neutralize it. If the products of this reaction are water and aluminum chloride, what is the balanced chemical equation for this reaction?
- 7. Sulfuric acid is made in a three-step process: (1) the combustion of elemental sulfur to produce sulfur dioxide, (2) the continued reaction of sulfur dioxide with oxygen to produce sulfur trioxide, and (3) the reaction of sulfur trioxide with water to make sulfuric acid (H₂SO₄). Write balanced chemical equations for all three reactions.
- 8. If the products of glucose metabolism are carbon dioxide and water, what is the balanced chemical equation for the overall process? What is the stoichiometric ratio between the number of CO₂ molecules made to the number of H₂O molecules made?
- 9. Historically, the first true battery was the Leclanché cell, named after its discoverer, Georges Leclanché. It was based on the following reaction:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

Identify what is being oxidized, what is being reduced, and the respective reducing and oxidizing agents.

ANSWERS

- $1.\ 2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O$
- 3. A combination reaction makes a new substance from more than one reactant; a redox reaction rearranges electrons. Not all combination reactions are redox reactions, and not all redox reactions are combination reactions.
- 5. Your friend is incorrect because the number of electrons transferring is not balanced.

7. (1) $S + O_2 \rightarrow SO_2$; (2) $2SO_2 + O_2 \rightarrow 2SO_3$; (3) $SO_3 + H_2O \rightarrow H_2SO_4$

9. oxidized and reducing agent: Zn; reduced and oxidizing agent: Cu²⁺



7.9: INTRODUCTION TO CHEMICAL REACTIONS (SUMMARY)

To ensure that you understand the material in this chapter, you should review the meanings of the following bold terms in the following summary and ask yourself how they relate to the topics in the chapter.

Scientific **laws** are general statements that apply to a wide variety of circumstances. One important law in chemistry is the **law of conservation of matter**, which states that in any closed system, the amount of matter stays constant.

Chemical equations are used to represent **chemical reactions**. **Reactants** change chemically into **products**. The law of conservation of matter requires that a proper chemical equation be **balanced**. **Coefficients** are used to show the relative numbers of reactant and product molecules.

In **stoichiometry**, quantities of reactants and/or products can be related to each other using the balanced chemical equation. The coefficients in a balanced chemical reaction are used to devise the proper ratios that relate the number of molecules of one substance to the number of molecules of another substance.

Chemical reactions can be classified by type. **Combination reactions** (also called **composition reactions**) make a substance from other substances. **Decomposition reactions** break one substance down into multiple substances. **Combustion reactions** combine molecular oxygen with the atoms of another reactant.

Oxidation reactions are reactions in which an atom loses an electron. **Reduction reactions** are reactions in which an atom gains an electron. These two processes always occur together, so they are collectively referred to as **oxidation-reduction** (or **redox**) **reactions**. The species being oxidized it called the **reducing agent**, while the species being reduced is the **oxidizing agent**. Alternate definitions of oxidation and reduction focus on the gain or loss of oxygen atoms, or the loss or gain of hydrogen atoms. Redox reactions are easily balanced if the overall reaction is first separated into **half reactions**, which are individually balanced.

Oxidation-reduction reactions are common in organic and biological chemistry. **Respiration**, the process by which we inhale and metabolize oxygen, is a series of redox reactions. In the absence of oxygen, redox reactions still occur in a process called **anaerobic metabolism**. **Antioxidants** such as ascorbic acid also play a part in the human diet, acting as reducing agents in various biochemical reactions. **Photosynthesis**, the process by which plants convert water and carbon dioxide to glucose, is also based on redox reactions.



8: QUANTITIES IN CHEMICAL REACTIONS

Although this works, most of the reactions occurring around us involve much larger amounts of chemicals. Even a tiny sample of a substance will contain millions, billions, or a hundred billion billions of atoms and molecules. How do we compare amounts of substances to each other in chemical terms when it is so difficult to count to a hundred billion billion? Actually, there are ways to do this, which we will explore in this chapter.

8.1: PRELUDE TO QUANTITIES IN CHEMICAL REACTIONS

Amounts do matter and in a variety of circumstances. The chapter-opening essay in Chapter 1 tells the story of a nurse who mistakenly read "2–3 mg" as "23 mg" and administered the higher and potentially fatal dose of morphine to a child. Food scientists who work in test kitchens must keep track of specific amounts of ingredients as they develop new products for us to eat. Quality control technicians measure amounts of substances in manufactured products to ensure that the products meet company o

8.2: THE MOLE

A mole is 6.022×10^{23} things.

8.3: ATOMIC AND MOLAR MASSES

The mass of moles of atoms and molecules is expressed in units of grams.

8.4: MOLE-MASS CONVERSIONS

It is possible to convert between moles of material and mass of material.

8.5: MOLE-MOLE RELATIONSHIPS IN CHEMICAL REACTIONS

The balanced chemical reaction can be used to determine molar relationships between substances.

8.6: MOLE-MASS AND MASS-MASS PROBLEMS

A balanced chemical equation can be used to relate masses or moles of different substances in a reaction.

8.7: QUANTITIES IN CHEMICAL REACTIONS (EXERCISE)

Select problems and solution.

8.8: QUANTITIES IN CHEMICAL REACTIONS (SUMMARY)

To ensure that you understand the material in this chapter, you should review the meanings of the following bold terms in the following summary and ask yourself how they relate to the topics in the chapter.

8.9: BOND ENERGIES

Atoms are held together by a certain amount of energy called bond energy. Chemical processes are labeled as exothermic or endothermic based on whether they give off or absorb energy, respectively.

8.10: THE ENERGY OF BIOCHEMICAL REACTIONS Energy to power the human body comes from chemical reactions.

8.11: ENERGY AND CHEMICAL PROCESSES (EXERCISES) Problems and Solutions to accompany the chapter.

8.12: ENERGY AND CHEMICAL PROCESSES (SUMMARY)

To ensure that you understand the material in this chapter, you should review the meanings of the following bold terms in the following summary and ask yourself how they relate to the topics in the chapter.



8.1: PRELUDE TO QUANTITIES IN CHEMICAL REACTIONS

When the disengaged gasses are carefully examined, they are found to weigh **113.7 grs.**; these are of two kinds, viz. **144 cubical inches** of carbonic acid gas, weighing **100 grs.** and **380 cubical inches** of a very light gas, weighing only **13.7 grs.**..and, when the water which has passed over into the bottle [labeled] H is carefully examined, it is found to have lost **85.7 grs.** of its weight. Thus, in this experiment, **85.7 grs.** of water, joined to **28 grs.** of charcoal, have combined in such a way as to form **100 grs.** of carbonic acid, and **13.7 grs.** of a particular gas capable of being burnt. (Bold emphasis added.)

In this paragraph from the *Elements of Chemistry*, Antoine Lavoisier (1743–94) is explaining an experiment in which he was trying to demonstrate that water is not an element but instead is composed of hydrogen (the gas "capable of being burnt") and oxygen. This is a historical account of a groundbreaking experiment and illustrates the importance of amounts in chemistry. Lavoisier was pointing out that the initial total mass of water and charcoal, 85.7 g plus 28 g, equals the final total mass of carbonic acid and the particular gas, 100 g plus 13.7 g. In this way, he was illustrating the law of conservation of matter. It is another way of saying that *amounts matter*.

Amounts do matter and in a variety of circumstances. The chapter-opening essay in Chapter 1 tells the story of a nurse who mistakenly read "2–3 mg" as "23 mg" and administered the higher and potentially fatal dose of morphine to a child. Food scientists who work in test kitchens must keep track of specific amounts of ingredients as they develop new products for us to eat. Quality control technicians measure amounts of substances in manufactured products to ensure that the products meet company or government standards. Supermarkets routinely weigh meat and produce and charge consumers by the ounce or the pound.



8.2: THE MOLE

Learning Objectives	
	_

• To define the mole unit.

Figure 8.2.1 shows that we need 2 hydrogen atoms and 1 oxygen atom to make 1 water molecule. If we want to make 2 water molecules, we will need 4 hydrogen atoms and 2 oxygen atoms. If we want to make 5 molecules of water, we need 10 hydrogen atoms and 5 oxygen atoms. The ratio of atoms we will need to make any number of water molecules is the same: 2 hydrogen atoms to 1 oxygen atom.



Figure 8.2.1 Water Molecules. The ratio of hydrogen atoms to oxygen atoms used to make water molecules is always 2:1, no matter how many water molecules are being made.

One problem we have, however, is that it is extremely difficult, if not impossible, to organize atoms one at a time. As stated in the introduction, we deal with billions of atoms at a time. How can we keep track of so many atoms (and molecules) at a time? We do it by using mass rather than by counting individual atoms.

A hydrogen atom has a mass of approximately 1 u. An oxygen atom has a mass of approximately 16 u. The ratio of the mass of an oxygen atom to the mass of a hydrogen atom is therefore approximately 16:1.

If we have 2 atoms of each element, the ratio of their masses is approximately 32:2, which reduces to 16:1—the same ratio. If we have 12 atoms of each element, the ratio of their total masses is approximately $(12 \times 16):(12 \times 1)$, or 192:12, which also reduces to 16:1. If we have 100 atoms of each element, the ratio of the masses is approximately 1,600:100, which again reduces to 16:1. As long as we have equal numbers of hydrogen and oxygen atoms, the ratio of the masses will always be 16:1.

The same consistency is seen when ratios of the masses of other elements are compared. For example, the ratio of the masses of silicon atoms to equal numbers of hydrogen atoms is always approximately 28:1, while the ratio of the masses of calcium atoms to equal numbers of lithium atoms is approximately 40:7.

So we have established that the masses of atoms are constant with respect to each other, as long as we have the same number of each type of atom. Consider a more macroscopic example. If a sample contains 40 g of Ca, this sample has the same number of atoms as



there are in a sample of 7 g of Li. What we need, then, is a number that represents a convenient quantity of atoms so we can relate macroscopic quantities of substances. Clearly even 12 atoms are too few because atoms themselves are so small. We need a number that represents billions and billions of atoms.

Chemists use the term mole to represent a large number of atoms or molecules. Just as a dozen implies 12 things, a mole (mol) represents 6.022×10^{23} things. The number 6.022×10^{23} , called Avogadro's number after the 19th-century chemist Amedeo Avogadro, is the number we use in chemistry to represent macroscopic amounts of atoms and molecules. Thus, if we have 6.022×10^{23} O atoms, we say we have 1 mol of O atoms. If we have 2 mol of Na atoms, we have $2 \times (6.022 \times 10^{23})$ Na atoms, or 1.2044×10^{24} Na atoms. Similarly, if we have 0.5 mol of benzene (C₆H₆) molecules, we have $0.5 \times (6.022 \times 10^{23})$ C₆H₆ molecules, or 3.011×10^{23} C₆H₆ molecules.

A mole represents a very large number! If 1 mol of quarters were stacked in a column, it could stretch back and forth between Earth and the sun *6.8 billion* times.

Notice that we are applying the mole unit to different types of chemical entities. In these examples, we cited moles of atoms *and* moles of molecules. The word *mole* represents a number of things— 6.022×10^{23} of them—but does not by itself specify what "they" are. They can be atoms, formula units (of ionic compounds), or molecules. That information still needs to be specified.

Because 1 H₂ molecule contains 2 H atoms, 1 mol of H₂ molecules (6.022×10^{23} molecules) has 2 mol of H atoms. Using formulas to indicate how many atoms of each element we have in a substance, we can relate the number of moles of molecules to the number of moles of atoms. For example, in 1 mol of ethanol (C₂H₆O), we can construct the following relationships (Table 8.2.1):

Table 8.2.1: Molecular Relationships

1 Molecule of $C_2 H_6 O$ Has	1 Mol of $C_2 H_6 O$ Has	Molecular Relationships
2 C atoms	2 mol of C atoms	$\frac{2 \operatorname{mol} C \operatorname{atoms}}{1 \operatorname{mol} C_2 H_6 O \operatorname{molecules}} \text{ or } \frac{1 \operatorname{mol} C_2 H_6 O \operatorname{molecules}}{2 \operatorname{mol} C \operatorname{atoms}}$
6 H atoms	6 mol of H atoms	$\frac{6 \text{ mol H atoms}}{1 \text{ mol } C_2 H_6 O \text{ molecules}} \text{ or } \frac{1 \text{ mol } C_2 H_6 O \text{ molecules}}{6 \text{ mol H atoms}}$
1 O atom	1 mol of O atoms	$\frac{1 \operatorname{mol} O \operatorname{atoms}}{1 \operatorname{mol} C_2 H_6 O \operatorname{molecules}} \text{ or } \frac{1 \operatorname{mol} C_2 H_6 O \operatorname{molecules}}{1 \operatorname{mol} O \operatorname{atoms}}$

The following example illustrates how we can use these relationships as conversion factors.

Example 8.2.1

If a sample consists of 2.5 mol of ethanol (C_2H_6O), how many moles of carbon atoms, hydrogen atoms, and oxygen atoms does it have?

SOLUTION

Using the relationships in Table 8.2.1, we apply the appropriate conversion factor for each element:

2.5 mol
$$C_2H_6O$$
 motecules $\times \frac{2 \text{ mol C atoms}}{1 \text{ mol } C_2H_6O \text{ motecules}} = 5.0 \text{ mol C atoms}$

Note how the unit *mol* C_2H_6O *molecules* cancels algebraically. Similar equations can be constructed for determining the number of H and O atoms:

$$2.5 ext{ mol } C_2H_6O ext{ molecules} imes rac{6 ext{ mol } H ext{ atoms}}{1 ext{ mol } C_2H_6O ext{ molecules}} = 15 ext{ mol } H ext{ atoms}$$

 $2.5 ext{ mol } C_2H_6O ext{ molecules} imes rac{1 ext{ mol } O ext{ atoms}}{1 ext{ mol } C_2H_6O ext{ molecules}} = 2.5 ext{ mol } O ext{ atoms}$

Exercise 8.2.1

If a sample contains 6.75 mol of Na₂SO₄, how many moles of sodium atoms, sulfur atoms, and oxygen atoms does it have?

The fact that 1 mol equals 6.022×10^{23} items can also be used as a conversion factor.

Example 8.2.2

How many formula units are present in 2.34 mol of NaCl? How many ions are in 2.34 mol?

SOLUTION

Typically in a problem like this, we start with what we are given and apply the appropriate conversion factor. Here, we are given a quantity of 2.34 mol of NaCl, to which we can apply the definition of a mole as a conversion factor:



$$2.34 ext{ mol NaCl} imes rac{6.022 imes 10^{23} ext{ NaCl units}}{1 ext{ mol NaCl}} = 1.41 imes 10^{24} ext{ NaCl units}$$

Because there are two ions per formula unit, there are

$$1.41 imes 10^{24} ext{ NaCl units} imes rac{2 ext{ ions}}{ ext{NaCl units}} = 2.82 imes 10^{24} ext{ ions}$$

in the sample.

Exercise 8.2.2

How many molecules are present in 16.02 mol of C₄H₁₀? How many atoms are in 16.02 mol?

CONCEPT REVIEW EXERCISE

1. What is a mole?

ANSWER

1. A mole is 6.022×10^{23} things.

KEY TAKEAWAY

• A mole is 6.022×10^{23} things.

EXERCISES

- 1. How many dozens are in 1 mol? Express your answer in proper scientific notation.
- 2. A gross is a dozen dozen, or 144 things. How many gross are in 1 mol? Express your answer in proper scientific notation.
- 3. How many moles of each type of atom are in 1.0 mol of $C_6H_{12}O_6$?
- 4. How many moles of each type of atom are in 1.0 mol of K₂Cr₂O₇?
- 5. How many moles of each type of atom are in 2.58 mol of Na₂SO₄?
- 6. How many moles of each type of atom are in 0.683 mol of C₃₄H₃₂FeN₄O₄? (This is the formula of heme, a component of hemoglobin.)
- 7. How many molecules are in 16.8 mol of H₂O?
- 8. How many formula units are in 0.778 mol of iron(III) nitrate?
- 9. A sample of gold contains 7.02×10^{24} atoms. How many moles of gold is this?
- 10. A flask of mercury contains 3.77×10^{22} atoms. How many moles of mercury are in the flask?
- 11. An intravenous solution of normal saline may contain 1.72 mol of sodium chloride (NaCl). How many sodium and chlorine atoms are present in the solution?
- 12. A lethal dose of arsenic is 1.00×10^{21} atoms. How many moles of arsenic is this?

- 1. 5.018 \times 10²² dozens
- 3. 6.0 mol of C atoms, 12.0 mol of H atoms, and 6.0 mol of O atoms
- 5. 5.16 mol of Na atoms, 2.58 mol of S atoms, and 10.32 mol of O atoms
- 7. 1.012×10^{25} molecules
- 9. 11.7 mol
- 11. 1.04×10^{24} Na atoms and 1.04×10^{24} Cl atoms



8.3: ATOMIC AND MOLAR MASSES

LEARNING OBJECTIVES

• To learn how the masses of moles of atoms and molecules are expressed.

Now that we have introduced the mole and practiced using it as a conversion factor, we ask the obvious question: why is the mole *that particular* number of things? Why is it 6.022×10^{23} and not 1×10^{23} or even 1×10^{20} ?

The number in a mole, Avogadro's number, is related to the relative sizes of the atomic mass unit and gram mass units. Whereas one hydrogen atom has a mass of approximately 1 u, 1 mol of H atoms has a mass of approximately 1 *gram*. And whereas one sodium atom has an approximate mass of 23 u, 1 mol of Na atoms has an approximate mass of 23 *grams*.

One mole of a substance has the same mass in grams that one atom or molecule has in atomic mass units. The numbers in the periodic table that we identified as the atomic masses of the atoms not only tell us the mass of one atom in u but also tell us the mass of 1 mol of atoms in grams.

One mole of a substance has the same mass in grams that one atom or molecule has in atomic mass units.

Example 8.3.1: Moles to Mass Conversion with Elements

What is the mass of each quantity?

- a. 1 mol of Al atoms
- b. 2 mol of U atoms

SOLUTION

- a. One mole of Al atoms has a mass in grams that is numerically equivalent to the atomic mass of aluminum. The periodic table shows that the atomic mass (rounded to two decimal points) of Al is 26.98, so 1 mol of Al atoms has a mass of 26.98 g.
- b. According to the periodic table, 1 mol of U has a mass of 238.03 g, so the mass of 2 mol is twice that, or 476.06 g.

Exercise 8.3.1: Moles to Mass Conversion with Elements

What is the mass of each quantity?

a. 1 mol of Au atoms

b. 5 mol of Br atoms

The mole concept can be extended to masses of formula units and molecules as well. The mass of 1 mol of molecules (or formula units) in grams is numerically equivalent to the mass of one molecule (or formula unit) in atomic mass units. For example, a single molecule of O_2 has a mass of 32.00 u, and 1 mol of O_2 molecules has a mass of 32.00 g. As with atomic mass unit–based masses, to obtain the mass of 1 mol of a substance, we simply sum the masses of the individual atoms in the formula of that substance. The mass of 1 mol of a substance is referred to as its molar mass, whether the substance is an element, an ionic compound, or a covalent compound.

Example 8.3.2: Moles to Mass Conversion with Compounds			
What is the mass of 1 mol of each substance?			
1. NaCl			
2. bilirubin ($C_{33}H_{36}N_4O_6$), the principal pigment present in bile (a liver secretion)			
SOLUTION			
1. Summing the molar masses of the atoms in the NaCl formula unit gives			
1 Na molar mass:	23.00 g		
1 Cl molar mass:	35.45 g		
Total:	58.45 g		



The mass of 1 mol of NaCl is 58.45 g.

2. Multiplying the molar mass of each atom by the number of atoms of that type in bilirubin's formula and adding the results, we get

33 C molar mass:	33 × 12.01 g	396.33 g
36 H molar mass:	36 × 1.01 =	36.36 g
4 N molar mass:	4 × 14.00 =	56.00 g
6 O molar mass:	6 × 16.00 =	96.00 g
Total:		584.69 g

The mass of 1 mol of bilirubin is 584.69 g.

EXERCISE 8.3.2: MOLES TO MASS CONVERSION WITH COMPOUNDS

What is the mass of 1 mol of each substance?

a. barium sulfate (BaSO₄), used to take X rays of the gastrointestional tract

b. adenosine $(C_{10}H_{13}N_5O_4)$, a component of cell nuclei crucial for cell division

Be careful when counting atoms. In formulas with polyatomic ions in parentheses, the subscript outside the parentheses is applied to every atom inside the parentheses. For example, the molar mass of $Ba(OH)_2$ requires the sum of 1 mass of Ba, 2 masses of O, and 2 masses of H:

1 Ba molar mass:	1 × 137.33 g =	137.33 g
2 O molar mass:	2 × 16.00 g =	32.00 g
2 H molar mass:	2 × 1.01 g =	2.02 g
Total:		171.35 g

Because molar mass is defined as the mass for 1 mol of a substance, we can refer to molar mass as grams per mole (g/mol). The division sign (/) implies "per," and "1" is implied in the denominator. Thus, the molar mass of bilirubin can be expressed as 584.05 g/mol, which is read as "five hundred eighty four point zero five grams per mole."

CONCEPT REVIEW EXERCISES

- 1. How are molar masses of the elements determined?
- 2. How are molar masses of compounds determined?

ANSWERS

- 1. Molar masses of the elements are the same numeric value as the masses of a single atom in atomic mass units but in units of grams instead.
- 2. Molar masses of compounds are calculated by adding the molar masses of their atoms.

KEY TAKEAWAY

• The mass of moles of atoms and molecules is expressed in units of grams.

EXERCISES

- 1. What is the molar mass of Si? What is the molar mass of U?
- 2. What is the molar mass of Mn? What is the molar mass of Mg?
- 3. What is the molar mass of FeCl₂? What is the molar mass of FeCl₃?
- 4. What is the molar mass of C_6H_6 ? What is the molar mass of $C_6H_5CH_3$?
- 5. What is the molar mass of (NH₄)₂S? What is the molar mass of Ca(OH)₂?
- 6. What is the molar mass of $(NH_4)_3PO_4$? What is the molar mass of $Sr(HCO_3)_2$?
- 7. Aspirin (C₉H₈O₄) is an analgesic (painkiller) and antipyretic (fever reducer). What is the molar mass of aspirin?
- 8. Ibuprofen ($C_{13}H_{18}O_2$) is an analgesic (painkiller). What is the molar mass of ibuprofen?
- 9. Morphine (C₁₇H₁₉NO₃) is a narcotic painkiller. What is the mass of 1 mol of morphine?



10. Heroin ($C_{21}H_{23}NO_5$) is a narcotic drug that is a derivative of morphine. What is the mass of 1 mol of heroin?

- 1. 28.09 g/mol; 238.00 g/mol
- 3. 126.75 g/mol; 162.20 g/mol
- 5. 68.15 g/mol; 74.10 g/mol
- 7. 180.17 g/mol
- 9 285.36 g



8.4: MOLE-MASS CONVERSIONS

LEARNING OBJECTIVES

• s to convert quantities between mass units and mole units.

A previous Example stated that the mass of 2 mol of U is twice the molar mass of uranium. Such a straightforward exercise does not require any formal mathematical treatment. Many questions concerning mass are not so straightforward, however, and require some mathematical manipulations.

The simplest type of manipulation using molar mass as a conversion factor is a mole-mass conversion (or its reverse, a mass-mole conversion). In such a conversion, we use the molar mass of a substance as a conversion factor to convert mole units into mass units (or, conversely, mass units into mole units).

We also established that 1 mol of Al has a mass of 26.98 g (Example). Stated mathematically,

We can divide both sides of this expression by either side to get one of two possible conversion factors:

$$\frac{1 \operatorname{mol} \mathrm{Al}}{26.98 \operatorname{g} \mathrm{Al}} \operatorname{and} \frac{26.98 \operatorname{g} \mathrm{Al}}{1 \operatorname{mol} \mathrm{Al}}$$

$$(8.4.1)$$

The first conversion factor can be used to convert from mass to moles, and the second converts from moles to mass. Both can be used to solve problems that would be hard to do "by eye."

Example
$$8.4.1$$

What is the mass of 3.987 mol of Al?

SOLUTION

The first step in a conversion problem is to decide what conversion factor to use. Because we are starting with mole units, we want a conversion factor that will cancel the mole unit and introduce the unit for mass in the numerator. Therefore, we should use the 26.98 g Al

 $\frac{20000 \text{ g m}}{1 \text{ mol Al}}$ conversion factor. We start with the given quantity and multiply by the conversion factor:

$$3.987 \ mol \ Al \times \frac{26.98 \ g \ Al}{1 \ mol \ Al}$$

Note that the mol units cancel algebraically. (The quantity 3.987 mol is understood to be in the numerator of a fraction that has 1 in the unwritten denominator.) Canceling and solving gives

$$3.987 ext{ mol Al} imes rac{26.98 ext{ g Al}}{1 ext{ mol Al}} = 107.6 ext{ g Al}$$

Our final answer is expressed to four significant figures.

Exercise 8.4.1

How many moles are present in 100.0 g of Al? (Hint: you will have to use the other conversion factor we obtained for aluminum.)

Conversions like this are possible for any substance, as long as the proper atomic mass, formula mass, or molar mass is known (or can be determined) and expressed in grams per mole. Figure 8.4.1 is a chart for determining what conversion factor is needed, and Figure 8.4.2 is a flow diagram for the steps needed to perform a conversion.



Figure 8.4.1 A Simple Flowchart for Converting between Mass and Moles of a Substance. It takes one mathematical step to convert from moles to mass or from mass to moles.





Figure 8.4.2 A Flowchart Illustrating the Steps in Performing a Unit Conversion. When performing many unit conversions, the same logical steps can be taken.

Example 8.4.2

A biochemist needs 0.00655 mol of bilirubin ($C_{33}H_{36}N_4O_6$) for an experiment. How many grams of bilirubin will that be?

SOLUTION

To convert from moles to mass, we need the molar mass of bilirubin, which we can determine from its chemical formula:

33 C molar mass:	33 × 12.01 g =	396.33 g
36 H molar mass:	36 × 1.01 g =	36.36 g
4 N molar mass:	4 × 14.00 g =	56.00 g
6 O molar mass:	6 × 16.00 g =	96.00 g
Total:		584.69 g

The molar mass of bilirubin is 584.69 g. Using the relationship

1 mol bilirubin = 584.69 g bilirubin

we can construct the appropriate conversion factor for determining how many grams there are in 0.00655 mol. Following the steps from Figure 8.4.2

$$0.00655 ext{ mol bilirubin} imes rac{584.69 ext{ g bilirubin}}{ ext{ mol bilirubin}} = 3.83 ext{ g bilirubin}$$

The mol bilirubin unit cancels. The biochemist needs 3.83 g of bilirubin.

Exercise 8.4.2

A chemist needs 457.8 g of KMnO₄ to make a solution. How many moles of KMnO₄ is that?

TO YOUR HEALTH: MINERALS

For our bodies to function properly, we need to ingest certain substances from our diets. Among our dietary needs are minerals, the noncarbon elements our body uses for a variety of functions, such developing bone or ensuring proper nerve transmission. The US Department of Agriculture has established some recommendations for the RDIs of various minerals. The accompanying table lists the RDIs for minerals, both in mass and moles, assuming a 2,000-calorie daily diet.

Mineral	Male (ag	Male (age 19–30 y)		Female (age 19–30 y)	
Ca	1,000 mg	0.025 mol	1,000 mg	0.025 mol	
Cr	35 µg	$6.7 \times 10^{-7} \text{ mol}$	25 μg	$4.8 \times 10^{-7} \text{ mol}$	
Cu	900 µg	1.4×10^{-5} mol	900 µg	1.4×10^{-5} mol	
F	4 mg	2.1×10^{-4} mol	3 mg	1.5×10^{-4} mol	
Ι	150 µg	1.2×10^{-6} mol	150 µg	1.2×10^{-6} mol	
Fe	8 mg	1.4×10^{-4} mol	18 mg	3.2×10^{-4} mol	
K	3,500 mg	9.0×10^{-2} mol	3,500 mg	9.0×10^{-2} mol	
Mg	400 mg	1.6×10^{-2} mol	310 mg	1.3×10^{-2} mol	
Mn	2.3 mg	4.2×10^{-5} mol	1.8 mg	3.3×10^{-5} mol	
Мо	45 mg	4.7×10^{-7} mol	45 mg	4.7×10^{-7} mol	
Na	2,400 mg	$1.0 imes 10^{-1} ext{ mol}$	2,400 mg	$1.0 imes 10^{-1} ext{ mol}$	
Р	700 mg	2.3×10^{-2} mol	700 mg	2.3×10^{-2} mol	
Se	55 µg	$7.0 \times 10^{-7} \mathrm{mol}$	55 µg	7.0×10^{-7} mol	
Zn	11 mg	1.7×10^{-4} mol	8 mg	1.2×10^{-4} mol	

Table 8.4.1 illustrates several things. First, the needs of men and women for some minerals are different. The extreme case is for iron; women need over twice as much as men do. In all other cases where there is a different RDI, men need more than women.

Second, the amounts of the various minerals needed on a daily basis vary widely—both on a mass scale and a molar scale. The average person needs 0.1 mol of Na a day, which is about 2.5 g. On the other hand, a person needs only about 25–35 µg of Cr per day, which is under one millionth of a mole. As small as this amount is, a deficiency of chromium in the diet can lead to diabetes-like symptoms or

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neurological problems, especially in the extremities (hands and feet). For some minerals, the body does not require much to keep itself operating properly.

Although a properly balanced diet will provide all the necessary minerals, some people take dietary supplements. However, too much of a good thing, even minerals, is not good. Exposure to too much chromium, for example, causes a skin irritation, and certain forms of chromium are known to cause cancer (as presented in the movie *Erin Brockovich*).

CONCEPT REVIEW EXERCISES

- 1. What relationship is needed to perform mole-mass conversions?
- 2. What information determines which conversion factor is used in a mole-mass conversion?

ANSWERS

- 1. The atomic or molar mass is needed for a mole-mass conversion.
- 2. The unit of the initial quantity determines which conversion factor is used.

KEY TAKEAWAY

• It is possible to convert between moles of material and mass of material.

EXERCISES

- 1. What is the mass of 8.603 mol of Fe metal?
- 2. What is the mass of 0.552 mol of Ag metal?
- 3. What is the mass of 6.24×10^4 mol of Cl₂ gas?
- 4. What is the mass of 0.661 mol of O₂ gas?
- 5. What is the mass of 20.77 mol of CaCO₃?
- 6. What is the mass of 9.02×10^{-3} mol of the hormone epinephrine (C₉H₁₃NO₃)?
- 7. How many moles are present in 977.4 g of NaHCO₃?
- 8. How many moles of erythromycin ($C_{37}H_{67}NO_{13}$), a widely used antibiotic, are in 1.00×10^3 g of the substance?
- 9. Cortisone (C₂₁H₂₈O₅) is a synthetic steroid that is used as an anti-inflammatory drug. How many moles of cortisone are present in one 10.0 mg tablet?
- 10. Recent research suggests that the daily ingestion of 85 mg of aspirin (also known as acetylsalicylic acid, C₉H₈O₄) will reduce a person's risk of heart disease. How many moles of aspirin is that?

- 1. 480.5 g
- 3. 4.42×10^{6} g
- 5. 2,079 g
- 7. 11.63 mol
- 9. 2.77 × 10^{-5} mol



8.5: MOLE-MOLE RELATIONSHIPS IN CHEMICAL REACTIONS

LEARNING OBJECTIVES

• To use a balanced chemical reaction to determine molar relationships between the substances.

In Chapter 5, you learned to balance chemical equations by comparing the numbers of each type of atom in the reactants and products. The coefficients in front of the chemical formulas represent the numbers of molecules or formula units (depending on the type of substance). Here, we will extend the meaning of the coefficients in a chemical equation.

Consider the simple chemical equation

$$2 H_2 + O_2 \rightarrow 2 H_2 O$$
 (8.5.1)

The convention for writing balanced chemical equations is to use the <u>lowest whole-number ratio</u> for the coefficients. However, the equation is balanced as long as the coefficients are in a 2:1:2 ratio. For example, this equation is also balanced if we write it as

$$4 H_2 + 2 O_2 \rightarrow 4 H_2 O$$
 (8.5.2)

The ratio of the coefficients is 4:2:4, which reduces to 2:1:2. The equation is also balanced if we were to write it as

$$22 H_2 + 11 O_2 \rightarrow 22 H_2 O$$
 (8.5.3)

because 22:11:22 also reduces to 2:1:2.

Suppose we want to use larger numbers. Consider the following coefficients:

$$12.044 \times 10^{23} H_2 + 6.022 \times 10^{23} O_2 \rightarrow 12.044 \times 10^{23} H_2 O \tag{8.5.4}$$

These coefficients also have the ratio 2:1:2 (check it and see), so this equation is balanced. But 6.022×10^{23} is 1 mol, while 12.044×10^{23} is 2 mol (and the number is written that way to make this more obvious), so we can simplify this version of the equation by writing it as

$$2 \mod \mathrm{H}_2 + 1 \mod \mathrm{O}_2 \to 2 \mod \mathrm{H}_2\mathrm{O} \tag{8.5.5}$$

We can leave out the word mol and not write the 1 coefficient (as is our habit), so the final form of the equation, still balanced, is

$$2 H_2 + O_2 \rightarrow 2 H_2 O$$
 (8.5.6)

Now we interpret the coefficients as referring to molar amounts, not individual molecules. The lesson? *Balanced chemical equations are balanced not only at the molecular level but also in terms of molar amounts of reactants and products*. Thus, we can read this reaction as "two moles of hydrogen react with one mole of oxygen to produce two moles of water."

By the same token, the ratios we constructed to describe molecules reaction can also be constructed in terms of moles rather than molecules. For the reaction in which hydrogen and oxygen combine to make water, for example, we can construct the following ratios:

$$\frac{2 \operatorname{mol} \mathrm{H}_2}{1 \operatorname{mol} \mathrm{O}_2} \operatorname{or} \frac{1 \operatorname{mol} \mathrm{O}_2}{2 \operatorname{mol} \mathrm{H}_2}$$

$$(8.5.7)$$

$$\frac{2 \operatorname{mol} H_2 O}{1 \operatorname{mol} O_2} \operatorname{or} \frac{1 \operatorname{mol} O_2}{2 \operatorname{mol} H_2 O}$$
(8.5.8)

$$\frac{2 \operatorname{mol} H_2}{2 \operatorname{mol} H_2 O} \operatorname{or} \frac{2 \operatorname{mol} H_2 O}{2 \operatorname{mol} H_2}$$
(8.5.9)

We can use these ratios to determine what amount of a substance, in moles, will react with or produce a given number of moles of a different substance. The study of the numerical relationships between the reactants and the products in balanced chemical reactions is called *stoichiometry*.

Example 8.5.1

How many moles of oxygen react with hydrogen to produce 27.6 mol of H₂O? The balanced equation is as follows:

 $2\,\mathrm{H}_2 + \mathrm{O}_2 \longrightarrow 2\,\mathrm{H}_2\mathrm{O}$

SOLUTION



Because we are dealing with quantities of H_2O and O_2 , we will use a ratio that relates those two substances. Because we are given an amount of H_2O and want to determine an amount of O_2 , we will use the ratio that has H_2O in the denominator (so it cancels) and O_2 in the numerator (so it is introduced in the answer). Thus,

$$27.6 ext{ mol } ext{H}_2 ext{O} imes rac{1 ext{ mol } ext{O}_2}{2 ext{ mol } ext{H}_2 ext{O}} = 13.8 ext{ mol } ext{O}_2$$

To produce 27.6 mol of H₂O, 13.8 mol of O₂ react.

Exercise 8.5.1

Using $2H_2 + O_2 \rightarrow 2H_2O$, how many moles of hydrogen react with 3.07 mol of oxygen to produce H_2O ?

CONCEPT REVIEW EXERCISE

1. How do we relate molar amounts of substances in chemical reactions?

ANSWER

1. Amounts of substances in chemical reactions are related by their coefficients in the balanced chemical equation.

KEY TAKEAWAY

The balanced chemical reaction can be used to determine molar relationships between substances.

EXERCISES

1. List the molar ratios you can derive from this balanced chemical equation:

$$NH_3 + 2O_2 \rightarrow HNO_3 + H_2O$$

2. List the molar ratios you can derive from this balanced chemical equation

$$2C_2H_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O$$

3. Given the following balanced chemical equation,

 $6NaOH + 3Cl_2 \rightarrow NaClO_3 + 5NaCl + 3H_2O$

how many moles of NaCl can be formed if 3.77 mol of NaOH were to react?

4. Given the following balanced chemical equation,

$$\rm C_5H_{12} + 8O_2 \ \rightarrow \ 5CO_2 + 6H_2O$$

how many moles of H₂O can be formed if 0.0652 mol of C₅H₁₂ were to react?

5. Balance the following unbalanced equation and determine how many moles of H₂O are produced when 1.65 mol of NH₃ react.

$$NH_3 + O_2 \rightarrow N_2 + H_2O$$

6. Trinitrotoluene $[C_6H_2(NO_2)_2CH_3]$, also known as TNT, is formed by reacting nitric acid (HNO₃) with toluene ($C_6H_5CH_3$):

$$HNO_3 + C_6H_5CH_3 \rightarrow C_6H_2(NO_2)_2CH_3 + H_2O$$

Balance the equation and determine how many moles of TNT are produced when 4.903 mol of HNO₃ react.

- 7. Chemical reactions are balanced in terms of molecules and in terms of moles. Are they balanced in terms of dozens? Defend your answer.
- 8. Explain how a chemical reaction balanced in terms of moles satisfies the law of conservation of matter.

- 1. 1 mol NH₃:2 mol O₂:1 mol HNO₃:1 mol H₂O
- 3. 3.14 mol
- 5. $4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$; 2.48 mol
- 7. Yes, they are still balanced.



8.6: MOLE-MASS AND MASS-MASS PROBLEMS

LEARNING OBJECTIVES

• To convert from mass or moles of one substance to mass or moles of another substance in a chemical reaction.

We have established that a balanced chemical equation is balanced in terms of moles as well as atoms or molecules. We have used balanced equations to set up ratios, now in terms of moles of materials, that we can use as conversion factors to answer stoichiometric questions, such as how many moles of substance A react with so many moles of reactant B. We can extend this technique even further. Recall that we can relate a molar amount to a mass amount using molar mass. We can use that ability to answer stoichiometry questions in terms of the masses of a particular substance, in addition to moles. We do this using the following sequence:



Collectively, these conversions are called mole-mass calculations.

As an example, consider the balanced chemical equation

$$Fe_2O_3 + 3SO_3 \to Fe_2(SO_4)_3$$
 (8.6.1)

If we have 3.59 mol of Fe_2O_3 , how many grams of SO_3 can react with it? Using the mole-mass calculation sequence, we can determine the required mass of SO_3 in two steps. First, we construct the appropriate molar ratio, determined from the balanced chemical equation, to calculate the number of moles of SO_3 needed. Then using the molar mass of SO_3 as a conversion factor, we determine the mass that this number of moles of SO_3 has.

The first step resembles the exercises we did in Section 6.4 "Mole-Mole Relationships in Chemical Reactions". As usual, we start with the quantity we were given:

$$3.59 \text{ mol Fe}_2\text{O}_3 imes rac{3 \text{ mol SO}_3}{1 \text{ mol Fe}_2\text{O}_3} = 10.77 \text{ mol SO}_3$$

$$(8.6.2)$$

The mol Fe_2O_3 units cancel, leaving mol SO_3 unit. Now, we take this answer and convert it to grams of SO_3 , using the molar mass of SO_3 as the conversion factor:

$$10.77 \text{ mol } \mathrm{SO}_3 imes rac{80.06 \text{ g } \mathrm{SO}_3}{1 \text{ mol } \mathrm{SO}_3} = 862 \text{ g } \mathrm{SO}_3$$
 (8.6.3)

Our final answer is expressed to three significant figures. Thus, in a two-step process, we find that 862 g of SO₃ will react with 3.59 mol of Fe₂O₃. Many problems of this type can be answered in this manner.

The same two-step problem can also be worked out in a single line, rather than as two separate steps, as follows:

$$3.59 \text{ mol Fe}_2 O_3 \times \underbrace{\frac{3 \text{ mol SO}_3}{1 \text{ mol Fe}_2 O_3}}_{\text{converts to moles of SO}_3} \times \underbrace{\frac{80.06 \text{ g SO}_3}{1 \text{ mol SO}_3}}_{\text{converts to grams of SO}_3} = 862 \text{ g SO}_3$$

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)

(8.6.5)

We get exactly the same answer when combining all the math steps together as we do when we calculate one step at a time.

Example
$$8.6.1$$

How many grams of CO₂ are produced if 2.09 mol of HCl are reacted according to this balanced chemical equation?

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O \tag{8.6.4}$$

SOLUTION

Our strategy will be to convert from moles of HCl to moles of CO_2 and then from moles of CO_2 to grams of CO_2 . We will need the molar mass of CO_2 , which is 44.01 g/mol. Performing these two conversions in a single-line gives 46.0 g of CO_2 :

$$2.09 \text{ molHCI} \times \frac{1 \text{ mol} \text{CO}_2}{2 \text{ molHCI}} \times \frac{44.01 \text{ g} \text{ CO}_2}{1 \text{ mol} \text{CO}_2} = 46.0 \text{ g} \text{ CO}_2$$

from the coefficients
of the balanced
equation

The molar ratio between CO₂ and HCl comes from the balanced chemical equation.

Exercise

How many grams of glucose ($C_6H_{12}O_6$) are produced if 17.3 mol of H_2O are reacted according to this balanced chemical equation?

$$6CO_2 + 6H_2O
ightarrow C_6H_{12}O_6 + 6O_2$$

It is a small step from mole-mass calculations to mass-mass calculations. If we start with a known mass of one substance in a chemical reaction (instead of a known number of moles), we can calculate the corresponding masses of other substances in the reaction. The first step in this case is to convert the known mass into moles, using the substance's molar mass as the conversion factor. Then—and only then—we use the balanced chemical equation to construct a conversion factor to convert that quantity to moles of another substance, which in turn can be converted to a corresponding mass. Sequentially, the process is as follows:



This three-part process can be carried out in three discrete steps or combined into a single calculation that contains three conversion factors. The following example illustrates both techniques.

Example 8.6.2 : Chlorination of Carbon

Methane can react with elemental chlorine to make carbon tetrachloride (CCl₄). The balanced chemical equation is as follows:

$$CH_4 + 4Cl_2 \rightarrow CCl_4 + 4HCl \tag{8.6.6}$$

How many grams of HCl are produced by the reaction of 100.0 g of CH₄?

SOLUTION

First, let us work the problem in stepwise fashion. We begin by converting the mass of CH_4 to moles of CH_4 , using the molar mass of CH_4 (16.05 g/mol) as the conversion factor:



$100.0 \ \mathrm{g \ CH_4} \times \frac{1 \ \mathrm{mol \ CH_4}}{16.05 \ \mathrm{g \ CH_4}} \!=\! 6.231 \ \mathrm{mol \ CH_4}$

Note that we inverted the molar mass so that the gram units cancel, giving us an answer in moles. Next, we use the balanced chemical equation to determine the ratio of moles CH_4 and moles HCl and convert our first result into moles of HCl:

$$6.231 ext{ mol CH}_4 imes rac{4 ext{ mol HCl}}{1 ext{ mol CH}_4} = 24.92 ext{ mol HCl}$$

Finally, we use the molar mass of HCl (36.46 g/mol) as a conversion factor to calculate the mass of 24.92 mol of HCl:

$$24.92 \text{ mol HCl} \times \frac{36.46 \text{ g HCl}}{1 \text{ mol HCl}} = 908.5 \text{ g HCl}$$

In each step, we have limited the answer to the proper number of significant figures. If desired, we can do all three conversions on a single line:

$$100.0 \ge \mathrm{CH}_4 \times \frac{1 \ \mathrm{mol} \ \mathrm{CH}_4}{16.05 \ge \mathrm{CH}_4} \times \frac{4 \ \mathrm{mol} \ \mathrm{HCl}}{1 \ \mathrm{mol} \ \mathrm{CH}_4} \times \frac{36.46 \ge \mathrm{HCl}}{1 \ \mathrm{mol} \ \mathrm{HCl}} = 908.7 \ge \mathrm{HCl}$$

This final answer is slightly different from our first answer because only the final answer is restricted to the proper number of significant figures. In the first answer, we limited each intermediate quantity to the proper number of significant figures. As you can see, both answers are essentially the same.

EXERCISE 8.6.2: OXIDATION OF PROPANAL

The oxidation of propanal (CH₃CH₂CHO) to propionic acid (CH₃CH₂COOH) has the following chemical equation:

 $CH_3CH_2CHO + 2K_2Cr_2O_7 \rightarrow CH_3CH_2COOH + other products$

How many grams of propionic acid are produced by the reaction of 135.8 g of K₂Cr₂O₇?

TO YOUR HEALTH: THE SYNTHESIS OF TAXOL

Taxol is a powerful anticancer drug that was originally extracted from the Pacific yew tree (*Taxus brevifolia*). As you can see from the accompanying figure, taxol is a very complicated molecule, with a molecular formula of $C_{47}H_{51}NO_{14}$. Isolating taxol from its natural source presents certain challenges, mainly that the Pacific yew is a slow-growing tree, and the equivalent of six trees must be harvested to provide enough taxol to treat a single patient. Although related species of yew trees also produce taxol in small amounts, there is significant interest in synthesizing this complex molecule in the laboratory.

After a 20-year effort, two research groups announced the complete laboratory synthesis of taxol in 1994. However, each synthesis required over 30 separate chemical reactions, with an overall efficiency of less than 0.05%. To put this in perspective, to obtain a single 300 mg dose of taxol, you would have to begin with 600 g of starting material. To treat the 26,000 women who are diagnosed with ovarian cancer each year with one dose, almost 16,000 kg (over 17 tons) of starting material must be converted to taxol. Taxol is also used to treat breast cancer, with which 200,000 women in the United States are diagnosed every year. This only increases the amount of starting material needed.

Clearly, there is intense interest in increasing the overall efficiency of the taxol synthesis. An improved synthesis not only will be easier but also will produce less waste materials, which will allow more people to take advantage of this potentially life-saving drug.



Figure 8.6.1 The Structure of the Cancer Drug Taxol. Because of the complexity of the molecule, hydrogen atoms are not shown, but they are present on every atom to give the atom the correct number of covalent bonds (four bonds for each carbon atom).

CONCEPT REVIEW EXERCISES

1. What is the general sequence of conversions for a mole-mass calculation?

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2. What is the general sequence of conversions for a mass-mass calculation?

ANSWERS

- 1. mol first substance \rightarrow mol second substance \rightarrow mass second substance
- 2. mass first substance \rightarrow mol first substance \rightarrow mol second substance \rightarrow mass second substance

KEY TAKEAWAY

• A balanced chemical equation can be used to relate masses or moles of different substances in a reaction.

EXERCISES

1. Given the following unbalanced chemical equation,

$$H_3PO_4 + NaOH \rightarrow H_2O + Na_3PO_4$$

what mass of H₂O is produced by the reaction of 2.35 mol of H₃PO₄?

2. Given the following unbalanced chemical equation,

 $C_2H_6 + Br_2 \rightarrow C_2H_4Br_2 + HBr$

what mass of HBr is produced if 0.884 mol of C_2H_6 is reacted?

3. Certain fats are used to make soap, the first step being to react the fat with water to make glycerol (also known as glycerin) and compounds called fatty acids. One example is as follows:

$$\begin{array}{c} \mathrm{C_3H_5}(\mathrm{OOC}(\mathrm{CH_2})_{14}\mathrm{CH_3})_3 + 3\mathrm{H_2O} \rightarrow \mathrm{C_3H_5}(\mathrm{OH})_3 + 3\mathrm{CH_3}(\mathrm{CH_2})_{14}\mathrm{COOH} \\ \mathrm{a\ fat} & \mathrm{glycerol} & \mathrm{fatty\ acid} \end{array}$$

How many moles of glycerol can be made from the reaction of 1,000.0 g of C₃H₅(OOC(CH₂)₁₄CH₃)₃?

4. Photosynthesis in plants leads to the general overall reaction for producing glucose ($C_6H_{12}O_6$):

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$$

How many moles of glucose can be made from the reaction of 544 g of CO₂?

5. Precipitation reactions, in which a solid (called a precipitate) is a product, are commonly used to remove certain ions from solution. One such reaction is as follows:

$$Ba(NO_3)_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaNO_3(aq)$$

How many grams of Na₂SO₄ are needed to precipitate all the barium ions produced by 43.9 g of Ba(NO₃)₂?

6. Nitroglycerin $[C_3H_5(ONO_2)_3]$ is made by reacting nitric acid (HNO₃) with glycerol $[C_3H_5(OH)_3]$ according to this reaction:

$$C_3H_5(OH)_3 + 3HNO_3 \rightarrow C_3H_5(ONO_2)_3 + 3H_2O$$

If 87.4 g of HNO₃ are reacted with excess glycerol, what mass of nitroglycerin can be made?

7. Antacids are bases that neutralize acids in the digestive tract. Magnesium hydroxide [Mg(OH)₂] is one such antacid. It reacts with hydrochloric acid in the stomach according to the following reaction:

$$Mg(OH)_2 + 2HCl \rightarrow MgCl_2 + 2H_2O$$

How many grams of HCl can a 200 mg dose of Mg(OH)₂ neutralize?

8. Acid rain is caused by the reaction of nonmetal oxides with water in the atmosphere. One such reaction involves nitrogen dioxide (NO₂) and produces nitric acid (HNO₃):

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO_3$$

If 1.82×10^{13} g of NO₂ enter the atmosphere every year due to human activities, potentially how many grams of HNO₃ can be produced annually?

9. A simplified version of the processing of iron ore into iron metal is as follows:

$$2Fe_2O_3 + 3C \rightarrow 4Fe + 3CO_2$$

How many grams of C are needed to produce 1.00×10^9 g of Fe?

10. The *SS Hindenburg* contained about 5.33×10^5 g of H₂ gas when it burned at Lakehurst, New Jersey, in 1937. The chemical reaction is as follows:

$$2H_2 + O_2 \rightarrow 2H_2O$$

How many grams of H₂O were produced?



- 1. 127 g
- 3. 1.236 mol
- 5. 23.9 g
- 7. 0.251 g
- 9. 1.61×10^8 g



8.7: QUANTITIES IN CHEMICAL REACTIONS (EXERCISE)

ADDITIONAL EXERCISES

- 1. If the average male has a body mass of 70 kg, of which 60% is water, how many moles of water are in an average male?
- 2. If the average female is 60.0 kg and contains 0.00174% iron, how many moles of iron are in an average female?
- 3. How many moles of each element are present in 2.67 mol of each compound?
 - a. HCl
 - b. H₂SO₄
 - c. Al(NO₃)₃
 - d. $Ga_2(SO_4)_3$

4. How many moles of each element are present in 0.00445 mol of each compound?

- a. HCl
- b. H₂SO₄
- c. Al₂(CO₃)₃
- d. Ga₂(SO₄)₃
- 5. What is the mass of one hydrogen atom in grams? What is the mass of one oxygen atom in grams? Do these masses have a 1:16 ratio, as expected?
- 6. What is the mass of one sodium atom in grams?
- 7. If 6.63×10^{-6} mol of a compound has a mass of 2.151 mg, what is the molar mass of the compound?
- 8. Hemoglobin (molar mass is approximately 64,000 g/mol) is the major component of red blood cells that transports oxygen and carbon dioxide in the body. How many moles are in 0.034 g of hemoglobin?

- 1. 2,330 mol
- 3. a. 2.67 mol of H and 2.67 mol of Cl
 - b. 5.34 mol of H, 2.67 mol of S, and 10.68 mol of O
 - c. 2.67 mol of Al, 8.01 mol of N, and 24.03 mol of O $\,$
 - d. 5.34 mol of Ga, 8.01 mol of S, and 32.04 mol of O
- 5. H = 1.66×10^{-24} g and O = 2.66×10^{-23} g; yes, they are in a 1:16 ratio.
- 7. 324 g/mol



8.8: QUANTITIES IN CHEMICAL REACTIONS (SUMMARY)

To ensure that you understand the material in this chapter, you should review the meanings of the following bold terms in the following summary and ask yourself how they relate to the topics in the chapter.

Chemical reactions relate quantities of reactants and products. Chemists use the **mole** unit to represent 6.022×10^{23} things, whether the things are atoms of elements or molecules of compounds. This number, called **Avogadro's number**, is important because this number of atoms or molecules has the same mass in grams as one atom or molecule has in atomic mass units. **Molar masses** of substances can be determined by summing the appropriate masses from the periodic table; the final molar mass will have units of grams.

Because one mole of a substance will have a certain mass, we can use that relationship to construct conversion factors that will convert a mole amount into a mass amount, or vice versa. Such **mole-mass conversions** typically take one algebraic step.

Chemical reactions list reactants and products in molar amounts, not just molecular amounts. We can use the coefficients of a balanced chemical equation to relate moles of one substance in the reaction to moles of other substances (stoichiometry). Chemical reactions obey the Law of Conservation of Mass. To balance a chemical reaction, the coefficients in front of each compound can be adjusted until the total number of atoms of each elements is equal on both sides of the reaction arrow.

Collision Theory can be used to described the energetic aspects of chemical reactions. The reactants and products of a chemical reaction store potential energy in the form of chemical bonds and intermolecular forces. The energy difference in the bond energies of the reactants and products is called "Enthalpy". When the products are lower in potential energy than the reactants, then this excess energy is released as heat and the reaction is described as exothermic. When the products are higher in potential energy than the reactants, then energy must be added to the reaction as heat for it to occur and the reaction is described as endothermic.

The rate of a chemical reaction is influenced by its activation energy. The larger the activation energy, the slower the reaction rate. Catalysts can be added to reactions to lower the activation energy and increase the reaction rate.

Not all reactions go to completion. For some reactions, both the forward and reverse reaction can occur simultaneously. When the forward and reverse reaction rates are equal, the reaction is described as being "at equilibrium". Another way to recognize when a system is at equilibrium is when the concentration of reactants and products remain constant. Le Chatlier's principle states that the direction of an equilibrium reaction will shift to reduce the stress.



8.9: BOND ENERGIES

LEARNING OBJECTIVES

The Learning Objectives of this Module are to:

- Define *bond energy*.
- Determine if a chemical process is exothermic or endothermic.

What happens when you take a basketball, place it halfway up a playground slide, and then let it go? The basketball rolls down the slide. What happens if you do it again? Does the basketball roll down the slide? It should.

If you were to perform this experiment over and over again, do you think the basketball would ever roll *up* the slide? Probably not. Why not? Well, for starters, in all of our experience, the basketball has always moved to a lower position when given the opportunity. The gravitational attraction of Earth exerts a force on the basketball, and given the chance, the basketball will move down. We say that the basketball is going to a lower *gravitational potential energy*. The basketball can move up the slide, but only if someone exerts some effort (that is, work) on the basketball. A general statement, based on countless observations over centuries of study, is that all objects tend to move spontaneously to a position of minimum energy unless acted on by some other force or object.

A similar statement can be made about atoms in compounds. Atoms bond together to form compounds because in doing so they attain lower energies than they possess as individual atoms. A quantity of energy, equal to the difference between the energies of the bonded atoms and the energies of the separated atoms, is released, usually as heat. That is, the bonded atoms have a lower energy than the individual atoms do. *When atoms combine to make a compound, energy is always given off, and the compound has a lower overall energy.* In making compounds, atoms act like a basketball on a playground slide; they move in the direction of decreasing energy.

We can reverse the process, just as with the basketball. If we put energy into a molecule, we can cause its bonds to break, separating a molecule into individual atoms. Bonds between certain specific elements usually have a characteristic energy, called the bond energy, that is needed to break the bond. The same amount of energy was liberated when the atoms made the chemical bond in the first place. The term *bond energy* is usually used to describe the strength of interactions between atoms that make covalent bonds. For atoms in ionic compounds attracted by opposite charges, the term lattice energy is used. For now, we will deal with covalent bonds in molecules.

Although each molecule has its own characteristic bond energy, some generalizations are possible. For example, although the exact value of a C–H bond energy depends on the particular molecule, all C–H bonds have a bond energy of roughly the same value because they are all C–H bonds. It takes roughly 100 kcal of energy to break 1 mol of C–H bonds, so we speak of the bond energy of a C–H bond as being about 100 kcal/mol. A C–C bond has an approximate bond energy of 80 kcal/mol, while a C=C has a bond energy of about 145 kcal/mol. Table 8.9.1 lists the approximate bond energies of various covalent bonds.

Table 8.0.1. Approximate Dand Energies

Bond	Bond Energy (kcal/mol)
C-H	100
CO	86
C=0	190
C–N	70
CC	85
C=C	145
C≡C	200
N-H	93
H–H	105

When a chemical reaction occurs, the atoms in the reactants rearrange their chemical bonds to make products. The new arrangement of bonds does not have the same total energy as the bonds in the reactants. Therefore, when chemical reactions occur, *there will always be an accompanying energy change*.



In some reactions, the energy of the products is lower than the energy of the reactants. Thus, in the course of the reaction, the substances lose energy to the surrounding environment. Such reactions are exothermic and can be represented by an *energy-level diagram* like the one in Figure 8.9.1. In most cases, the energy is given off as heat (although a few reactions give off energy as light).



Figure 8.9.1: Exothermic Reactions. For an exothermic chemical reaction, energy is given off as reactants are converted to products. In chemical reactions where the products have a higher energy than the reactants, the reactants must absorb energy from their environment to react. These reactions are endothermic and can be represented by an energy-level diagram like the one shown in Figure 8.9.2



Figure 8.9.2: Endothermic Reactions. For an endothermic chemical reaction, energy is absorbed as reactants are converted to products.

Exothermic and endothermic reactions can be thought of as having energy as either a product of the reaction or a reactant. Exothermic reactions give off energy, so energy is a product. Endothermic reactions require energy, so energy is a reactant.

Example 8.9.1

Is each chemical reaction exothermic or endothermic?

a. $2H_2(g) + O_2(g) \rightarrow 2H_2O(\ell) + 135$ kcal

b. $N_2(g) + O_2(g) + 45 \text{ kcal} \rightarrow 2\text{NO}(g)$

SOLUTION

a. Because energy is a product, energy is given off by the reaction. Therefore, this reaction is exothermic.

b. Because energy is a reactant, energy is absorbed by the reaction. Therefore, this reaction is endothermic.

Exercise 8.9.1

Is each chemical reaction exothermic or endothermic?



a. $H_2(g) + F_2(g) \rightarrow 2HF(g) + 130$ kcal b. $2C(s) + H_2(g) + 5.3$ kcal $\rightarrow C_2H_2(g)$

CONCEPT REVIEW EXERCISES

- 1. What is the connection between energy and chemical bonds?
- 2. Why does energy change during the course of a chemical reaction?

ANSWERS

- 1. Chemical bonds have a certain energy that is dependent on the elements in the bond and the number of bonds between the atoms.
- 2. Energy changes because bonds rearrange to make new bonds with different energies.

KEY TAKEAWAYS

- Atoms are held together by a certain amount of energy called bond energy.
- Chemical processes are labeled as exothermic or endothermic based on whether they give off or absorb energy, respectively.

EXERCISES

- 1. Using the data in Table 7.5, calculate the energy of one C–H bond (as opposed to 1 mol of C–H bonds).
- 2. Using the data in Table 7.5, calculate the energy of one C=C bond (as opposed to 1 mol of C=C bonds).
- 3. Is a bond-breaking process exothermic or endothermic?
- 4. Is a bond-making process exothermic or endothermic?
- 5. Is each chemical reaction exothermic or endothermic?
 - a. $2SnCl_2(s) + 33 \text{ kcal} \rightarrow Sn(s) + SnCl_4(s)$ b. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell) + 213 \text{ kcal}$
- 6. Is each chemical reaction exothermic or endothermic?
 - a. $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g) + 137 \text{ kJ}$
 - b. C(s, graphite) + 1.9 kJ \rightarrow C(s, diamond)

- 1. 1.661×10^{-19} cal
- 3. endothermic
- 5. a. endothermic b. exothermic



8.10: THE ENERGY OF BIOCHEMICAL REACTIONS

LEARNING OBJECTIVES

• The Learning Objective of this Module is to relate the concept of energy change to chemical reactions that occur in the body.

The chemistry of the human body, or any living organism, is very complex. Even so, the chemical reactions found in the human body follow the same principles of energy that other chemical reactions follow.

Where does the energy that powers our bodies come from? The details are complex, but we can look at some simple processes at the heart of cellular activity.

An important reaction that provides energy for our bodies is the oxidation of glucose ($C_6H_{12}O_6$):

$$C_6H_{12}O_{6(s)} + 6O_{2(q)} \to 6CO_{2(q)} + 6H_2O_{(\ell)} + 670 \text{ kcal}$$
(8.10.1)

Considering that 1 mol of $C_6H_{12}O_6(s)$ has a volume of about 115 mL, we can see that glucose is a compact source of energy.

Glucose and other sugars are examples of carbohydrates, which are one of the three main dietary components of a human diet. All carbohydrates supply approximately 4 kcal/g. You can verify that by taking the heat of reaction for glucose oxidation and dividing it by its molar mass. Proteins, the building blocks of structural tissues like muscle and skin, also supply about 4 kcal/g. Other important energy sources for the body are fats, which are largely hydrocarbon chains. Fats provide even more energy per gram, about 9 kcal/g.

Another important reaction is the conversion of adenosine triphosphate (ATP) to adenosine diphosphate (ADP), which is shown in Figure 8.10.1. Under physiological conditions, the breaking of an O–P bond and the formation of an O–P and two O–H bonds gives off about 7.5 kcal/mol of ATP. This may not seem like much energy, especially compared to the amount of energy given off when glucose reacts. It is enough energy, however, to fuel other biochemically important chemical reactions in our cells.



Figure 8.10.1: ATP to ADP. The conversion of ATP (top) to ADP (bottom) provides energy for the cells of the body.

Even complex biological reactions must obey the basic rules of chemistry.

CAREER FOCUS: DIETITIAN

A dietitian is a nutrition expert who communicates food-related information to the general public. In doing so, dietitians promote the general well-being among the population and help individuals recover from nutritionally related illnesses.

Our diet does not just supply us with energy. We also get vitamins, minerals, and even water from what we eat. Eating too much, too little, or not enough of the right foods can lead to a variety of problems. Dietitians are trained to make specific dietary recommendations to address particular issues relating to health. For example, a dietitian might work with a person to develop an overall diet that would help that person lose weight or control diabetes. Hospitals employ dietitians in planning menus for patients, and many dietitians work with community organizations to improve the eating habits of large groups of people.

CONCEPT REVIEW EXERCISE

1. What is the energy content per gram of proteins, carbohydrates, and fats?

ANSWER

1. proteins and carbohydrates: 4 kcal/g; fats: 9 kcal/g


KEY TAKEAWAY

• Energy to power the human body comes from chemical reactions.

EXERCISES

- 1. An 8 oz serving of whole milk has 8.0 g of fat, 8.0 g of protein, and 13 g of carbohydrates. Approximately how many kilocalories does it contain?
- 2. A serving of potato chips has 160 kcal. If the chips have 15 g of carbohydrates and 2.0 g of protein, about how many grams of fat are in a serving of potato chips?
- 3. The average body temperature of a person is 37°C, while the average surrounding temperature is 22°C. Is overall human metabolism exothermic or endothermic?
- 4. Cold-blooded animals absorb heat from the environment for part of the energy they need to survive. Is this an exothermic or an endothermic process?
- 5. If the reaction ATP \rightarrow ADP gives off 7.5 kcal/mol, then the reverse process, ADP \rightarrow ATP requires 7.5 kcal/mol to proceed. How many moles of ADP can be converted to ATP using the energy from 1 serving of potato chips (see Exercise 2)?
- 6. If the oxidation of glucose yields 670 kcal of energy per mole of glucose oxidized, how many servings of potato chips (see Exercise 2) are needed to provide the same amount of energy?

ANSWERS

- 1. 156 kcal
- 3. exothermic
- 5. 21.3 mol



8.11: ENERGY AND CHEMICAL PROCESSES (EXERCISES)

ADDITIONAL EXERCISES

- 1. Sulfur dioxide (SO₂) is a pollutant gas that is one cause of acid rain. It is oxidized in the atmosphere to sulfur trioxide (SO₃), which then combines with water to make sulfuric acid (H₂SO₄).
 - a. Write the balanced reaction for the oxidation of SO₂ to make SO₃. (The other reactant is diatomic oxygen.)
 - b. When 1 mol of SO₂ reacts to make SO₃, 23.6 kcal of energy are given off. If 100 lb (1 lb = 454 g) of SO₂ were converted to SO₃, what would be the total energy change?
- 2. Ammonia (NH₃) is made by the direct combination of H₂ and N₂ gases according to this reaction:

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) + 22.0 \text{ kcal}$$

a. Is this reaction endothermic or exothermic?

- b. What is the overall energy change if 1,500 g of N_2 are reacted to make ammonia?
- 3. A 5.69 g sample of iron metal was heated in boiling water to 99.8°C. Then it was dropped into a beaker containing 100.0 g of H₂O at 22.6°C. Assuming that the water gained all the heat lost by the iron, what is the final temperature of the H₂O and Fe?
- 4. A 5.69 g sample of copper metal was heated in boiling water to 99.8°C. Then it was dropped into a beaker containing 100.0 g of H_2O at 22.6°C. Assuming that the water gained all the heat lost by the copper, what is the final temperature of the H_2O and Cu?
- 5. When 1 g of steam condenses, 540 cal of energy is released. How many grams of ice can be melted with 540 cal?
- 6. When 1 g of water freezes, 79.9 cal of energy is released. How many grams of water can be boiled with 79.9 cal?
- 7. The change in energy is +65.3 kJ for each mole of calcium hydroxide [Ca(OH)₂] according to the following reaction:

$$Ca(OH)_2(s) \rightarrow CaO(s) + H_2O(g)$$

How many grams of Ca(OH)₂ could be reacted if 575 kJ of energy were available?

8. The thermite reaction gives off so much energy that the elemental iron formed as a product is typically produced in the liquid state:

$$2Al(s) + Fe_2O_3(s) \rightarrow Al_2O_3(s) + 2Fe(\ell) + 204 \text{ kcal}$$

How much heat will be given off if 250 g of Fe are to be produced?

- 9. A normal adult male requires 2,500 kcal per day to maintain his metabolism.
 - a. Nutritionists recommend that no more than 30% of the calories in a person's diet come from fat. At 9 kcal/g, what is the maximum mass of fat an adult male should consume daily?
 - b. At 4 kcal/g each, how many grams of protein and carbohydrates should an adult male consume daily?
- 10. A normal adult male requires 2,500 kcal per day to maintain his metabolism.
 - a. At 9 kcal/g, what mass of fat would provide that many kilocalories if the diet was composed of nothing but fats?
 - b. At 4 kcal/g each, what mass of protein and/or carbohydrates is needed to provide that many kilocalories?
- 11. The volume of the world's oceans is approximately $1.34\times 10^{24}\,\text{cm}^3.$
 - a. How much energy would be needed to increase the temperature of the world's oceans by 1°C? Assume that the heat capacity of the oceans is the same as pure water.
 - b. If Earth receives 6.0×10^{22} J of energy per day from the sun, how many days would it take to warm the oceans by 1°C, assuming all the energy went into warming the water?
- 12. Does a substance that has a small specific heat require a small or large amount of energy to change temperature? Explain.
- 13. Some biology textbooks represent the conversion of adenosine triphosphate (ATP) to adenosine diphosphate (ADP) and phosphate ions as follows:

ATP \rightarrow ADP + phosphate + energy

What is wrong with this reaction?

14. Assuming that energy changes are additive, how much energy is required to change 15.0 g of ice at -15°C to 15.0 g of steam at 115°C? (Hint: you will have five processes to consider.)

ANSWERS

- 1. a. $2SO_2 + O_2 \rightarrow 2SO_3$ b. 16,700 kcal
- 3. about 23.1°C



- 5. 6.76 g
- 7. 652 g
- 9. a. 83.3 g b. 438 g
- 11. a. 1.34 × 10²⁴ cal b. 93 days
- 13. A reactant is missing: H₂O is missing.7



8.12: ENERGY AND CHEMICAL PROCESSES (SUMMARY)

To ensure that you understand the material in this chapter, you should review the meanings of the following bold terms in the following summary and ask yourself how they relate to the topics in the chapter.

Energy is the ability to do work. The transfer of energy from one place to another is **heat**. Heat and energy are measured in units of **joules**, **calories**, or kilocalories (equal to 1,000 calories). The amount of heat gained or lost when the temperature of an object changes can be related to its mass and a constant called the **specific heat** of the substance.

The transfer of energy can also cause a substance to change from one phase to another. During the transition, called a **phase change**, heat is either added or lost. Despite the fact that heat is going into or coming out of a substance during a phase change, the temperature of the substance does not change until the phase change is complete; that is, phase changes are **isothermal**. Analogous to specific heat, a constant called the **heat of fusion** of a substance describes how much heat must be transferred for a substance to melt or solidify (that is, to change between solid and liquid phases), while the **heat of vaporization** describes the amount of heat transferred in a boiling or condensation process (that is, to change between liquid and gas phases).

Every chemical change is accompanied by an energy change. This is because the interaction between atoms bonding to each other has a certain **bond energy**, the energy required to break the bond (called **lattice energy** for ionic compounds), and the bond energies of the reactants will not be the same as the bond energies of the products. Reactions that give off energy are called **exothermic**, while reactions that absorb energy are called **endothermic**. Energy-level diagrams can be used to illustrate the energy changes that accompany chemical reactions.

Even complex biochemical reactions have to follow the rules of simple chemistry, including rules involving energy change. Reactions of **carbohydrates** and **proteins** provide our bodies with about 4 kcal of energy per gram, while **fats** provide about 9 kcal per gram.



9: GASES

In everyday life, we commonly come in contact with water as a solid (ice), as a liquid, and as a gas (steam). Under the proper conditions of temperature and pressure, many substances—not only water—can experience the three different phases. An understanding of the phases of matter is important for our understanding of all matter. In this chapter, we will explore the three phases of matter.

9.1: GASES AND PRESSURE

The gas phase is unique among the three states of matter in that there are some simple models we can use to predict the physical behavior of all gases—independent of their identities. We cannot do this for the solid and liquid states. Initial advances in the understanding of gas behavior were made in the mid 1600s by Robert Boyle, an English scientist who founded the Royal Society (one of the world's oldest scientific organizations).

9.2: GAS LAWS

The physical properties of gases are predictable using mathematical formulas known as gas laws.

9.3: GASES (EXERCISES)

Problems and select solutions to this chapter.

9.4: SOLIDS, LIQUIDS, AND GASES (SUMMARY)

To ensure that you understand the material in this chapter, you should review the meanings of the following bold terms in the following summary and ask yourself how they relate to the topics in the chapter.



9.1: GASES AND PRESSURE

LEARNING OBJECTIVES

• To describe the gas phase.

The gas phase is unique among the three states of matter in that there are some simple models we can use to predict the physical behavior of all gases—independent of their identities. We cannot do this for the solid and liquid states. In fact, the development of this understanding of the behavior of gases represents the historical dividing point between alchemy and modern chemistry. Initial advances in the understanding of gas behavior were made in the mid 1600s by Robert Boyle, an English scientist who founded the Royal Society (one of the world's oldest scientific organizations).

How is it that we can model all gases independent of their chemical identity? The answer is in a group of statements called the kinetic theory of gases:

- Gases are composed of tiny particles that are separated by large distances.
- Gas particles are constantly moving, experiencing collisions with other gas particles and the walls of their container.
- The velocity of gas particles is related to the temperature of a gas.
- Gas particles do not experience any force of attraction or repulsion with each other.

Did you notice that none of these statements relates to the identity of the gas? This means that all gases should behave similarly. A gas that follows these statements perfectly is called an *ideal gas*. Most gases show slight deviations from these statements and are called *real gases*. However, the existence of real gases does not diminish the importance of the kinetic theory of gases.

One of the statements of the kinetic theory mentions collisions. As gas particles are constantly moving, they are also constantly colliding with each other and with the walls of their container. There are forces involved as gas particles bounce off the container walls (Figure 9.1.1). The force generated by gas particles divided by the area of the container walls yields pressure. Pressure is a property we can measure for a gas, but we typically do not consider pressure for solids or liquids.



Figure 9.1.1: Gas Pressure. Pressure is what results when gas particles rebound off the walls of their container.

The basic unit of pressure is the newton per square meter (N/m²). This combined unit is redefined as a pascal (Pa). One pascal is not a very large amount of pressure. A more useful unit of pressure is the bar, which is 100,000 Pa (1 bar = 100,000 Pa). Other common units of pressure are the atmosphere (atm), which was originally defined as the average pressure of Earth's atmosphere at sea level; and mmHg (millimeters of mercury), which is the pressure generated by a column of mercury 1 mm high. The unit millimeters of mercury is also called a torr, named after the Italian scientist Evangelista Torricelli, who invented the barometer in the mid-1600s. A more precise definition of atmosphere, in terms of torr, is that there are exactly 760 torr in 1 atm. A bar equals 1.01325 atm. Given all the relationships between these pressure units, the ability to convert from one pressure unit to another is a useful skill.

EXAMPLE 9.1.1: CONVERTING PRESSURES

Write a conversion factor to determine how many atmospheres are in 1,547 mmHg.

SOLUTION

Because 1 mmHg equals 1 torr, the given pressure is also equal to 1,547 torr. Because there are 760 torr in 1 atm, we can use this conversion factor to do the mathematical conversion:

$$1,547 \operatorname{torr} imes rac{1 \operatorname{atm}}{760 \operatorname{torr}} = 2.04 \operatorname{atm}$$

Note how the torr units cancel algebraically.

EXERCISE 9.1.1: CONVERTING PRESSURES



Write a conversion factor to determine how many millimeters of mercury are in 9.65 atm.

The kinetic theory also states that there is no interaction between individual gas particles. Although we know that there are, in fact, intermolecular interactions in real gases, the kinetic theory assumes that gas particles are so far apart that the individual particles don't "feel" each other. Thus, we can treat gas particles as tiny bits of matter whose identity isn't important to certain physical properties.

CONCEPT REVIEW EXERCISE

1. What is pressure, and what units do we use to express it?

ANSWER

1. Pressure is the force per unit area; its units can be pascals, torr, millimeters of mercury, or atmospheres.

KEY TAKEAWAY

• The gas phase has certain general properties characteristic of that phase.

EXERCISES

- 1. What is the kinetic theory of gases?
- 2. According to the kinetic theory of gases, the individual gas particles are (always, frequently, never) moving.
- 3. Why does a gas exert pressure?
- 4. Why does the kinetic theory of gases allow us to presume that all gases will show similar behavior?
- 5. Arrange the following pressure quantities in order from smallest to largest: 1 mmHg, 1 Pa, and 1 atm.
- 6. Which unit of pressure is larger—the torr or the atmosphere?
- 7. How many torr are there in 1.56 atm?
- 8. Convert 760 torr into pascals.
- 9. Blood pressures are expressed in millimeters of mercury. What would be the blood pressure in atmospheres if a patient's systolic blood pressure is 120 mmHg and the diastolic blood pressure is 82 mmHg? (In medicine, such a blood pressure would be reported as "120/82," spoken as "one hundred twenty over eighty-two.")
- 10. In weather forecasting, barometric pressure is expressed in inches of mercury (in. Hg), where there are exactly 25.4 mmHg in every 1 in. Hg. What is the barometric pressure in millimeters of mercury if the barometric pressure is reported as 30.21 in. Hg?

ANSWERS

- 1. Gases are composed of tiny particles that are separated by large distances. Gas particles are constantly moving, experiencing collisions with other gas particles and the walls of their container. The velocity of gas particles is related to the temperature of a gas. Gas particles do not experience any force of attraction or repulsion with each other.
- 3. A gas exerts pressure as its particles rebound off the walls of its container.
- 5. 1 Pa, 1 mmHg, and 1 atm
- 7. 1,190 torr
- 9. 0.158 atm; 0.108 atm



9.2: GAS LAWS

LEARNING OBJECTIVES

• To predict the properties of gases using the gas laws.

Experience has shown that several properties of a gas can be related to each other under certain conditions. The properties are pressure (P), volume (V), temperature (T, in kelvins), and amount of material expressed in moles (n). What we find is that a sample of gas cannot have any random values for these properties. Instead, only certain values, dictated by some simple mathematical relationships, will occur.

BOYLE'S LAW

The first simple relationship, referred to as a gas law, is between the pressure of a gas and its volume. If the amount of gas in a sample and its temperature are kept constant, then as the pressure of a gas is increased, the volume of the gas decreases proportionately. Mathematically, this is written as

$$P \propto \frac{1}{V}$$
 (9.2.1)

where the " α " symbol means "is proportional to." This is one form of Boyle's law, which relates the pressure of a gas to its volume.

A more useful form of Boyle's law involves a change in conditions of a gas. For a given amount of gas at a constant temperature, if we know the initial pressure and volume of a gas sample and the pressure or volume changes, we can calculate what the new volume or pressure will be. That form of Boyle's law is written

$$P_i V_i = P_f V_f \tag{9.2.2}$$

where the subscript i refers to initial conditions and the subscript f refers to final conditions.

To use 9.2.2 you need to know any three of the variables so that you can algebraically calculate the fourth variable. Also, the pressure quantities must have the same units, as must the two volume quantities. If the two similar variables don't have the same variables, one value must be converted to the other value's unit.

Example 9.2.1: Increasing Pressure in a Gas

What happens to the volume of a gas if its pressure is increased? Assume all other conditions remain the same.

SOLUTION

If the pressure of a gas is increased, the volume decreases in response.

EXERCISE 9.2.1: INCREASING VOLUME IN A GAS

What happens to the pressure of a gas if its volume is increased? Assume all other conditions remain the same.

Example 9.2.2: Gas Compression

If a sample of gas has an initial pressure of 1.56 atm and an initial volume of 7.02 L, what is the final volume if the pressure is reduced to 0.987 atm? Assume that the amount and the temperature of the gas remain constant.

SOLUTION

The key in problems like this is to be able to identify which quantities represent which variables from the relevant equation. The way the question is worded, you should be able to tell that 1.56 atm is P_i , 7.02 L is V_i , and 0.987 atm is P_f . What we are looking for is the final volume— V_f . Therefore, substituting these values into $P_iV_i = P_fV_f$:

$$(1.56 \text{ atm})(7.02 \text{ L}) = (0.987 \text{ atm}) \times V_{4}$$

The expression has atmospheres on both sides of the equation, so they cancel algebraically:

$$(1.56)(7.02 \text{ L}) = (0.987) \times V_{\text{f}}$$

Now we divide both sides of the expression by 0.987 to isolate $V_{\rm f}$, the quantity we are seeking:

$$rac{(1.56)(7.02~{
m L})}{0.987} = {
m V_f}$$

Performing the multiplication and division, we get the value of $V_{\rm f}$, which is 11.1 L. The volume increases. This should make sense because the pressure decreases, so pressure and volume are inversely related.



Exercise 9.2.2

If a sample of gas has an initial pressure of 3.66 atm and an initial volume of 11.8 L, what is the final pressure if the volume is reduced to 5.09 L? Assume that the amount and the temperature of the gas remain constant.

If the units of similar quantities are not the same, one of them must be converted to the other quantity's units for the calculation to work out properly. It does not matter which quantity is converted to a different unit; the only thing that matters is that the conversion and subsequent algebra are performed properly. The following example illustrates this process.

Example 9.2.3

If a sample of gas has an initial pressure of 1.56 atm and an initial volume of 7.02 L, what is the final volume if the pressure is changed to 1,775 torr? Does the answer make sense? Assume that the amount and the temperature of the gas remain constant.

SOLUTION

This example is similar to Example 9.2.2 except now the final pressure is expressed in torr. For the math to work out properly, one of the pressure values must be converted to the other unit. Let us change the initial pressure to torr:

$$1.56~\mathrm{atm} imes rac{760~\mathrm{torr}}{1~\mathrm{atm}} = 1,190~\mathrm{torr}$$

Now we can use Boyle's law:

$$(1,190 \text{ torr})(7.02 \text{ L}) = (1,775 \text{ torr}) \times V_{\text{f}}$$

Torr cancels algebraically from both sides of the equation, leaving

$$(1,190)(7.02 \text{ L}) = (1,775) \times V_{\text{f}}$$

Now we divide both sides of the equation by 1,775 to isolate $V_{\rm f}$ on one side. Solving for the final volume,

$$V_{f} = rac{(1, 190)(7.02 \text{ L})}{1,775} = 4.71 \text{ L}$$

Because the pressure increases, it makes sense that the volume decreases.

The answer for the final volume is essentially the same if we converted the 1,775 torr to atmospheres: 1,775 torr $\times \frac{1 \text{ atm}}{760 \text{ torr}} = 2.336 \text{ atm}$. Using Boyle's law: (1.56 atm)(7.02 L) = (2.335 atm) $\times V_{\rm f}$; $V_{\rm f} = \frac{(1.56 \text{ atm})(7.02 \text{ L})}{2.336 \text{ atm}} = 4.69 \text{ L}.$

Exercise 9.2.3

If a sample of gas has an initial pressure of 375 torr and an initial volume of 7.02 L, what is the final pressure if the volume is changed to 4,577 mL? Does the answer make sense? Assume that amount and the temperature of the gas remain constant.

To Your Health: Breathing

Breathing certainly is a major contribution to your health! Without breathing, we could not survive. Curiously, the act of breathing itself is little more than an application of Boyle's law.

The lungs are a series of ever-narrowing tubes that end in a myriad of tiny sacs called alveoli. It is in the alveoli that oxygen from the air transfers to the bloodstream and carbon dioxide from the bloodstream transfers to the lungs for exhalation. For air to move in and out of the lungs, the pressure inside the lungs must change, forcing the lungs to change volume—just as predicted by Boyle's law.

The pressure change is caused by the diaphragm, a muscle that covers the bottom of the lungs. When the diaphragm moves down, it expands the size of our lungs. When this happens, the air pressure inside our lungs decreases slightly. This causes new air to rush in, and we inhale. The pressure decrease is slight—only 3 torr, or about 0.4% of an atmosphere. We inhale only 0.5–1.0 L of air per normal breath.

Exhaling air requires that we relax the diaphragm, which pushes against the lungs and slightly decreases the volume of the lungs. This slightly increases the pressure of the air in the lungs, and air is forced out; we exhale. Only 1–2 torr of extra pressure is needed to exhale. So with every breath, our own bodies are performing an experimental test of Boyle's law.

CHARLES'S LAW

Another simple gas law relates the volume of a gas to its temperature. Experiments indicate that as the temperature of a gas sample is increased, its volume increases as long as the pressure and the amount of gas remain constant. The way to write this mathematically is



(9.2.3)

 $\mathbf{V}\propto T$

At this point, the concept of temperature must be clarified. Although the Kelvin scale is the preferred temperature scale, the Celsius scale is also a common temperature scale used in science. The Celsius scale is based on the melting and boiling points of water and is actually the common temperature scale used by most countries around the world (except for the United States, which still uses the Fahrenheit scale). The value of a Celsius temperature is directly related to its Kelvin value by a simple expression:

Kelvin temperature = Celsius temperature + 273

Thus, it is easy to convert from one temperature scale to another.

The Kelvin scale is sometimes referred to as the absolute scale because the zero point on the Kelvin scale is at absolute zero, the coldest possible temperature. On the other temperature scales, absolute zero is -260° C or -459° F.

The expression relating a gas volume to its temperature begs the following question: to which temperature scale is the volume of a gas related? The answer is that gas volumes are directly related to the *Kelvin temperature*. Therefore, the temperature of a gas sample should always be expressed in (or converted to) a Kelvin temperature.

Example 9.2.4: Increasing Temperature

What happens to the volume of a gas if its temperature is decreased? Assume that all other conditions remain constant.

SOLUTION

If the temperature of a gas sample is decreased, the volume decreases as well.

Exercise 9.2.4

What happens to the temperature of a gas if its volume is increased? Assume that all other conditions remain constant.

As with Boyle's law, the relationship between volume and temperature can be expressed in terms of initial and final values of volume and temperature, as follows:

$$\frac{V_i}{T_i} = \frac{V_f}{T_f}$$
(9.2.4)

where V_i and T_i are the initial volume and temperature, and V_f and T_f are the final volume and temperature. This is Charles's law. The restriction on its use is that the pressure of the gas and the amount of gas must remain constant. (Charles's law is sometimes referred to as Gay-Lussac's law, after the scientist who promoted Charles's work.)

Example 9.2.5

A gas sample at 20°C has an initial volume of 20.0 L. What is its volume if the temperature is changed to 60°C? Does the answer make sense? Assume that the pressure and the amount of the gas remain constant.

SOLUTION

Although the temperatures are given in degrees Celsius, we must convert them to the kelvins before we can use Charles's law. Thus,

$$20^{\circ}\text{C} + 273 = 293 \text{ K} = T_{i} 60^{\circ}\text{C} + 273 = 333 \text{ K} = T_{f}$$

Now we can substitute these values into Charles's law, along with the initial volume of 20.0 L:

$$\frac{20.0 \text{ L}}{293 \text{ K}} = \frac{\text{V}_{\text{f}}}{333 \text{ K}}$$

Multiplying the 333 K to the other side of the equation, we see that our temperature units will cancel:

$$\frac{(333 \text{ K})(20.0 \text{ L})}{293 \text{ K}} = \text{V}$$

Solving for the final volume, V_f = 22.7 L. So, as the temperature is increased, the volume increases. This makes sense because volume is directly proportional to the absolute temperature (as long as the pressure and the amount of the remain constant).

Exercise 9.2.5

A gas sample at 35°C has an initial volume of 5.06 L. What is its volume if the temperature is changed to -35°C? Does the answer make sense? Assume that the pressure and the amount of the gas remain constant.

COMBINED GAS LAW



Other gas laws can be constructed, but we will focus on only two more. The combined gas law brings Boyle's and Charles's laws together to relate pressure, volume, and temperature changes of a gas sample:

$$\frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f}$$
(9.2.5)

To apply this gas law, the amount of gas should remain constant. As with the other gas laws, the temperature must be expressed in kelvins, and the units on the similar quantities should be the same. Because of the dependence on three quantities at the same time, it is difficult to tell in advance what will happen to one property of a gas sample as two other properties change. The best way to know is to work it out mathematically.

Example 9.2.6

A sample of gas has P_i = 1.50 atm, V_i = 10.5 L, and T_i = 300 K. What is the final volume if P_f = 0.750 atm and T_f = 350 K?

SOLUTION

Using the combined gas law, substitute for five of the quantities:

 $\frac{(1.50 \; \mathrm{atm})(10.5 \; \mathrm{L})}{300 \; \mathrm{K}} = \frac{(0.750 \; \mathrm{atm})(\mathrm{V_f})}{350 \; \mathrm{K}}$

We algebraically rearrange this expression to isolate $V_{\rm f}$ on one side of the equation:

$$(1.50 \text{ atm})(10.5 \text{ L})(350 \text{ K})$$

$$V_{\rm f} = \frac{1}{(300 \text{ K})(0.750 \text{ atm})} = 24.5 \text{ L}$$

Note how all the units cancel except the unit for volume.

Exercise 9.2.6

A sample of gas has $P_i = 0.768$ atm, $V_i = 10.5$ L, and $T_i = 300$ K. What is the final pressure if $V_f = 7.85$ L and $T_f = 250$ K?

Example 9.2.7

A balloon containing a sample of gas has a temperature of 22°C and a pressure of 1.09 atm in an airport in Cleveland. The balloon has a volume of 1,070 mL. The balloon is transported by plane to Denver, where the temperature is 11°C and the pressure is 655 torr. What is the new volume of the balloon?

SOLUTION

The first task is to convert all quantities to the proper and consistent units. The temperatures must be expressed in kelvins, and the pressure units are different so one of the quantities must be converted. Let us convert the atmospheres to torr:

$$22^{\circ}C + 273 = 295 \text{ K} = T_{i}$$

$$11^{\circ}C + 273 = 284 \text{ K} = T_{f}$$

$$1.09 \text{ atm} \times \frac{760 \text{ torr}}{1 \text{ atm}} = 828 \text{ torr} = P_{i}$$

Now we can substitute the quantities into the combined has law:

$$\frac{(828 \text{ torr})(1,070 \text{ mL})}{295 \text{ K}} = \frac{(655 \text{ torr}) \times \text{V}_{\text{f}}}{284 \text{ K}}$$

To solve for $V_{\rm f}$, we multiply the 284 K in the denominator of the right side into the numerator on the left, and we divide 655 torr in the numerator of the right side into the denominator on the left:

$$rac{(828 ext{ torr})(1,070 ext{ mL})(284 ext{ K})}{(295 ext{ K})(655 ext{ torr})} = ext{V}_{ ext{f}}$$

Notice that torr and kelvins cancel, as they are found in both the numerator and denominator. The only unit that remains is milliliters, which is a unit of volume. So $V_{\rm f}$ = 1,300 mL. The overall change is that the volume of the balloon has increased by 230 mL.

Exercise 9.2.7

A balloon used to lift weather instruments into the atmosphere contains gas having a volume of 1,150 L on the ground, where the pressure is 0.977 atm and the temperature is 18°C. Aloft, this gas has a pressure of 6.88 torr and a temperature of -15°C. What is the new volume of the gas?



THE IDEAL GAS LAW

So far, the gas laws we have used have focused on changing one or more properties of the gas, such as its volume, pressure, or temperature. There is one gas law that relates all the independent properties of a gas under any particular condition, rather than a change in conditions. This gas law is called the ideal gas law. The formula of this law is as follows:

$$PV = nRT \tag{9.2.6}$$

In this equation, P is pressure, V is volume, n is amount of moles, and T is temperature. R is called the ideal gas law constant and is a proportionality constant that relates the values of pressure, volume, amount, and temperature of a gas sample. The variables in this equation do not have the subscripts i and f to indicate an initial condition and a final condition. The ideal gas law relates the four independent properties of a gas under *any* conditions.

The value of R depends on what units are used to express the other quantities. If volume is expressed in liters and pressure in atmospheres, then the proper value of R is as follows:

$$R = 0.08205 \frac{L \cdot atm}{mol \cdot K}$$
(9.2.7)

This may seem like a strange unit, but that is what is required for the units to work out algebraically.

Example 9.2.8

What is the volume in liters of 1.45 mol of N_2 gas at 298 K and 3.995 atm?

SOLUTION

Using the ideal gas law where P = 3.995 atm, n = 1.45, and T = 298,

$$(3.995 ext{ atm}) imes \mathrm{V} = (1.45 ext{ mol}) \left(0.08205 \ rac{\mathrm{L} \cdot \mathrm{atm}}{\mathrm{mol} \cdot \mathrm{K}}
ight) (298 ext{ K})$$

On the right side, the moles and kelvins cancel. Also, because atmospheres appear in the numerator on both sides of the equation, they also cancel. The only remaining unit is liters, a unit of volume. So

$$3.995 \times V = (1.45)(0.08205)(298)$$
 L

Dividing both sides of the equation by 3.995 and evaluating, we get V = 8.87 L. Note that the conditions of the gas are not changing. Rather, the ideal gas law allows us to determine what the fourth property of a gas (here, volume) *must* be if three other properties (here, amount, pressure, and temperature) are known.

EXERCISE 9.2.8

What is the pressure of a sample of CO_2 gas if 0.557 mol is held in a 20.0 L container at 451 K?

For convenience, scientists have selected 273 K (0°C) and 1.00 atm pressure as a set of standard conditions for gases. This combination of conditions is called standard temperature and pressure (STP). Under these conditions, 1 mol of any gas has about the same volume. We can use the ideal gas law to determine the volume of 1 mol of gas at STP:

$$(1.00 \text{ atm}) \times V = (1.00 \text{ mol}) \left(0.08205 \ \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right) (273 \text{ K})$$
 (9.2.8)

This volume is 22.4 L. Because this volume is independent of the identity of a gas, the idea that 1 mol of gas has a volume of 22.4 L at STP makes a convenient conversion factor:

Example 9.2.9

Cyclopropane (C_3H_6) is a gas that formerly was used as an anesthetic. How many moles of gas are there in a 100.0 L sample if the gas is at STP?

SOLUTION

We can set up a simple, one-step conversion that relates moles and liters:

$$100.0 \ {
m L} \ {
m C}_3 {
m H}_6 imes {1
m mol} {22.4
m L} = 4.46 \ {
m mol} \ {
m C}_3 {
m H}_6$$

There are almost 4.5 mol of gas in 100.0 L.

Note: Because of its flammability, cyclopropane is no longer used as an anesthetic gas.



Exercise 9.2.9

Freon is a trade name for a series of fluorine- and chlorine-containing gases that formerly were used in refrigeration systems. What volume does 8.75 mol of Freon have at STP?

Note: Many gases known as Freon are no longer used because their presence in the atmosphere destroys the ozone layer, which protects us from ultraviolet light from the sun.

DALTON'S LAW OF PARTIAL PRESSURES

The ideal gas equation of state applies to mixtures just as to pure gases. It was in fact with a gas mixture, ordinary air, that Boyle, Gay-Lussac and Charles did their early experiments. The only new concept we need in order to deal with gas mixtures is the *partial pressure*, a concept invented by the famous English chemist John Dalton (1766-1844). Dalton reasoned that the low density and high compressibility of gases indicates that they consist mostly of empty space; from this it follows that when two or more different gases occupy the same volume, they behave entirely independently. The contribution that each component of a gaseous mixture makes to the total pressure of the gas is known as the *partial pressure* of that gas.

The definition of Dalton's Law of Partial Pressures that address this is:

The total pressure of a gas is the sum of the partial pressures of its components

which is expressed algebraically as

$$P_{total} = P_1 + P_2 + P_3 \dots = \sum_i P_i$$
 (9.2.9)

or, equivalently

$$P_{total} = \frac{RT}{V} \sum_{i} n_i \tag{9.2.10}$$

There is also a similar relationship based on *volume fractions*, known as *Amagat's law of partial volumes*. It is exactly analogous to Dalton's law, in that it states that the total volume of a mixture is just the sum of the partial volumes of its components. But there are two important differences: Amagat's law holds only for ideal gases which must all be at the same temperature and pressure. Dalton's law has neither of these restrictions. Although Amagat's law seems intuitively obvious, it sometimes proves useful in chemical engineering applications. We will make no use of it in this course.

Example 9.2.10

Three flasks having different volumes and containing different gases at various pressures are connected by stopcocks as shown. When the stopcocks are opened,

a. What will be the pressure in the system?

b. Which gas will be most abundant in the mixture?

Assume that the temperature is uniform and that the volume of the connecting tubes is negligible.

SOLUTION

The trick here is to note that the total number of moles n_T and the temperature remain unchanged, so we can make use of Boyle's law PV = constant. We will work out the details for CO₂ only, denoted by subscripts *a*.

For CO₂,

$$P_a V_a = (2.13 \ atm)(1.50 \ L) = 3.19 \ L \cdot atm \tag{9.2.11}$$

Adding the *PV* products for each separate container, we obtain

$$\sum_{i} P_i V_i = 6.36 \ L \cdot atm = n_T R T \tag{9.2.12}$$

We will call this sum P_1V_1 . After the stopcocks have been opened and the gases mix, the new conditions are denoted by P_2V_2 . From Boyle's law (9.2.2,

$$P_1 V_1 = P_2 V_2 = 6.36 \ L \cdot atm \tag{9.2.13}$$

$$V_2 = \sum_i V_i = 4.50 \ L \tag{9.2.14}$$



Solving for the final pressure P_2 we obtain (6.36 L-atm)/(4.50 L) = **1.41 atm**.

For part (*b*), note that the number of moles of each gas is n = PV/RT. The mole fraction if any one gas is $X_i = n_i/n_T$. For CO₂, this works out to (3.19/*RT*) / (6.36/*RT*) = 0.501. Because this exceeds 0.5, we know that this is the most abundant gas in the final mixture.

Dalton's law states that in a gas mixture (P_{total}) each gas will exert a pressure independent of the other gases (P_n) and each gas will behave as if it alone occupies the total volume. By extension, the partial pressure of each gas can be calculated by multiplying the total pressure (P_{total}) by the gas percentage (%).

$$P_{Total} = P_1 + P_2 + P_3 + P_4 + \ldots + P_n \tag{9.2.15}$$

or

$P_n = rac{\% ext{ of individual } ext{gas}_n}{P_{Total}}$	(9.2.16)
Table 0.9.1. Dential Decouver for the same in since a territed dec	

Gas	Partial Pressure (mm Hg)	Percentage (%)
Nitrogen, (N_2\)	P_{N_2} = 594	78
Oxygen, O_2	$P_{O_2} = 160$	21
Carbon Dioxide, CO_2	$P_{CO_2} = 0.25$	0.033
Water Vapor, H_2O	$P_{H_{2}O}$ = 5.7	0.75
Other trace gases	P_{Other} = 0.05	0.22
Total air	P_{Total} = 760	1

HENRY'S LAW

Henry's law is one of the gas laws formulated by William Henry in 1803. It states: "At a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid." An equivalent way of stating the law is that the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas above the liquid.

To explain this law, Henry derived the equation:

$$C = kP_{qas} \tag{9.2.17}$$

where

- *C* is the solubility of a gas at a fixed temperature in a particular solvent (in units of M or mL gas/L)
- *k* is Henry's law constant (often in units of M/atm)
- P_{gas} is the partial pressure of the gas (often in units of Atm)

Henry's Law tells us that the greater the pressure of gas above the surface of a liquid, the higher the concentration of the gas in the liquid. Also, Henry's law tells us that gases diffuse from areas of high gas concentration to areas of low gas concentration.

APPLICABILITY OF HENRY'S LAW

- Henry's law only works if the molecules are at equilibrium.
- Henry's law does not work for gases at high pressures (e.g., *N*_{2 (*g*)} at high pressure becomes very soluble and harmful when in the blood supply).
- Henry's law does not work if there is a chemical reaction between the solute and solvent (e.g., $HCl_{(g)}$ reacts with water by a dissociation reaction to generate H_3O^+ and Cl^- ions).

COLLECTING GASES OVER WATER

A common laboratory method of collecting the gaseous product of a chemical reaction is to conduct it into an inverted tube or bottle filled with water, the opening of which is immersed in a larger container of water. This arrangement is called a *pneumatic trough*, and was widely used in the early days of chemistry. As the gas enters the bottle it displaces the water and becomes trapped in the upper part.





Figure 9.2.1:An Apparatus for Collecting Gases by the Displacement of Water

The volume of the gas can be observed by means of a calibrated scale on the bottle, but what about its pressure? The total pressure confining the gas is just that of the atmosphere transmitting its force through the water. (An exact calculation would also have to take into account the height of the water column in the inverted tube.) But liquid water itself is always in equilibrium with its vapor, so the space in the top of the tube is a mixture of two gases: the gas being collected, and gaseous H_2O . The partial pressure of H_2O is known as the vapor pressure of water and it depends on the temperature. In order to determine the quantity of gas we have collected, we must use Dalton's Law to find the partial pressure of that gas.

Example 9.2.11

Oxygen gas was collected over water as shown above. The atmospheric pressure was 754 torr, the temperature was 22°C, and the volume of the gas was 155 mL. The vapor pressure of water at 22°C is 19.8 torr. Use this information to estimate the number of moles of O_2 produced.

SOLUTION

From Dalton's law,

$$P_{O_2} = P_{total} - P_{H_2O} = 754 - 19.8 = 734 \ torr = 0.966 \ atm$$

Now use the Ideal Gas Law to convert to moles

$$n = rac{PV}{RT} = rac{(0.966 \; atm)(0.155 \; L)}{(0.082 \; Latmmol^{-1}K^{-1})(295 \; K)} = 0.00619 \; mol$$

SCUBA DIVING

Our respiratory systems are designed to maintain the proper oxygen concentration in the blood when the partial pressure of O_2 is 0.21 atm, its normal sea-level value. Below the water surface, the pressure increases by 1 atm for each 10.3 m increase in depth; thus a scuba diver at 10.3 m experiences a total of 2 atm pressure pressing on the body. In order to prevent the lungs from collapsing, the air the diver breathes should also be at about the same pressure.



Figure 9.2.2: Scuba Dviging actively takes into account both Henry's and Dalton's Laws

But at a total pressure of 2 atm, the partial pressure of O_2 in ordinary air would be 0.42 atm; at a depth of 100 ft (about 30 m), the O_2 pressure of 0.8 atm would be far too high for health. For this reason, the air mixture in the pressurized tanks that scuba divers wear



must contain a smaller fraction of O_2 . This can be achieved most simply by raising the nitrogen content, but high partial pressures of N_2 can also be dangerous, resulting in a condition known as nitrogen narcosis. The preferred diluting agent for sustained deep diving is helium, which has very little tendency to dissolve in the blood even at high pressures.

CAREER FOCUS: RESPIRATORY THERAPIST

Certain diseases—such as emphysema, lung cancer, and severe asthma—primarily affect the lungs. Respiratory therapists help patients with breathing-related problems. They can evaluate, help diagnose, and treat breathing disorders and even help provide emergency assistance in acute illness where breathing is compromised.

Most respiratory therapists must complete at least two years of college and earn an associate's degree, although therapists can assume more responsibility if they have a college degree. Therapists must also pass state or national certification exams. Once certified, respiratory therapists can work in hospitals, doctor's offices, nursing homes, or patient's homes. Therapists work with equipment such as oxygen tanks and respirators, may sometimes dispense medication to aid in breathing, perform tests, and educate patients in breathing exercises and other therapy.

Because respiratory therapists work directly with patients, the ability to work well with others is a must for this career. It is an important job because it deals with one of the most crucial functions of the body.

CONCEPT REVIEW EXERCISES

- 1. What properties do the gas laws help us predict?
- 2. What makes the ideal gas law different from the other gas laws?

ANSWERS

- 1. Gas laws relate four properties: pressure, volume, temperature, and number of moles.
- 2. The ideal gas law does not require that the properties of a gas change.

KEY TAKEAWAY

• The physical properties of gases are predictable using mathematical formulas known as gas laws.

EXERCISES

- 1. What conditions of a gas sample should remain constant for Boyle's law to be used?
- 2. What conditions of a gas sample should remain constant for Charles's law to be used?
- 3. Does the identity of a gas matter when using Boyle's law? Why or why not?
- 4. Does the identity of a gas matter when using Charles's law? Why or why not?
- 5. A sample of nitrogen gas is confined to a balloon that has a volume of 1.88 L and a pressure of 1.334 atm. What will be the volume of the balloon if the pressure is changed to 0.662 atm? Assume that the temperature and the amount of the gas remain constant.
- 6. A sample of helium gas in a piston has a volume of 86.4 mL under a pressure of 447 torr. What will be the volume of the helium if the pressure on the piston is increased to 1,240 torr? Assume that the temperature and the amount of the gas remain constant.
- 7. If a gas has an initial pressure of 24,650 Pa and an initial volume of 376 mL, what is the final volume if the pressure of the gas is changed to 775 torr? Assume that the amount and the temperature of the gas remain constant.
- 8. A gas sample has an initial volume of 0.9550 L and an initial pressure of 564.5 torr. What would the final pressure of the gas be if the volume is changed to 587.0 mL? Assume that the amount and the temperature of the gas remain constant.
- 9. A person draws a normal breath of about 1.00 L. If the initial temperature of the air is 18°C and the air warms to 37°C, what is the new volume of the air? Assume that the pressure and amount of the gas remain constant.
- 10. A person draws a normal breath of about 1.00 L. If the initial temperature of the air is -10°C and the air warms to 37°C, what is the new volume of the air? Assume that the pressure and the amount of the gas remain constant.
- 11. An air/gas vapor mix in an automobile cylinder has an initial temperature of 450 K and a volume of 12.7 cm³. The gas mix is heated to 565°C. If pressure and amount are held constant, what is the final volume of the gas in cubic centimeters?
- 12. Given the following conditions for a gas: $V_i = 0.665 \text{ L}$, $T_i = 23.6^{\circ}\text{C}$, $V_f = 1.034 \text{ L}$. What is T_f in degrees Celsius and kelvins?
- 13. Assuming the amount remains the same, what must be the final volume of a gas that has an initial volume of 387 mL, an initial pressure of 456 torr, an initial temperature of 65.0°C, a final pressure of 1.00 atm, and a final temperature of 300 K?
- 14. When the nozzle of a spray can is depressed, 0.15 mL of gas expands to 0.44 mL, and its pressure drops from 788 torr to 1.00 atm. If the initial temperature of the gas is 22.0°C, what is the final temperature of the gas?
- 15. Use the ideal gas law to show that 1 mol of a gas at STP has a volume of about 22.4 L.



- 16. Use a standard conversion factor to determine a value of the ideal gas law constant *R* that has units of L•torr/mol•K.
- 17. How many moles of gas are there in a 27.6 L sample at 298 K and a pressure of 1.44 atm?
- 18. How many moles of gas are there in a 0.066 L sample at 298 K and a pressure of 0.154 atm?
- 19. A 0.334 mol sample of carbon dioxide gas is confined to a volume of 20.0 L and has a pressure of 0.555 atm. What is the temperature of the carbon dioxide in kelvins and degrees Celsius?
- 20. What must *V* be for a gas sample if n = 4.55 mol, P = 7.32 atm, and T = 285 K?
- 21. What is the pressure of 0.0456 mol of Ne gas contained in a 7.50 L volume at 29°C?
 - 22. What is the pressure of 1.00 mol of Ar gas that has a volume of 843.0 mL and a temperature of -86.0°C?
- 23. A mixture of the gases N_2 , O_2 , and Ar has a total pressure of 760 mm Hg. If the partial pressure of N_2 is 220 mm Hg and of O_2 is 470 mm Hg, What is the partial pressure of Ar?
- 24. What percent of the gas above is Ar?
- 25. Apply Henry's Law to the diagram below to explain:

why oxygen diffuses from the alveoli of the lungs into the blood and from the blood into the tissues of the body. why carbon dioxide diffuses from the tissues into the blood and from the blood into the alveoli and then finally out into the atmosphere.



ANSWERS

- 1. temperature and amount of the gas
- 3. The identity does not matter because the variables of Boyle's law do not identify the gas.
- 5. 3.89 L
- 7. 92.1 mL
- 9. 1.07 L
- 11. 23.7 cm³
- 13. 206 mL
- 15. The ideal gas law confirms that 22.4 L equals 1 mol.
- 17. 1.63 mol
- 19. 405 K; 132°C
- 21. 0.151 atm



9.3: GASES (EXERCISES)

ADDITIONAL EXERCISES

- 1. How many grams of oxygen gas are needed to fill a 25.0 L container at 0.966 atm and 22°C?
- 2. A breath of air is about 1.00 L in volume. If the pressure is 1.00 atm and the temperature is 37°C, what mass of air is contained in each breath? Use an average molar mass of 28.8 g/mol for air.
- 3. The balanced chemical equation for the combustion of propane is as follows:

$$C_3H_{8(g)} + 5O_{2(g)} \to 3CO_{2(g)} + 4H_2O_{(\ell)}$$

$$(9.3.1)$$

a. If 100.0 g of propane are combusted, how many moles of oxygen gas are necessary for the reaction to occur?

- b. At STP, how many liters of oxygen gas would that be?
- 4. The equation for the formation of ammonia gas (NH₃) is as follows:

$$N_{2(g)} + 3H_{2(g)} \to 2NH_{3(g)}$$
 (9.3.2)

At 500°C and 1.00 atm, 10.0 L of N_2 gas are reacted to make ammonia.

- a. If the pressures and temperatures of H_2 and NH_3 were the same as those of N_2 , what volume of H_2 would be needed to react with N_2 , and what volume of NH_3 gas would be produced?
- b. Compare your answers to the balanced chemical equation. Can you devise a "shortcut" method to answer Exercise 4a?
- 5. At 20°C, 1 g of liquid H₂O has a volume of 1.002 mL. What volume will 1 g of water vapor occupy at 20°C if its pressure is 17.54 mmHg? By what factor has the water expanded in going from the liquid phase to the gas phase?
- 6. At 100°C, 1 g of liquid H₂O has a volume of 1.043 mL. What volume will 1 g of steam occupy at 100°C if its pressure is 760.0 mmHg? By what factor has the water expanded in going from the liquid phase to the gas phase?
- 7. Predict whether NaCl or NaI will have the higher melting point. Explain. (Hint: consider the relative strengths of the intermolecular interactions of the two compounds.)
- 8. Predict whether CH₄ or CH₃OH will have the lower boiling point. Explain. (Hint: consider the relative strengths of the intermolecular interactions of the two compounds.)
- 9. A standard automobile tire has a volume of about 3.2 ft³ (where 1 ft³ equals 28.32 L). Tires are typically inflated to an absolute pressure of 45.0 pounds per square inch (psi), where 1 atm equals 14.7 psi. Using this information with the ideal gas law, determine the number of moles of air needed to fill a tire if the air temperature is 18.0°C.
- 10. Another gas law, Amontons's law, relates pressure and temperature under conditions of constant amount and volume:

$$\frac{P_i}{T_i} = \frac{P_f}{T_f}$$

If an automobile tire (see Exercise 9) is inflated to 45.0 psi at 18.0°C, what will be its pressure if the operating temperature (i.e., the temperature the tire reaches when the automobile is on the road) is 45.0°C? Assume that the volume and the amount of the gas remain constant.

ANSWERS

1. 31.9 g

- 3. a. 11.4 mol b. 255 L
- 5. 57.81 L; an expansion of 57,700 times
- 7. NaCl; with smaller anions, NaCl likely experiences stronger ionic bonding.
- 9. 11.6 mol



9.4: SOLIDS, LIQUIDS, AND GASES (SUMMARY)

To ensure that you understand the material in this chapter, you should review the meanings of the following bold terms in the following summary and ask yourself how they relate to the topics in the chapter.

A **phase** is a certain form of matter that has the same physical properties throughout. Three phases are common: the solid, the liquid, and the gas phase. What determines the phase of a substance? Generally, the strength of the **intermolecular interactions** determines whether a substance is a solid, liquid, or gas under any particular conditions. **Covalent network bonding** is a very strong form of intermolecular interaction. Diamond is one example of a substance that has this intermolecular interaction. **Ionic interactions**, the forces of attraction due to oppositely charged ions, are also relatively strong. Covalent bonds are another type of interaction within molecules, but if the bonds are **polar covalent bonds**, then the unequal sharing of electrons can cause charge imbalances within molecules that cause interactions between molecules. These molecules are described as **polar**, and these interactions are called **dipole-dipole interactions**. A certain rather strong type of dipole-dipole interaction, involving a hydrogen atom, is called **hydrogen bonding**. On the other hand, equal sharing of electrons forms **nonpolar covalent bonds**, and the interactions between different molecules is less because the molecules are nonpolar. All substances have very weak **dispersion forces** (also called **London forces**) caused by the movement of electrons within the bonds themselves.

In the solid phase, intermolecular interactions are so strong that they hold the individual atoms or molecules in place. In many solids, the regular three-dimensional arrangement of particles makes a **crystal**. In other solids, the irregular arrangement of particles makes an **amorphous** solid. In liquids, the intermolecular interactions are strong enough to keep the particles of substance together but not in place. Thus, the particles are free to move over each other but still remain in contact.

In gases, the intermolecular interactions are weak enough that the individual particles are separated from each other in space. The **kinetic theory of gases** is a collection of statements that describe the fundamental behavior of all gases. Among other properties, gases exert a **pressure** on their container. Pressure is measured using units like **pascal**, **bar**, **atmosphere**, or **mmHg** (also called a **torr**).

There are several simple relationships between the variables used to describe a quantity of gas. These relationships are called **gas laws**. **Boyle's law** relates the pressure and volume of a gas, while **Charles's law** relates the volume and absolute temperature of a gas. The **combined gas law** relates the volume, pressure, and absolute temperature of a gas sample. All of these gas laws allow us to understand the changing conditions of a gas. The **ideal gas law** relates the pressure, volume, amount, and absolute temperature of a gas under any conditions. These four variables are related to the **ideal gas law constant**, which is the proportionality constant used to calculate the conditions of a gas. Because the conditions of a gas can change, a set of benchmark conditions called **standard temperature and pressure (STP)** is defined. Standard temperature is 0°C, and standard pressure is 1.00 atm.



10: SOLUTIONS

Solutions are a large part of everyday life. A lot of the chemistry occurring around us happens in solution. In fact, much of the chemistry that occurs in our own bodies takes place in solution, and many solutions are important for our health. In our understanding of chemistry, we need to understand a little bit about solutions. In this chapter, you will learn about the special characteristics of solutions, how solutions are characterized, and some of their properties.

10.1: PRELUDE TO SOLUTIONS

10.2: SOLUTIONS

Solutions form because a solute and a solvent experience similar intermolecular interactions.

10.3: THE DISSOLUTION PROCESS

When a solute dissolves, its individual particles are surrounded by solvent molecules and are separated from each other.

10.4: CONCENTRATION

Various concentration units are used to express the amounts of solute in a solution. Concentration units can be used as conversion factors in stoichiometry problems. New concentrations can be easily calculated if a solution is diluted.

10.5: COLLIGATIVE PROPERTIES OF SOLUTIONS

Colligative properties depend only on the number of dissolved particles (that is, the concentration), not their identity. Raoult's law is concerned with the vapor pressure depression of solutions. The boiling points of solutions are always higher, and the freezing points of solutions are always lower, than those of the pure solvent.

10.6: COLLIGATIVE PROPERTIES OF IONIC SOLUTES

For ionic solutes, the calculation of colligative properties must include the fact that the solutes separate into multiple particles when they dissolve. The equations for calculating colligative properties of solutions of ionic solvents include the van't Hoff factor, i.

10.7: SOLUTIONS (EXERCISES)

Problems and select solutions to this chapter.

10.8: SOLUTIONS (EXERCISES)

10.9: SOLUTIONS (SUMMARY)

To ensure that you understand the material in this chapter, you should review the meanings of the bold terms in the following summary and ask yourself how they relate to the topics in the chapter.



10.1: PRELUDE TO SOLUTIONS

If you watch any of the medical dramas on television, you may have heard a doctor (actually an actor) call for an intravenous solution of "Ringer's lactate" (or "lactated Ringer's"). So what is Ringer's lactate?

Intravenous (IV) solutions are administered for two main reasons:

- 1. to introduce necessary substances into the bloodstream, such as ions for proper body function, sugar and other food substances for energy, or drugs to treat a medical condition, and
- 2. to increase the volume of the bloodstream.

Many people with acute or long-term medical conditions have received some type of an IV solution.

One basic IV solution, called a *normal saline solution*, is simply a dilute solution of NaCl dissolved in water. Normal saline is 9.0 g of NaCl dissolved in each liter of solution. *Ringer's lactate* is a normal saline solution that also has small amounts of potassium and calcium ions mixed in. In addition, it contains about 2.5 g of lactate ions ($C_3H_5O_3^-$) per liter of solution. The liver metabolizes lactate ions into bicarbonate (HCO_3^-) ions, which help maintain the acid-base balance of blood. Many medical problems, such as heart attacks and shock, affect the acid-base balance of blood, and the presence of lactate in the IV solution eases problems caused by this imbalance.

Physicians can select from a range of premade IV solutions, in accordance with a patient's particular needs. Ringer's lactate is commonly used when a patient's blood volume must be increased quickly. Another frequently used IV solution, called D5W, is a 5% solution of dextrose (a form of sugar) in water.



10.2: SOLUTIONS

LEARNING OBJECTIVES

• To understand what causes solutions to form.

A solution is another name for a homogeneous mixture. A *mixture* as a material composed of two or more substances. In a solution, the combination is so intimate that the different substances cannot be differentiated by sight, even with a microscope. Compare, for example, a mixture of salt and pepper and another mixture consisting of salt and water. In the first mixture, we can readily see individual grains of salt and the flecks of pepper. A mixture of salt and pepper is not a solution. However, in the second mixture, no matter how carefully we look, we cannot see two different substances. Salt dissolved in water is a solution.

The major component of a solution, called the solvent, is typically the same phase as the solution itself. Each minor component of a solution (and there may be more than one) is called the solute. In most of the solutions we will describe in this textbook, there will be no ambiguity about whether a component is the solvent or the solute.) For example, in a solution of salt in water, the solute is salt, and solvent is water.

Solutions come in all phases, and the solvent and the solute do not have to be in the same phase to form a solution (such as salt and water). For example, air is a gaseous solution of about 80% nitrogen and about 20% oxygen, with some other gases present in much smaller amounts. An alloy is a solid solution consisting of a metal (like iron) with some other metals or nonmetals dissolved in it. Steel, an alloy of iron and carbon and small amounts of other metals, is an example of a solid solution. Table 10.2.1 lists some common types of solutions, with examples of each.

Table 10.2.1: Types of Solutions				
Solvent Phase	Solute Phase	Example		
gas	gas	air		
liquid	gas	carbonated beverages		
liquid	liquid	ethanol (C ₂ H ₅ OH) in H ₂ O (alcoholic beverages)		
liquid	solid	saltwater		
solid	gas	H ₂ gas absorbed by Pd metal		
solid	liquid	$\operatorname{Hg}(\ell)$ in dental fillings		
solid	solid	steel alloys		

What causes a solution to form? The simple answer is that the solvent and the solute must have similar intermolecular interactions. When this is the case, the individual particles of solvent and solute can easily mix so intimately that each particle of solute is surrounded by particles of solute, forming a solution. However, if two substances have very different intermolecular interactions, large amounts of energy are required to force their individual particles to mix intimately, so a solution does not form.

This process leads to a simple rule of thumb: *like dissolves like*. Solvents that are very polar will dissolve solutes that are very polar or even ionic. Solvents that are nonpolar will dissolve nonpolar solutes. Thus water, being polar, is a good solvent for ionic compounds and polar solutes like ethanol (C_2H_5OH). However, water does not dissolve nonpolar solutes, such as many oils and greases (Figure 10.2.1).





Figure 10.2.1: A beaker holds water with blue food dye (upper liquid layer) and a much more dense perfluoroheptane (a fluorocarbon) lower liquid layer. The two fluids cannot mix and the dye cannot dissolve in fluorocarbon. A goldfish and a crab have been introduced into the water. The goldfish cannot penetrate the dense fluorocarbon. The crab floats at the liquid boundary with only parts of his legs penetrating the fluorocarbon fluid, unable to sink to the bottom of the beaker. Quarter coins rest on the bottom of the beaker. Animals were rescued from their predicament after the photo was taken. Figure used with permission from Wikipedia (Sbharris (Steven B. Harris)).

We use the word soluble to describe a solute that dissolves in a particular solvent, and the word insoluble for a solute that does not dissolve in a solvent. Thus, we say that sodium chloride is soluble in water but insoluble in hexane (C_6H_{14}). If the solute and the solvent are both liquids and soluble in any proportion, we use the word miscible, and the word immiscible if they are not.

Example 10.2.1

Water is considered a polar solvent. Which substances should dissolve in water?

- 1. methanol (CH₃OH)
- 2. sodium sulfate (Na₂SO₄)
- 3. octane (C_8H_{18})

SOLUTION

Because water is polar, substances that are polar or ionic will dissolve in it.

- 1. Because of the OH group in methanol, we expect its molecules to be polar. Thus, we expect it to be soluble in water. As both water and methanol are liquids, the word *miscible* can be used in place of *soluble*.
- 2. Sodium sulfate is an ionic compound, so we expect it to be soluble in water.
- 3. Like other hydrocarbons, octane is nonpolar, so we expect that it would not be soluble in water.

Exercise 10.2.1

Toluene (C₆H₅CH₃) is widely used in industry as a nonpolar solvent. Which substances should dissolve in toluene?

- a. water (H₂O)
- b. sodium sulfate (Na₂SO₄)
- c. octane (C_8H_{18})

CONCEPT REVIEW EXERCISES

- 1. What causes a solution to form?
- 2. How does the phrase like dissolves like relate to solutions?

ANSWERS

- 1. Solutions form because a solute and a solvent have similar intermolecular interactions.
- 2. It means that substances with similar intermolecular interactions will dissolve in each other.

KEY TAKEAWAY

• Solutions form because a solute and a solvent experience similar intermolecular interactions.

EXERCISES

1. Define solution.



- 2. Give several examples of solutions.
- 3. What is the difference between a solvent and a solute?
- 4. Can a solution have more than one solute in it? Can you give an example?
- 5. Does a solution have to be a liquid? Give several examples to support your answer.
- 6. Give at least two examples of solutions found in the human body.
- 7. Which substances will probably be soluble in water, a very polar solvent?
 - a. sodium nitrate (NaNO₃)
 - b. hexane (C_6H_{14})
 - c. isopropyl alcohol [(CH₃)₂CHOH]
 - d. benzene (C_6H_6)
- 8. Which substances will probably be soluble in toluene (C₆H₅CH₃), a nonpolar solvent?
 - a. sodium nitrate (NaNO₃)
 - b. hexane (C_6H_{14})
 - c. isopropyl alcohol [(CH₃)₂CHOH]
 - d. benzene (C₆H₆)
- 9. The solubility of alcohols in water varies with the length of carbon chain. For example, ethanol (CH₃CH₂OH) is soluble in water in any ratio, while only 0.0008 mL of heptanol (CH₃CH₂CH₂CH₂CH₂CH₂CH₂CH₂OH) will dissolve in 100 mL of water. Propose an explanation for this behavior.
- 10. Dimethyl sulfoxide [(CH₃)₂SO] is a polar liquid. Based on the information in Exercise 9, which do you think will be more soluble in it—ethanol or heptanol?

ANSWERS

- 1. a homogeneous mixture
- 3. A solvent is the majority component of a solution; a solute is the minority component of a solution.
- 5. A solution does not have to be liquid; air is a gaseous solution, while some alloys are solid solutions (answers will vary).
- 7. a. probably soluble
 - b. probably not soluble
 - c. probably soluble
 - d. probably not soluble
- 9. Small alcohol molecules have strong polar intermolecular interactions, so they dissolve in water. In large alcohol molecules, the nonpolar end overwhelms the polar end, so they do not dissolve very well in water.



10.3: THE DISSOLUTION PROCESS

LEARNING OBJECTIVES

• To describe the dissolution process at the molecular level

THE DISSOLUTION PROCESS

What occurs at the molecular level to cause a solute to dissolve in a solvent? The answer depends in part on the solute, but there are some similarities common to all solutes.

Recall the rule that *like dissolves like*. This means that substances must have similar intermolecular forces to form solutions. When a soluble solute is introduced into a solvent, the particles of solute can interact with the particles of solvent. In the case of a solid or liquid solute, the interactions between the solute particles and the solvent particles are so strong that the individual solute particles separate from each other and, surrounded by solvent molecules, enter the solution. (Gaseous solutes already have their constituent particles separated, but the concept of being surrounded by solvent particles still applies.) This process is called solvation and is illustrated in Figure 10.3.1 When the solvent is water, the word hydration, rather than solvation, is used.



Figure 10.3.1: Solvation. When a solute dissolves, the individual particles of solute become surrounded by solvent particles. Eventually the particle detaches from the remaining solute, surrounded by solvent molecules in solution. Source: Photo © Thinkstock

IONIC COMPOUNDS AND COVALENT COMPOUNDS AS SOLUTES

In the case of molecular solutes like glucose, the solute particles are individual molecules. However, if the solute is ionic, the individual ions separate from each other and become surrounded by solvent particles. That is, the cations and anions of an ionic solute separate when the solute dissolves. This process is referred to as dissociation (Figure 10.3.1).

The dissociation of soluble ionic compounds gives solutions of these compounds an interesting property: they conduct electricity. Because of this property, soluble ionic compounds are referred to as electrolytes. Many ionic compounds dissociate completely and are therefore called strong electrolytes. Sodium chloride is an example of a strong electrolyte. Some compounds dissolve but dissociate only partially, and solutions of such solutes may conduct electricity only weakly. These solutes are called weak electrolytes. Acetic acid (CH₃COOH), the compound in vinegar, is a weak electrolyte. Solutes that dissolve into individual neutral molecules without dissociation do not impart additional electrical conductivity to their solutions and are called nonelectrolytes. Table sugar ($C_{12}H_{22}O_{11}$) is an example of a nonelectrolyte.

The link below will connect you to an animation that illustrates the differences between ionic compounds (electroytes) and covalent compounds (non-electrolytes) dissolved in water.

The term electrolyte is used in medicine to mean any of the important ions that are dissolved in aqueous solution in the body. Important physiological electrolytes include Na^+ , K^+ , Ca^{2+} , Mg^{2+} , and Cl^{-} .

Example 10.3.1

The following substances all dissolve to some extent in water. Classify each as an electrolyte or a nonelectrolyte.

1. potassium chloride (KCl)



2. fructose ($C_6H_{12}O_6$)

- 3. isopropyl alcohol [CH₃CH(OH)CH₃]
- 4. magnesium hydroxide [Mg(OH)₂]

SOLUTION

Each substance can be classified as an ionic solute or a nonionic solute. Ionic solutes are electrolytes, and nonionic solutes are nonelectrolytes.

- 1. Potassium chloride is an ionic compound; therefore, when it dissolves, its ions separate, making it an electrolyte.
- 2. Fructose is a sugar similar to glucose. (In fact, it has the same molecular formula as glucose.) Because it is a molecular compound, we expect it to be a nonelectrolyte.
- 3. Isopropyl alcohol is an organic molecule containing the alcohol functional group. The bonding in the compound is all covalent, so when isopropyl alcohol dissolves, it separates into individual molecules but not ions. Thus, it is a nonelectrolyte
- 4. Magnesium hydroxide is an ionic compound, so when it dissolves it dissociates. Thus, magnesium hydroxide is an electrolyte.

Exercise 10.3.1

The following substances all dissolve to some extent in water. Classify each as an electrolyte or a nonelectrolyte.

a. acetone (CH_3COCH_3)

b. iron(III) nitrate [Fe(NO₃)₃]

- c. elemental bromine (Br₂)
- d. sodium hydroxide (NaOH)

CONCEPT REVIEW EXERCISE

1. Explain how the solvation process describes the dissolution of a solute in a solvent.

ANSWER

1. Each particle of the solute is surrounded by particles of the solvent, carrying the solute from its original phase.

KEY TAKEAWAY

• When a solute dissolves, its individual particles are surrounded by solvent molecules and are separated from each other.

EXERCISES

1. Describe what happens when an ionic solute like Na₂SO₄ dissolves in a polar solvent.

2. Describe what happens when a molecular solute like sucrose $(C_{12}H_{22}O_{11})$ dissolves in a polar solvent.

3. Classify each substance as an electrolyte or a nonelectrolyte. Each substance dissolves in H_2O to some extent.

- a. NH₄NO₃ b. CO₂
- c. NH_2CONH_2
- d. HCl

4. Classify each substance as an electrolyte or a nonelectrolyte. Each substance dissolves in H₂O to some extent.

- a. CH₃CH₂CH₂OH
 b. Ca(CH₃CO₂)₂
 c. I₂
 d. KOH
 5. Will solutions of each solute conduct electricity when dissolved?
 - a. AgNO₃ b. CHCl₃ c. BaCl₂ d. Li₂O

6. Will solutions of each solute conduct electricity when dissolved?

```
a. CH<sub>3</sub>COCH<sub>3</sub>
b. N(CH<sub>3</sub>)<sub>3</sub>
c. CH<sub>3</sub>CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>
```



d. FeCl₂

ANSWERS

- 1. Each ion of the ionic solute is surrounded by particles of solvent, carrying the ion from its associated crystal.
- 3. a. electrolyte
 - b. nonelectrolyte
 - c. nonelectrolyte
 - d. electrolyte
- 5. a. yes
 - b. no
 - c. yes
 - d. yes



10.4: CONCENTRATION

LEARNING OBJECTIVES

- Express the amount of solute in a solution in various concentration units.
- Use molarity to determine quantities in chemical reactions.
- Determine the resulting concentration of a diluted solution.

To define a solution precisely, we need to state its concentration: how much solute is dissolved in a certain amount of solvent. Words such as *dilute* or *concentrated* are used to describe solutions that have a little or a lot of dissolved solute, respectively, but these are relative terms whose meanings depend on various factors.

SOLUBILITY

There is usually a limit to how much solute will dissolve in a given amount of solvent. This limit is called the solubility of the solute. Some solutes have a very small solubility, while other solutes are soluble in all proportions. Table 10.4.1 lists the solubilities of various solutes in water. Solubilities vary with temperature, so Table 10.4.1 includes the temperature at which the solubility was determined.

Substance	Substance Solubility (g in 100 mL of H2O)		
AgCl(s)	0.019		
$C_6H_6(\ell)$ (benzene)	0.178		
$CH_4(g)$	0.0023		
CO ₂ (g)	0.150		
CaCO ₃ (s)	0.058		
CaF ₂ (s)	0.0016		
Ca(NO ₃) ₂ (s)	143.9		
$C_6H_{12}O_6$ (glucose)	120.3 (at 30°C)		
KBr(s)	67.8		
MgCO ₃ (s)	2.20		
NaCl(s)	36.0		
NaHCO ₃ (s)	8.41		
$C_{12}H_{22}O_{11}$ (sucrose)	204.0 (at 20°C)		

If a solution contains so much solute that its solubility limit is reached, the solution is said to be saturated, and its concentration is known from information contained in Table 10.4.1 If a solution contains less solute than the solubility limit, it is unsaturated. Under special circumstances, more solute can be dissolved even after the normal solubility limit is reached; such solutions are called *supersaturated* and are not stable. If the solute is solid, excess solute can easily recrystallize. If the solute is a gas, it can bubble out of solution uncontrollably, like what happens when you shake a soda can and then immediately open it.

PRECIPITATION FROM SUPERSATURATED SOLUTIONS

Recrystallization of excess solute from a supersaturated solution usually gives off energy as heat. Commercial heat packs containing supersaturated sodium acetate ($NaC_2H_3O_2$) take advantage of this phenomenon. You can probably find them at your local drugstore.





Video 10.4.1: Watered-down sodium acetate trihydrate. Needle crystal is truly wonderful structures

Most solutions we encounter are unsaturated, so knowing the solubility of the solute does not accurately express the amount of solute in these solutions. There are several common ways of specifying the concentration of a solution.

PERCENT COMPOSITION

There are several ways of expressing the concentration of a solution by using a percentage. The mass/mass percent (% m/m) is defined as the mass of a solute divided by the mass of a solution times 100:

$$\% \text{ m/m} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\%$$
 (10.4.1)

If you can measure the masses of the solute and the solution, determining the mass/mass percent is easy. Each mass must be expressed in the same units to determine the proper concentration.

Example 10.4.1

A saline solution with a mass of 355 g has 36.5 g of NaCl dissolved in it. What is the mass/mass percent concentration of the solution?

SOLUTION

We can substitute the quantities given in the equation for mass/mass percent:

$$m \%~m/m = rac{36.5~
m g}{355~
m g} imes 100\% = 10.3\%$$

Exercise 10.4.1

A dextrose (also called D-glucose, $C_6H_{12}O_6$) solution with a mass of 2.00 × 10² g has 15.8 g of dextrose dissolved in it. What is the mass/mass percent concentration of the solution?

For gases and liquids, volumes are relatively easy to measure, so the concentration of a liquid or a gas solution can be expressed as a volume/volume percent (% v/v): the volume of a solute divided by the volume of a solution times 100:

$$\% v/v = \frac{\text{volume of solute}}{\text{volume of solution}} \times 100\%$$
(10.4.2)

Again, the units of the solute and the solution must be the same. A hybrid concentration unit, mass/volume percent (% m/v), is commonly used for intravenous (IV) fluids (Figure 10.4.1). It is defined as the mass in grams of a solute, divided by volume in milliliters of solution times 100:

$$\% \text{ m/v} = \frac{\text{mass of solute (g)}}{\text{volume of solution (mL)}} \times 100\%$$
(10.4.3)





Figure 10.4.1: Mass/Volume Percent.The 0.9% NaCl concentration on this IV bag is mass/volume percent (left). Such solution is used for other purposes and available in bottles (right). Figures used with permission from Wikipedia

Each percent concentration can be used to produce a conversion factor between the amount of solute, the amount of solution, and the percent. Furthermore, given any two quantities in any percent composition, the third quantity can be calculated, as the following example illustrates.

Example 10.4.2

A sample of 45.0% v/v solution of ethanol (C_2H_5OH) in water has a volume of 115 mL. What volume of ethanol solute does the sample contain?

SOLUTION

A percentage concentration is simply the number of parts of solute per 100 parts of solution. Thus, the percent concentration of 45.0% v/v implies the following:

$$45.0\%\,v/v \rightarrow \frac{45\,mL\,C_2H_5OH}{100\,mL\,solution}$$

That is, there are 45 mL of C_2H_5OH for every 100 mL of solution. We can use this fraction as a conversion factor to determine the amount of C_2H_5OH in 115 mL of solution:

$$115 \text{ mL solution} \times \frac{45 \text{ mL } C_2 H_5 \text{ OH}}{100 \text{ mL solution}} = 51.8 \text{ mL } C_2 H_5 \text{ OH}$$

The highest concentration of ethanol that can be obtained normally is 95% ethanol, which is actually 95% v/v.

Exercise 10.4.2

What volume of a 12.75% m/v solution of glucose ($C_6H_{12}O_6$) in water is needed to obtain 50.0 g of $C_6H_{12}O_6$?

Example 10.4.3

A normal saline IV solution contains 9.0 g of NaCl in every liter of solution. What is the mass/volume percent of normal saline?



SOLUTION

We can use the definition of mass/volume percent, but first we have to express the volume in milliliter units:

Because this is an exact relationship, it does not affect the significant figures of our result.

$$\% \text{ m/v} = rac{9.0 \text{ g NaCl}}{1,000 \text{ mL solution}} imes 100\% = 0.90\% \text{ m/v}$$

Exercise 10.4.3

The chlorine bleach that you might find in your laundry room is typically composed of 27.0 g of sodium hypochlorite (NaOCl), dissolved to make 500.0 mL of solution. What is the mass/volume percent of the bleach?

In addition to percentage units, the units for expressing the concentration of extremely dilute solutions are parts per million (ppm) and parts per billion (ppb). Both of these units are mass based and are defined as follows:

$$ppm = \frac{\text{mass of solute}}{\text{mass of solution}} \times 1,000,000$$
(10.4.4)

$$ppb = \frac{\text{mass of solute}}{\text{mass of solution}} \times 1,000,000,000$$
(10.4.5)

Similar to parts per million and parts per billion, related units include parts per thousand (ppth) and parts per trillion (ppt).

Concentrations of *trace elements* in the body—elements that are present in extremely low concentrations but are nonetheless necessary for life—are commonly expressed in parts per million or parts per billion. Concentrations of poisons and pollutants are also described in these units. For example, cobalt is present in the body at a concentration of 21 ppb, while the State of Oregon's Department of Agriculture limits the concentration of arsenic in fertilizers to 9 ppm.

In aqueous solutions, 1 ppm is essentially equal to 1 mg/L, and 1 ppb is equivalent to 1 μ g/L.

Example 10.4.4

If the concentration of cobalt in a human body is 21 ppb, what mass in grams of Co is present in a body having a mass of 70.0 kg? **SOLUTION**

A concentration of 21 ppb means "21 g of solute per 1,000,000,000 g of solution." Written as a conversion factor, this concentration of Co is as follows:

$$21 ext{ ppb Co}
ightarrow rac{21 ext{ g Co}}{1,000,000,000 ext{ g solution}}$$

We can use this as a conversion factor, but first we must convert 70.0 kg to gram units:

$$70.0 ext{ kg} imes rac{1,000 ext{ g}}{1 ext{ kg}} = 7.00 imes 10^4 ext{ g}$$

Now we determine the amount of Co:

$$7.00 imes 10^4 ext{ g solution} imes rac{21 ext{ g Co}}{1,000,000,000 ext{ g solution}} = 0.0015 ext{ g Co}$$

This is only 1.5 mg.

Exercise 10.4.4

An 85 kg body contains 0.012 g of Ni. What is the concentration of Ni in parts per million?

MOLARITY



Another way of expressing concentration is to give the number of moles of solute per unit volume of solution. Such concentration units are useful for discussing chemical reactions in which a solute is a product or a reactant. Molar mass can then be used as a conversion factor to convert amounts in moles to amounts in grams.

Molarity is defined as the number of moles of a solute dissolved per liter of solution:

$$molarity = \frac{number of moles of solute}{number of liters of solution}$$
(10.4.6)

Molarity is abbreviated M (often referred to as "molar"), and the units are often abbreviated as mol/L. It is important to remember that "mol" in this expression refers to moles of solute and that "L" refers to liters of solution. For example, if you have 1.5 mol of NaCl dissolved in 0.500 L of solution, its molarity is therefore

$$\frac{1.5 \text{ mol NaCl}}{0.500 \text{ L solution}} = 3.0 \text{ M NaCl}$$
(10.4.7)

which is read as "three point oh molar sodium chloride." Sometimes (aq) is added when the solvent is water, as in "3.0 M NaCl(aq)." Before a molarity concentration can be calculated, the amount of the solute must be expressed in moles, and the volume of the solution must be expressed in liters, as demonstrated in the following example.

Example 10.4.5

What is the molarity of an aqueous solution of 25.0 g of NaOH in 750 mL?

SOLUTION

Before we substitute these quantities into the definition of molarity, we must convert them to the proper units. The mass of NaOH must be converted to moles of NaOH. The molar mass of NaOH is 40.00 g/mol:

$$25.0 ext{ g NaOH} imes rac{1 ext{ mol NaOH}}{40.00 ext{ g NaOH}} = 0.625 ext{ mol NaOH}$$

Next, we convert the volume units from milliliters to liters:

$$750 \text{ mL} imes rac{1 \text{ L}}{1,000 \text{ mL}} = 0.750 \text{ L}$$

Now that the quantities are expressed in the proper units, we can substitute them into the definition of molarity:

$$M = \frac{0.625 \text{ mol NaOH}}{0.750 \text{ L}} = 0.833 \text{ M NaOH}$$

Exercise 10.4.5

If a 350 mL cup of coffee contains 0.150 g of caffeine ($C_8H_{10}N_4O_2$), what is the molarity of this caffeine solution?

The definition of molarity can also be used to calculate a needed volume of solution, given its concentration and the number of moles desired, or the number of moles of solute (and subsequently, the mass of the solute), given its concentration and volume. The following example illustrates this.

Example 10.4.6

1. What volume of a 0.0753 M solution of dimethylamine [(CH₃)₂NH] is needed to obtain 0.450 mol of the compound?

2. Ethylene glycol (C₂H₆O₂) is mixed with water to make auto engine coolants. How many grams of C₂H₆O₂ are in 5.00 L of a 6.00 M aqueous solution?

SOLUTION

In both parts, we will use the definition of molarity to solve for the desired quantity.

1. 0.0753 M =
$$\frac{0.450 \text{ mol } (\text{CH}_3)_2 \text{NH}}{\text{volume of solution}}$$

To solve for the volume of solution, we multiply both sides by volume of solution and divide both sides by the molarity value to isolate the volume of solution on one side of the equation:

$${
m volume \ of \ solution} = rac{0.450 \ {
m mol} \ ({
m CH}_3)_2 {
m NH}}{0.0753 \ {
m M}} = 5.98 \ {
m L}$$

Note that because the definition of molarity is mol/L, the division of mol by M yields L, a unit of volume.

2. The molar mass of C₂H₆O₂ is 62.08 g/mol., so



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$$6.00 \text{ M} = rac{ ext{moles of solute}}{5.00 \text{ L}}$$

To solve for the number of moles of solute, we multiply both sides by the volume:

moles of solute =
$$(6.00 \text{ M})(5.00 \text{ L}) = 30.0 \text{ mol}$$

Note that because the definition of molarity is mol/L, the product $M \times L$ gives mol, a unit of amount. Now, using the molar mass of $C_3H_8O_3$, we convert mol to g:

$$30.0 ext{ mol} imes rac{62.08 ext{ g}}{ ext{mol}} = 1,860 ext{ g}$$

Thus, there are 1,860 g of $C_2H_6O_2$ in the specified amount of engine coolant.

Note: Dimethylamine has a "fishy" odor. In fact, organic compounds called amines cause the odor of decaying fish.

Exercise 10.4.6

a. What volume of a 0.0902 M solution of formic acid (HCOOH) is needed to obtain 0.888 mol of HCOOH?

b. Acetic acid (HC₂H₃O₂) is the acid in vinegar. How many grams of HC₂H₃O₂ are in 0.565 L of a 0.955 M solution?

USING MOLARITY IN STOICHIOMETRY PROBLEMS

Of all the ways of expressing concentration, molarity is the one most commonly used in stoichiometry problems because it is directly related to the mole unit. Consider the following chemical equation:

 $HCl(aq) + NaOH(s) \rightarrow H_2O(\ell) + NaCl(aq)$

Suppose we want to know how many liters of aqueous HCl solution will react with a given mass of NaOH. A typical approach to answering this question is as follows:



Figure 10.4.2: Typical approach to solving Molarity problems

In itself, each step is a straightforward conversion. It is the combination of the steps that is a powerful quantitative tool for problem solving.

Example 10.4.7

How many milliliters of a 2.75 M HCl solution are needed to react with 185 g of NaOH? The balanced chemical equation for this reaction is as follows:

$$HCl(aq) + NaOH(s) \rightarrow H_2O(\ell) + NaCl(aq)$$

SOLUTION

We will follow the flowchart to answer this question. First, we convert the mass of NaOH to moles of NaOH using its molar mass, 40.00 g/mol:

$$185 \text{ g NaOH} imes rac{1 ext{ mol NaOH}}{40.00 ext{ g NaOH}} = 4.63 ext{ mol NaOH}$$

10.4.6



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Using the balanced chemical equation, we see that there is a one-to-one ratio of moles of HCl to moles of NaOH. We use this to determine the number of moles of HCl needed to react with the given amount of NaOH:

$$4.63 \text{ mol NaOH} imes rac{1 \text{ mol HCl}}{1 \text{ mol NaOH}} = 4.63 \text{ mol HCl}$$

Finally, we use the definition of molarity to determine the volume of 2.75 M HCl needed:

 $2.75 \text{ M HCl} = \frac{4.63 \text{ mol HCl}}{\text{volume of HCl solution}}$ volume of HCl = $\frac{4.63 \text{ mol HCl}}{2.75 \text{ M HCl}} = 1.68 \text{ L} \times \frac{1,000 \text{ mL}}{1 \text{ L}} = 1,680 \text{ mL}$

We need 1,680 mL of 2.75 M HCl to react with the NaOH.

Exercise 10.4.7

How many milliliters of a 1.04 M H₂SO₄ solution are needed to react with 98.5 g of Ca(OH)₂? The balanced chemical equation for the reaction is as follows:

$$H_2SO_{4(aq)}+Ca(OH)_{2(s)}
ightarrow 2H_2O_{(\ell)}+CaSO_{4(aq)}$$

The general steps for performing stoichiometry problems such as this are shown in Figure 10.4.3 You may want to consult this figure when working with solutions in chemical reactions. The double arrows in Figure 10.4.3 indicate that you can start at either end of the chart and, after a series of simple conversions, determine the quantity at the other end.



Figure 10.4.3: Diagram of Steps for Using Molarity in Stoichiometry Calculations. When using molarity in stoichiometry calculations, a specific sequence of steps usually leads you to the correct answer.

Many of the fluids found in our bodies are solutions. The solutes range from simple ionic compounds to complex proteins. Table 10.4.2 lists the typical concentrations of some of these solutes.





Solution	Solute	Concentration
		(M)
blood plasma stomach acid	Na ⁺	0.138
	K^+	0.005
	Ca ²⁺	0.004
	Mg ²⁺	0.003
	Cl^-	0.110
	HCO ₃ ⁻	0.030
	HCl	0.10
urine	NaCl	0.15
	PO4 ³⁻	0.05
	NH ₂ CONH (urea)	2 0.30
*Note: Concentrations are approximate and can vary widely.		

LOOKING CLOSER: THE DOSE MAKES THE POISON

Why is it that we can drink 1 qt of water when we are thirsty and not be harmed, but if we ingest 0.5 g of arsenic, we might die? There is an old saying: *the dose makes the poison*. This means that what may be dangerous in some amounts may not be dangerous in other amounts.

Take arsenic, for example. Some studies show that arsenic deprivation limits the growth of animals such as chickens, goats, and pigs, suggesting that arsenic is actually an essential trace element in the diet. Humans are constantly exposed to tiny amounts of arsenic from the environment, so studies of completely arsenic-free humans are not available; if arsenic is an essential trace mineral in human diets, it is probably required on the order of 50 ppb or less. A toxic dose of arsenic corresponds to about 7,000 ppb and higher, which is over 140 times the trace amount that may be required by the body. Thus, arsenic is not poisonous in and of itself. Rather, it is the amount that is dangerous: the dose makes the poison.

Similarly, as much as water is needed to keep us alive, too much of it is also risky to our health. Drinking too much water too fast can lead to a condition called water intoxication, which may be fatal. The danger in water intoxication is not that water itself becomes toxic. It is that the ingestion of too much water too fast dilutes sodium ions, potassium ions, and other salts in the bloodstream to concentrations that are not high enough to support brain, muscle, and heart functions. Military personnel, endurance athletes, and even desert hikers are susceptible to water intoxication if they drink water but do not replenish the salts lost in sweat. As this example shows, even the right substances in the wrong amounts can be dangerous!

EQUIVALENTS

Concentrations of ionic solutes are occasionally expressed in units called equivalents (Eq). One equivalent equals 1 mol of positive or negative charge. Thus, 1 mol/L of Na⁺(aq) is also 1 Eq/L because sodium has a 1+ charge. A 1 mol/L solution of $Ca^{2+}(aq)$ ions has a concentration of 2 Eq/L because calcium has a 2+ charge. Dilute solutions may be expressed in milliequivalents (mEq)—for example, human blood plasma has a total concentration of about 150 mEq/L. (For more information about the ions present in blood plasma, see Chapter 3 "Ionic Bonding and Simple Ionic Compounds", Section 3.3 "Formulas for Ionic Compounds".)

DILUTION

When solvent is added to dilute a solution, the volume of the solution changes, but the amount of solute does not change. Before dilution, the amount of solute was equal to its original concentration times its original volume:

amount in moles = (concentration × volume)_{initial}

After dilution, the same amount of solute is equal to the final concentration times the final volume:

amount in moles = $(concentration \times volume)_{final}$



To determine a concentration or amount after a dilution, we can use the following equation:

(concentration × volume)_{initial} = (concentration × volume)_{final}

Any units of concentration and volume can be used, as long as both concentrations and both volumes have the same unit.

Example 10.4.8

A 125 mL sample of 0.900 M NaCl is diluted to 1,125 mL. What is the final concentration of the diluted solution?

SOLUTION

Because the volume units are the same, and we are looking for the molarity of the final solution, we can use (concentration \times volume)_{initial} = (concentration \times volume)_{final}:

(0.900 M × 125 mL) = (concentration × 1,125 mL)

We solve by isolating the unknown concentration by itself on one side of the equation. Dividing by 1,125 mL gives

$$m concentration = rac{0.900 \ {
m M} imes 125 \ {
m mL}}{1,125 \ {
m mL}} = 0.100 \ {
m M}$$

as the final concentration.

Exercise 10.4.8

A nurse uses a syringe to inject 5.00 mL of 0.550 M heparin solution (heparin is an anticoagulant drug) into a 250 mL IV bag, for a final volume of 255 mL. What is the concentration of the resulting heparin solution?

KEY TAKEAWAYS

- Various concentration units are used to express the amounts of solute in a solution.
- Concentration units can be used as conversion factors in stoichiometry problems.
- New concentrations can be easily calculated if a solution is diluted.

CONCEPT REVIEW EXERCISES

- 1. What are some of the units used to express concentration?
- 2. Distinguish between the terms *solubility* and *concentration*.

ANSWERS

- 1. % m/m, % m/v, ppm, ppb, molarity, and Eq/L (answers will vary)
- 2. Solubility is typically a limit to how much solute can dissolve in a given amount of solvent. Concentration is the quantitative amount of solute dissolved at any concentration in a solvent.

EXERCISES

- 1. Define *solubility*. Do all solutes have the same solubility?
- 2. Explain why the terms *dilute* or *concentrated* are of limited usefulness in describing the concentration of solutions.
- 3. If the solubility of sodium chloride (NaCl) is 30.6 g/100 mL of H₂O at a given temperature, how many grams of NaCl can be dissolved in 250.0 mL of H₂O?
- 4. If the solubility of glucose (C₆H₁₂O₆) is 120.3 g/100 mL of H₂O at a given temperature, how many grams of C₆H₁₂O₆ can be dissolved in 75.0 mL of H₂O?
- 5. How many grams of sodium bicarbonate (NaHCO₃) can a 25.0°C saturated solution have if 150.0 mL of H₂O is used as the solvent?
- 6. If 75.0 g of potassium bromide (KBr) are dissolved in 125 mL of H₂O, is the solution saturated, unsaturated, or supersaturated?
- 7. Calculate the mass/mass percent of a saturated solution of NaCl. Use the data from Table 10.4.1"Solubilities of Various Solutes in Water at 25°C (Except as Noted)", assume that masses of the solute and the solvent are additive, and use the density of H₂O (1.00 g/mL) as a conversion factor.
- 8. Calculate the mass/mass percent of a saturated solution of MgCO₃ Use the data from Table 10.4.1"Solubilities of Various Solutes in Water at 25°C (Except as Noted)", assume that masses of the solute and the solvent are additive, and use the density of H₂O (1.00 g/mL) as a conversion factor.
- 9. Only 0.203 mL of C₆H₆ will dissolve in 100.000 mL of H₂O. Assuming that the volumes are additive, find the volume/volume percent of a saturated solution of benzene in water.
- 10. Only 35 mL of aniline (C₆H₅NH₂) will dissolve in 1,000 mL of H₂O. Assuming that the volumes are additive, find the volume/volume percent of a saturated solution of aniline in water.
- 11. A solution of ethyl alcohol (C_2H_5OH) in water has a concentration of 20.56% v/v. What volume of C_2H_5OH is present in 255 mL of solution?
- 12. What mass of KCl is present in 475 mL of a 1.09% m/v aqueous solution?
- 13. The average human body contains 5,830 g of blood. What mass of arsenic is present in the body if the amount in blood is 0.55 ppm?
- 14. The Occupational Safety and Health Administration has set a limit of 200 ppm as the maximum safe exposure level for carbon monoxide (CO). If an average breath has a mass of 1.286 g, what is the maximum mass of CO that can be inhaled at that maximum safe exposure level?
- 15. Which concentration is greater—15 ppm or 1,500 ppb?
- 16. Express the concentration 7,580 ppm in parts per billion.
- 17. What is the molarity of 0.500 L of a potassium chromate solution containing 0.0650 mol of K₂CrO₄?
- 18. What is the molarity of 4.50 L of a solution containing 0.206 mol of urea [(NH₂)₂CO]?
- 19. What is the molarity of a 2.66 L aqueous solution containing 56.9 g of NaBr?
- 20. If 3.08 g of Ca(OH)₂ is dissolved in enough water to make 0.875 L of solution, what is the molarity of the Ca(OH)₂?
- 21. What mass of HCl is present in 825 mL of a 1.25 M solution?
- 22. What mass of isopropyl alcohol (C_3H_8O) is dissolved in 2.050 L of a 4.45 M aqueous C_3H_8O solution?
- 23. What volume of 0.345 M NaCl solution is needed to obtain 10.0 g of NaCl?
- 24. How many milliliters of a 0.0015 M cocaine hydrochloride (C₁₇H₂₂ClNO₄) solution is needed to obtain 0.010 g of the solute?
- 25. Aqueous calcium chloride reacts with aqueous silver nitrate according to the following balanced chemical equation:

 $CaCl_2(aq) + 2AgNO_3(aq) \rightarrow 2AgCl(s) + Ca(NO_3)_2(aq)$

How many moles of AgCl(s) are made if 0.557 L of 0.235 M CaCl₂ react with excess AgNO₃? How many grams of AgCl are made?

26. Sodium bicarbonate (NaHCO₃) is used to react with acid spills. The reaction with sulfuric acid (H₂SO₄) is as follows:

$$2\text{NaHCO}_{3}(s) + \text{H}_{2}\text{SO}_{4}(aq) \rightarrow \text{Na}_{2}\text{SO}_{4}(aq) + 2\text{H}_{2}\text{O}(\ell) + 2\text{CO}_{2}(g)$$

If 27.6 mL of a 6.25 M H₂SO₄ solution were spilled, how many moles of NaHCO₃ would be needed to react with the acid? How many grams of NaHCO₃ is this?

27. The fermentation of glucose to make ethanol and carbon dioxide has the following overall chemical equation:

$$C_6H_{12}O_6(aq) \rightarrow 2C_2H_5OH(aq) + 2CO_2(g)$$

If 1.00 L of a 0.567 M solution of $C_6H_{12}O_6$ were completely fermented, what would be the resulting concentration of the C_2H_5OH solution? How many moles of CO_2 would be formed? How many grams is this? If each mole of CO_2 had a volume of 24.5 L, what volume of CO_2 is produced?

28. Aqueous sodium bisulfite gives off sulfur dioxide gas when heated:

$$2NaHSO_3(aq) \rightarrow Na_2SO_3(aq) + H_2O(\ell) + SO_2(g)$$

If 567 mL of a 1.005 M NaHSO₃ solution were heated until all the NaHSO₃ had reacted, what would be the resulting concentration of the Na₂SO₃ solution? How many moles of SO₂ would be formed? How many grams of SO₂ would be formed? If each mole of SO₂ had a volume of 25.78 L, what volume of SO₂ would be produced?

- 29. What is the concentration of a 1.0 M solution of K⁺(aq) ions in equivalents/liter?
- 30. What is the concentration of a 1.0 M solution of $SO_4^{2-}(aq)$ ions in equivalents/liter?
- 31. A solution having initial concentration of 0.445 M and initial volume of 45.0 mL is diluted to 100.0 mL. What is its final concentration?
- 32. A 50.0 mL sample of saltwater that is 3.0% m/v is diluted to 950 mL. What is its final mass/volume percent?

ANSWERS

- 1. Solubility is the amount of a solute that can dissolve in a given amount of solute, typically 100 mL. The solubility of solutes varies widely.
- 3. 76.5 g



- 5. 12.6 g
- 7.26.5%
- 9. 0.203%
- 11. 52.4 mL
- 13. 0.00321 g
- 15. 15 ppm
- 17. 0.130 M
- 19. 0.208 M
- 21. 37.6 g
- 23. 0.496 L
- 25. 0.262 mol; 37.5 g
- 27. 1.13 M C₂H₅OH; 1.13 mol of CO₂; 49.7 g of CO₂; 27.7 L of CO₂
- 29. 1.0 Eq/L
- 31. 0.200 M



10.5: COLLIGATIVE PROPERTIES OF SOLUTIONS

LEARNING OBJECTIVE

- Name the four colligative properties.
- Calculate changes in vapor pressure, melting point, and boiling point of solutions.
- Calculate the osmotic pressure of solutions.

The properties of solutions are very similar to the properties of their respective pure solvents. This makes sense because the majority of the solution *is* the solvent. However, some of the properties of solutions differ from pure solvents in measurable and predictable ways. The differences are proportional to the fraction that the solute particles occupy in the solution. These properties are called **colligative properties**; the word *colligative* comes from the Greek word meaning "related to the number," implying that these properties are related to the number of solute particles, not their identities.

Before we introduce the first colligative property, we need to introduce a new concentration unit. The **mole fraction** of the *i*th component in a solution, χ_i , is the number of moles of that component divided by the total number of moles in the sample:

$$\chi_i = \frac{moles\ of\ ith\ component}{total\ moles}\tag{10.5.1}$$

(χ is the lowercase Greek letter chi.) The mole fraction is always a number between 0 and 1 (inclusive) and has no units; it is just a number.

Example 10.5.1: Hydrocarbon Solution

A solution is made by mixing 12.0 g of C10H8 in 45.0 g of C6H6. What is the mole fraction of C10H8 in the solution?

Solution

We need to determine the number of moles of each substance, add them together to get the total number of moles, and then divide to determine the mole fraction of $C_{10}H_8$. The number of moles of $C_{10}H_8$ is as follows:

$$12.0g C_{10}H_8 \times \frac{1 \mod C_{10}H_8}{128.10g C_{10}H_8} = 0.0936 \mod C_{10}H_8 \tag{10.5.2}$$

The number of moles of C6H6 is as follows:

$$45.0g C_6 H_6 \times \frac{1 \mod C_6 H_6}{78.12g C_6 H_6} = 0.576 \mod C_6 H_6 \tag{10.5.3}$$

The total number of moles is

0.0936 mol + 0.576 mol = 0.670 mol

Now we can calculate the mole fraction of C10H8:

$$\chi_{C_{10}H_8} = \frac{0.0936mol}{0.670mol} = 0.140 \tag{10.5.4}$$

The mole fraction is a number between 0 and 1 and is unitless.

Exercise 10.5.1

A solution is made by mixing 33.8 g of CH3OH in 50.0 g of H2O. What is the mole fraction of CH3OH in the solution?

Answer

0.275

A useful thing to note is that the sum of the mole fractions of all substances in a mixture equals 1. Thus the mole fraction of $C_{6}H_{6}$ in Example 10.5.1 could be calculated by evaluating the definition of mole fraction a second time, or-because there are only two substances in this particular mixture-we can subtract the mole fraction of the $C_{10}H_{8}$ from 1 to get the mole fraction of $C_{6}H_{6}$.

Now that this new concentration unit has been introduced, the first colligative property can be considered. As was mentioned in Chapter 10, all pure liquids have a characteristic vapor pressure in equilibrium with the liquid phase, the partial pressure of which is dependent on temperature. Solutions, however, have a lower vapor pressure than the pure solvent has, and the amount of lowering is dependent on the fraction of solute particles, as long as the solute itself does not have a significant vapor pressure (the term *nonvolatile*



is used to describe such solutes). This colligative property is called **vapor pressure depression** (or *lowering*). The actual vapor pressure of the solution can be calculated as follows:

$$P_{soln} = \chi_{solv} P_{solv}^* \tag{10.5.5}$$

where P_{soln} is the vapor pressure of the solution, χ_{solv} is the mole fraction of the solvent particles, and P^*_{solv} is the vapor pressure of the pure solvent at that temperature (which is data that must be provided). This equation is known as **Raoult's law** (the approximate pronunciation is *rah-OOLT*). Vapor pressure depression is rationalized by presuming that solute particles take positions at the surface in place of solvent particles, so not as many solvent particles can evaporate.

Example 10.5.2: Vapor Pressure Reduction

A solution is made by mixing 12.0 g of $C_{10}H_8$ in 45.0 g of $C_{6}H_6$. If the vapor pressure of pure $C_{6}H_6$ is 95.3 torr, what is the vapor pressure of the solution?

Solution

This is the same solution that was in Example 15, but here we need the mole fraction of C6H6. The number of moles of C10H8 is as follows:

$$12.0g C_{10}H_8 \times \frac{1 \mod C_{10}H_8}{128.10g C_{10}H_8} = 0.0936 \mod C_{10}H_8$$
(10.5.6)

The number of moles of C₆H₆ is as follows:

$$45.0g C_6 H_6 \times \frac{1mol C_6 H_6}{78.12g C_6 H_6} = 0.576 mol C_6 H_6$$
(10.5.7)

So the total number of moles is

0.0936 mol + 0.576 mol = 0.670 mol

Now we can calculate the mole fraction of C_6H_6 :

$$\chi_{C_{10}H_8} = \frac{0.576mol}{0.670mol} = 0.860 \tag{10.5.8}$$

(The mole fraction of C10H8 calculated in Example 15 plus the mole fraction of C6H6 equals 1, which is mathematically required by the definition of mole fraction.) Now we can use Raoult's law to determine the vapor pressure in equilibrium with the solution:

P_{soln} = (0.860)(95.3 torr) = 82.0 torr

The solution has a lower vapor pressure than the pure solvent.

Exercise 10.5.2

A solution is made by mixing 33.8 g of $C_6H_{12}O_6$ in 50.0 g of H_2O . If the vapor pressure of pure water is 25.7 torr, what is the vapor pressure of the solution?

Answer

24.1 torr

Two colligative properties are related to solution concentration as expressed in molality. As a review, recall the definition of molality:

$$molality - = \frac{moles \ solute}{kilograms \ solvent} \tag{10.5.9}$$

Because the vapor pressure of a solution with a nonvolatile solute is depressed compared to that of the pure solvent, it requires a higher temperature for the solution's vapor pressure to reach 1.00 atm (760 torr). Recall that this is the definition of the normal boiling point: the temperature at which the vapor pressure of the liquid equals 1.00 atm. As such, the normal boiling point of the solution is higher than that of the pure solvent. This property is called **boiling point elevation**.

The change in boiling point (ΔT_b) is easily calculated:

$$\Delta T_b = mK_b \tag{10.5.10}$$

where *m* is the molality of the solution and K_b is called the **boiling point elevation constant,** which is a characteristic of the solvent. Several boiling point elevation constants (as well as boiling point temperatures) are listed in Table 10.5.1.



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Liquid	Boiling Point (°C)	<i>К</i> b (°С/ <i>m</i>)
НС2НЗО2	117.90	3.07
С6н6	80.10	2.53
CCl4	76.8	4.95
Н2О	100.00	0.512

Remember that what is initially calculated is the *change* in boiling point temperature, not the new boiling point temperature. Once the change in boiling point temperature is calculated, it must be added to the boiling point of the pure solvent-because boiling points are always elevated-to get the boiling point of the solution.

Example 10.5.3:

What is the boiling point of a 2.50 *m* solution of C6H4Cl2 in CCl4? Assume that C6H4Cl2 is not volatile.

Solution

Using the equation for the boiling point elevation,

 $\Delta T_{\rm b} = (2.50 \ m)(4.95^{\circ}{\rm C}/m) = 12.4^{\circ}{\rm C}$

Note how the molality units have canceled. However, we are not finished. We have calculated the change in the boiling point temperature, not the final boiling point temperature. If the boiling point goes up by 12.4°C, we need to add this to the normal boiling point of CCl4 to get the new boiling point of the solution:

 $TBP = 76.8^{\circ}C + 12.4^{\circ}C = 89.2^{\circ}C$

The boiling point of the solution is predicted to be 89.2°C.

Exercise 10.5.3

What is the boiling point of a 6.95 *m* solution of C12H22O11 in H2O?

Answer

103.6°C

The boiling point of a solution is higher than the boiling point of the pure solvent, but the opposite occurs with the freezing point. The freezing point of a solution is lower than the freezing point of the pure solvent. Think of this by assuming that solute particles interfere with solvent particles coming together to make a solid, so it takes a lower temperature to get the solvent particles to solidify. This is called **freezing point depression**.

The equation to calculate the change in the freezing point for a solution is similar to the equation for the boiling point elevation:

$$\Delta T_f = m K_f \tag{10.5.11}$$

where *m* is the molality of the solution and $K_{\rm f}$ is called the **freezing point depression constant**, which is also a characteristic of the solvent only. Several freezing point depression constants (as well as freezing point temperatures) are listed in Table 10.5.2

Liquid	Freezing Point (°C)	<i>K</i> f (°C/ <i>m</i>)
нс2н3о2	16.60	3.90
с6н6	5.51	4.90
С6н12	6.4	20.2
С10Н8	80.2	6.8
Н2О	0.00	1.86

Remember that this equation calculates the change in the freezing point, not the new freezing point. What is calculated needs to be subtracted from the normal freezing point of the solvent because freezing points always go down.

EXAMPLE 10.5.4: FREEZING POINT REDUCTION

What is the freezing point of a 1.77 *m* solution of CBr4 in C6H6?

Solution

We use the equation to calculate the change in the freezing point and then subtract this number from the normal freezing point of $C_{6}H_{6}$ to get the freezing point of the solution:

$\Delta T_{\rm f} = (1.77 \ m)(4.90^{\circ}{\rm C}/m) = 8.67^{\circ}{\rm C}$

Now we subtract this number from the normal freezing point of C₆H₆, which is 5.51°C:



5.51 - 8.67 = -3.16°C

The freezing point of the solution is −3.16°C.

Exercise 10.5.4

What is the freezing point of a 3.05 *m* solution of CBr4 in C10H8?

Answer

59.5°C

Freezing point depression is one colligative property we use in everyday life. Many antifreezes used in automobile radiators use solutions that have a lower freezing point than normal so that automobile engines can operate at subfreezing temperatures. We also take advantage of freezing point depression when we sprinkle various compounds on ice to thaw it in the winter for safety (Figure 10.5.1). The compounds make solutions that have a lower freezing point, so rather than forming slippery ice, any ice is liquefied and runs off, leaving a safer pavement behind.



Figure **10.5.1***:* Salt and Safety © Thinkstock Salt or other compounds take advantage of the freezing point depression to minimize the formation of ice on sidewalks and roads, thus increasing safety.

Before we introduce the final colligative property, we need to present a new concept. A **semipermeable membrane** is a thin membrane that will pass certain small molecules but not others. A thin sheet of cellophane, for example, acts as a semipermeable membrane. Consider the system in Figure 10.5.2



Figure 10.5.2: Osmosis. (a) Two solutions of differing concentrations are placed on either side of a semipermeable membrane. (b) When osmosis occurs, solvent molecules selectively pass through the membrane from the dilute solution to the concentrated solution, diluting it until the two concentrations are the same. The pressure exerted by the different height of the solution on the right is called the osmotic pressure.

a. A semipermeable membrane separates two solutions having the different concentrations marked. Curiously, this situation is not stable; there is a tendency for water molecules to move from the dilute side (on the left) to the concentrated side (on the right) until

10.5.4



the concentrations are equalized, as in Figure 10.5.2

b. This tendency is called **osmosis**. In osmosis, the solute remains in its original side of the system; only solvent molecules move through the semipermeable membrane. In the end, the two sides of the system will have different volumes. Because a column of liquid exerts a pressure, there is a pressure difference Π on the two sides of the system that is proportional to the height of the taller column. This pressure difference is called the **osmotic pressure**, which is a colligative property.

The osmotic pressure of a solution is easy to calculate:

$$\Pi = MRT \tag{10.5.12}$$

where Π is the osmotic pressure of a solution, *M* is the molarity of the solution, *R* is the ideal gas law constant, and *T* is the absolute temperature. This equation is reminiscent of the ideal gas law we considered in Chapter 6.

What is the osmotic pressure of a 0.333 M solution of $C_6H_{12}O_6$ at 25°C?

Solution

First we need to convert our temperature to kelvins:

$$T = 25 + 273 = 298 \text{ K}$$

Now we can substitute into the equation for osmotic pressure, recalling the value for *R*:

$$\prod = (0.333M) \left(0.08205 \frac{L.\,atm}{mol.\,K} \right) (298K) \tag{10.5.13}$$

The units may not make sense until we realize that molarity is defined as moles per liter:

$$\prod = \left(0.333 \frac{mol}{L}\right) \left(0.08205 \frac{L.\,atm}{mol.\,K}\right) (298K) \tag{10.5.14}$$

Now we see that the moles, liters, and kelvins cancel, leaving atmospheres, which is a unit of pressure. Solving,

 $\Pi = 8.14 \text{ atm}$

This is a substantial pressure! It is the equivalent of a column of water 84 m tall.

Exercise 10.5.5

What is the osmotic pressure of a 0.0522 M solution of C12H22O11 at 55°C?

Answer

1.40 atm

Osmotic pressure is important in biological systems because cell walls are semipermeable membranes. In particular, when a person is receiving intravenous (IV) fluids, the osmotic pressure of the fluid needs to be approximately the same as blood serum; otherwise bad things can happen. Figure 10.5.3 shows three red blood cells:

- a healthy red blood cell
- a red blood cell that has been exposed to a lower concentration than normal blood serum (a so-called *hypotonic* solution); the cell has plumped up as solvent moves into the cell to dilute the solutes inside.
- a red blood cell exposed to a higher concentration than normal blood serum (*hypertonic*); water leaves the red blood cell, so it collapses onto itself. Only when the solutions inside and outside the cell are the same (*isotonic*) will the red blood cell be able to do its job.





Figure 10.5.3: Osmotic Pressure and Red Blood Cells. (a) This is what a normal red blood cell looks like. (b) When a red blood cell is exposed to a hypotonic solution, solvent goes through the cell membrane and dilutes the inside of the cell. (c) When a red blood cell is exposed to a hypertonic solution, solvent goes from the cell to the surrounding solution, diluting the hypertonic solution and collapsing the cell. Neither of these last two cases is desirable, so IV solutions must be isotonic with blood serum to not cause deleterious effects.

Osmotic pressure is also the reason you should not drink seawater if you're stranded in a lifeboat on an ocean; seawater has a higher osmotic pressure than most of the fluids in your body. You *can* drink the water, but ingesting it will pull water out of your cells as osmosis works to dilute the seawater. Ironically, your cells will die of thirst, and you will also die. (It is OK to drink the water if you are stranded on a body of freshwater, at least from an osmotic pressure perspective.) Osmotic pressure is also thought to be important-in addition to capillary action-in getting water to the tops of tall trees.

SUMMARY

- Colligative properties depend only on the number of dissolved particles (that is, the concentration), not their identity.
- Raoult's law is concerned with the vapor pressure depression of solutions.
- The boiling points of solutions are always higher, and the freezing points of solutions are always lower, than those of the pure solvent.
- Osmotic pressure is caused by concentration differences between solutions separated by a semipermeable membrane and is an important biological issue.



10.6: COLLIGATIVE PROPERTIES OF IONIC SOLUTES

LEARNING OBJECTIVE

• Determine the colligative properties of solutions of ionic solutes.

In Section 11.6, we considered the colligative properties of solutions with molecular solutes. What about solutions with ionic solutes? Do they exhibit colligative properties?

There is a complicating factor: ionic solutes separate into ions when they dissolve. This increases the total number of particles dissolved in solution and *increases the impact on the resulting colligative property*. Historically, this greater-than-expected impact on colligative properties was one main piece of evidence for ionic compounds separating into ions (increased electrical conductivity was another piece of evidence).

For example, when NaCl dissolves, it separates into two ions:

 $\left(\left(e\{ NaCl(s) \rightarrow Na^{+}(aq) + Cl^{-}(aq) \right) \right) \right)$

This means that a 1 M solution of NaCl actually has a net particle concentration of 2 M. The observed colligative property will then be twice as large as expected for a 1 M solution.

It is easy to incorporate this concept into our equations to calculate the respective colligative property. We define the **van 't Hoff factor** (*i*) as the number of particles each solute formula unit breaks apart into when it dissolves. Previously, we have always tacitly assumed that the van't Hoff factor is simply 1. But for some ionic compounds, *i* is not 1, as shown in Table 11.7.1 - Ideal van't Hoff Factors for Ionic Compounds.

Table 11.7.1 Ideal van't Hoff Factors for Ionic Compounds

Compound	i
NaCl	2
KBr	2
LiNO3	2
CaCl2	3
Mg(C2H3O2)2	3
FeCl3	4
Al <u>2</u> (SO4)3	5

The ideal van't Hoff factor is equal to the number of ions that form when an ionic compound dissolves.

Example 10.6.1:
Predict the van't Hoff factor for Sr(OH)2.
Solution
When $Sr(OH)_2$ dissolves, it separates into one Sr^{2+} ion and two OH^- ions:
$Sr(OH)_2 \rightarrow Sr^{2+}(aq) + 2OH^{-}(aq)$
Because it breaks up into three ions, its van't Hoff factor is 3.
Exercise 10.6.1

What is the van't Hoff factor for Fe(NO3)3?

Answer

4

It is the "ideal" van't Hoff factor because this is what we expect from the ionic formula. However, this factor is usually correct only for dilute solutions (solutions less than 0.001 M). At concentrations greater than 0.001 M, there are enough interactions between ions of opposite charge that the net concentration of the ions is less than expected-sometimes significantly. The actual van't Hoff factor is thus less than the ideal one. Here, we will use ideal van't Hoff factors.

Revised equations to calculate the effect of ionization are then easily produced:

 $\Delta T_{b} = imK_{b}$ $\Delta T_{f} = imK_{g}$ $\Pi = iMRT$



where all variables have been previously defined. To calculate vapor pressure depression according to Raoult's law, the mole fraction of solvent particles must be recalculated to take into account the increased number of particles formed on ionization.

Example 10.6.2:

Determine the freezing point of a 1.77 *m* solution of NaCl in H₂O.

Solution

For NaCl, we need to remember to include the van't Hoff factor, which is 2. Otherwise, the calculation of the freezing point is straightforward:

 $\Delta T_{f} = (2)(1.77 m)(1.86^{\circ}C/m) = 6.58^{\circ}C$

This represents the change in the freezing point, which is decreasing. So we have to subtract this change from the normal freezing point of water, 0.00°C:

 $0.00 - 6.58 = -6.58^{\circ}C$

Exercise 10.6.2

Determine the boiling point of a 0.887 m solution of CaCl₂ in H₂O.

Answer

101.36°C

FOOD AND DRINK APP: SALTING PASTA COOKING WATER

When cooking dried pasta, many recipes call for salting the water before cooking the pasta. Some argue-with colligative properties on their side-that adding salt to the water raises the boiling point, thus cooking the pasta faster. Is there any truth to this?



Fig. 11.7.1 Cooking dried pasta © Thinkstock. Why do so many recipes call for adding salt to water when boiling pasta? Is it to raise the boiling temperature of the water?

To judge the veracity of this claim, we can calculate how much salt should be added to the water to raise the boiling temperature by 1.0°C, with the presumption that dried pasta cooks noticeably faster at 101°C than at 100°C (although a 1° difference may make only a negligible change in cooking times). We can calculate the molality that the water should have:

$1.0^{\circ}\text{C} = m(0.512^{\circ}\text{C}/m)m = 1.95$

We have ignored the van't Hoff factor in our estimation because this obviously is not a dilute solution. Let us further assume that we are using 4 L of water (which is very close to 4 qt, which in turn equals 1 gal). Because 4 L of water is about 4 kg (it is actually slightly less at 100°C), we can determine how much salt (NaCl) to add:





$$4 \ \ kgH_2O \times \frac{1.95 \ \ mol \ NaCl}{kgH_2O} \times \frac{58.5g \ NaCl}{\ \ mol \ NaCl} = 456.3g \ NaCl$$

$$(10.6.1)$$

This is just over 1 lb of salt and is equivalent to nearly 1 cup in the kitchen. In your experience, do you add almost a cup of salt to a pot of water to make pasta? Certainly not! A few pinches, perhaps one-fourth of a teaspoon, but not almost a cup! It is obvious that the little amount of salt that most people add to their pasta water is not going to significantly raise the boiling point of the water.

So why do people add some salt to boiling water? There are several possible reasons, the most obvious of which is taste: adding salt adds a little bit of salt flavor to the pasta. It cannot be much because most of the salt remains in the water, not in the cooked pasta. However, it may be enough to detect with our taste buds. The other obvious reason is habit; recipes tell us to add salt, so we do, even if there is little scientific or culinary reason to do so.

SUMMARY

For ionic solutes, the calculation of colligative properties must include the fact that the solutes separate into multiple particles when they dissolve. The equations for calculating colligative properties of solutions of ionic solvents include the van't Hoff factor, *i*.

Exercise 10.6.1

- 1. Explain why we need to consider a van't Hoff factor for ionic solutes but not for molecular solutes.
- 2. NaCl is often used in winter to melt ice on roads and sidewalks, but calcium chloride (CaCl₂) is also used. Which would be better (on a mole-by-mole basis), and why?
- 3. Calculate the boiling point of an aqueous solution of NaNO3 made by mixing 15.6 g of NaNO3 with 100.0 g of H₂O. Assume an ideal van't Hoff factor.
- 4. Many labs use a cleaning solution of KOH dissolved in C₂H₅OH. If 34.7 g of KOH were dissolved in 88.0 g of C₂H₅OH, what is the boiling point of this solution? The normal boiling point of C₂H₅OH is 78.4°C and its $K_b = 1.19$ °C/m. Assume an ideal van't Hoff factor.
- 5. What is the freezing point of a solution made by dissolving 345 g of CaCl₂ in 1,550 g of H₂O? Assume an ideal van't Hoff factor.
- 6. A classic homemade ice cream can be made by freezing the ice cream mixture using a solution of 250 g of NaCl dissolved in 1.25 kg of ice water. What is the temperature of this ice water? Assume an ideal van't Hoff factor.
- 7. Seawater can be approximated as a 3.5% NaCl solution by mass; that is, 3.5 g of NaCl are combined with 96.5 g H₂O. What is the osmotic pressure of seawater? Assume an ideal van't Hoff factor.
- 8. The osmotic pressure of blood is 7.65 atm at 37°C. If blood were considered a solution of NaCl, what is the molar concentration of NaCl in blood? Assume an ideal van't Hoff factor.
- 9. What is the vapor pressure of an aqueous solution of 36.4 g of KBr in 199.5 g of H₂O if the vapor pressure of H₂O at the same temperature is 32.55 torr? What other solute(s) would give a solution with the same vapor pressure? Assume an ideal van't Hoff factor.
- 10. Assuming an ideal van't Hoff factor, what mole fraction is required for a solution of Mg(NO3)2 to have a vapor pressure of 20.00 torr at 25.0°C? The vapor pressure of the solvent is 23.61 torr at this temperature.

Answers

- 1. Ionic solutes separate into more than one particle when they dissolve, whereas molecular solutes do not.
- 2.
- 3. 101.9°C
- 4.

5. −7.5°C

- 6.
- 7. 30.3 atm
- 8.
- 9. 30.86 torr; any two-ion salt should have the same effect.



10.7: SOLUTIONS (EXERCISES)

ADDITIONAL EXERCISES

1. Calcium nitrate reacts with sodium carbonate to precipitate solid calcium carbonate:

$$Ca(NO_3)_{2(aq)} + Na_2CO_{3(aq)} \rightarrow CaCO_{3(s)} + NaNO_{3(aq)}$$

$$(10.7.1)$$

- a. Balance the chemical equation.
- b. How many grams of Na₂CO₃ are needed to react with 50.0 mL of 0.450 M Ca(NO₃)₂?
- c. Assuming that the Na₂CO₃ has a negligible effect on the volume of the solution, find the osmolarity of the NaNO₃ solution remaining after the CaCO₃ precipitates from solution.
- 2. The compound HCl reacts with sodium carbonate to generate carbon dioxide gas:

$$[HCl_{(aq)} + Na_{2CO_{(aq)} \ ightarrow H_{2O_{(\ell)}} + CO_{(2(g))} + NaCl_{(aq)}]$$

- a. Balance the chemical equation.
- b. How many grams of Na₂CO₃ are needed to react with 250.0 mL of 0.755 M HCl?
- c. Assuming that the Na₂CO₃ has a negligible effect on the volume of the solution, find the osmolarity of the NaCl solution remaining after the reaction is complete.
- 3. Estimate the freezing point of concentrated aqueous HCl, which is usually sold as a 12 M solution. Assume complete ionization into H⁺ and Cl⁻ ions.
- 4. Estimate the boiling point of concentrated aqueous H₂SO₄, which is usually sold as an 18 M solution. Assume complete ionization into H⁺ and HSO₄⁻ ions.
- 5. Seawater can be approximated by a 3.0% m/m solution of NaCl in water. Determine the molarity and osmolarity of seawater. Assume a density of 1.0 g/mL.
- 6. Human blood can be approximated by a 0.90% m/m solution of NaCl in water. Determine the molarity and osmolarity of blood. Assume a density of 1.0 g/mL.
- 7. How much water must be added to 25.0 mL of a 1.00 M NaCl solution to make a resulting solution that has a concentration of 0.250 M?
- 8. Sports drinks like Gatorade are advertised as capable of resupplying the body with electrolytes lost by vigorous exercise. Find a label from a sports drink container and identify the electrolytes it contains. You should be able to identify several simple ionic compounds in the ingredients list.
- 9. Occasionally we hear a sensational news story about people stranded in a lifeboat on the ocean who had to drink their own urine to survive. While distasteful, this act was probably necessary for survival. Why not simply drink the ocean water? (Hint: See Exercise 5 and Exercise 6 above. What would happen if the two solutions in these exercises were on opposite sides of a semipermeable membrane, as we would find in our cell walls?)

ANSWERS

- 1. a. Ca(NO₃)₂(aq) + Na₂CO₃(aq) → CaCO₃(s) + 2NaNO₃(aq) b. 2.39 g c. 1.80 osmol
- 3. −45.6°C
- 5. 0.513 M; 1.026 osmol
- 7. 75.0 mL
- 9. The osmotic pressure of seawater is too high. Drinking seawater would cause water to go from inside our cells into the more concentrated seawater, ultimately killing the cells.



10.8: SOLUTIONS (EXERCISES)

Additional Exercises

- 1. One brand of ethyl alcohol (Everclear) is 95% ethyl alcohol, with the remaining 5% being water. What is the solvent and what is the solute of this solution?
- 2. Give an example of each type of solution from your own experience.
 - a. A solution composed of a gas solute in a liquid solvent.
 - b. A solution composed of a solid solute in a liquid solvent.
 - c. A solution composed of a liquid solute in a liquid solvent.
 - d. A solution composed of a solid solute in a solid solvent. (Hint: usually such solutions are made as liquids and then solidified.)
- 3. Differentiate between the terms *saturated* and *concentrated*.
- 4. Differentiate between the terms unsaturated and dilute.
- 5. What mass of FeCl2 is present in 445 mL of 0.0812 M FeCl2 solution?
- 6. What mass of SO₂ is present in 26.8 L of 1.22 M SO₂ solution?
- 7. What volume of 0.225 M Ca(OH)2 solution is needed to deliver 100.0 g of Ca(OH)2?
- 8. What volume of 12.0 M HCl solution is needed to obtain exactly 1.000 kg of HCl?
- 9. The World Health Organization recommends that the maximum fluoride ion concentration in drinking water is 1.0 ppm. Assuming water has the maximum concentration, if an average person drinks 1,920 mL of water per day, how many milligrams of fluoride ion are being ingested?
- 10. For sanitary reasons, water in pools should be chlorinated to a maximum level of 3.0 ppm. In a typical 5,000 gal pool that contains 21,200 kg of water, what mass of chlorine must be added to obtain this concentration?
- 11. Given its notoriety, you might think that uranium is very rare, but it is present at about 2–4 ppm of the earth's crust, which is more abundant than silver or mercury. If the earth's crust is estimated to have a mass of 8.50×10^{20} kg, what range of mass is thought to be uranium in the crust?
- 12. Chromium is thought to be an ultratrace element, with about 8.9 ng present in a human body. If the average body mass is 75.0 kg, what is the concentration of chromium in the body in pptr?
- 13. What mass of 3.00% H₂O₂ solution is needed to produce 35.7 g of O₂(g) at 295 K at 1.05 atm pressure?

 $2\text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\ell) + \text{O}_2(g)$

14. What volume of pool water is needed to generate 1.000 L of Cl₂(g) at standard temperature and pressure if the pool contains 4.0 ppm HOCl and the water is slightly acidic? The chemical reaction is as follows:

 $HOCl(aq) + HCl(aq) \rightarrow H2O(\ell) + Cl_2(g)$

Assume the pool water has a density of 1.00 g/mL.

- 15. A 0.500 *m* solution of MgCl₂ has a freezing point of -2.60° C. What is the true van't Hoff factor of this ionic compound? Why is it less than the ideal value?
- 16. The osmotic pressure of a 0.050 M LiCl solution at 25.0°C is 2.26 atm. What is the true van't Hoff factor of this ionic compound? Why is it less than the ideal value?
- 17. Order these solutions in order of increasing boiling point, assuming an ideal van't Hoff factor for each: 0.10 *m* C₆H₁₂O₆, 0.06 *m* NaCl, 0.4 *m* Au(NO₃)₃, and 0.4 *m* Al₂(SO₄)₃.
- Order these solutions in order of decreasing osmotic pressure, assuming an ideal van't Hoff factor: 0.1 M HCl, 0.1 M CaCl₂, 0.05 M MgBr₂, and 0.07 M Ga(C₂H₃O₂)₃

ANSWERS

3. Saturated means all the possible solute that can dissolve is dissolved, whereas concentrated implies that a lot of solute is dissolved.

4.

^{1.} solvent: ethyl alcohol; solute: water

^{2.}



5. 4.58 g6. 7. 6.00 L8. 9. 1.92 mg10. 11. $1.7 \times 10^{15} \text{ to } 3.4 \times 10^{15} \text{ kg}$ 12. 13. 2,530 g14. 15. 2.80; it is less than 3 because not all ions behave as independent particles. 16. 17. $0.10 \text{ m C}_{6H_{12}O_{6}} < 0.06 \text{ m NaCl} < 0.4 \text{ m Au}(NO_{3})_{3} < 0.4 \text{ m Al}_{2}(SO_{4})_{3}$



10.9: SOLUTIONS (SUMMARY)

To ensure that you understand the material in this chapter, you should review the meanings of the bold terms in the following summary and ask yourself how they relate to the topics in the chapter.

A **solution** is a homogeneous mixture. The major component is the **solvent**, while the minor component is the **solute**. Solutions can have any phase; for example, an **alloy** is a solid solution. Solutes are **soluble** or **insoluble**, meaning they dissolve or do not dissolve in a particular solvent. The terms **miscible** and **immiscible**, instead of soluble and insoluble, are used for liquid solutes and solvents. The statement *like dissolves like* is a useful guide to predicting whether a solute will dissolve in a given solvent.

The amount of solute in a solution is represented by the **concentration** of the solution. The maximum amount of solute that will dissolve in a given amount of solvent is called the **solubility** of the solute. Such solutions are **saturated**. Solutions that have less than the maximum amount are **unsaturated**. Most solutions are unsaturated, and there are various ways of stating their concentrations. **Mass/mass percent**, **volume/volume percent**, and **mass/volume percent** indicate the percentage of the overall solution that is solute. **Parts per million (ppm)** and **parts per billion (ppb)** are used to describe very small concentrations of a solute. **Molarity**, defined as the number of moles of solute per liter of solution, is a common concentration unit in the chemistry laboratory. **Equivalents** express concentrations in terms of moles of charge on ions. When a solution is diluted, we use the fact that the amount of solute remains constant to be able to determine the volume or concentration of the final diluted solution.

Dissolving occurs by **solvation**, the process in which particles of a solvent surround the individual particles of a solute, separating them to make a solution. For water solutions, the word **hydration** is used. If the solute is molecular, it dissolves into individual molecules. If the solute is ionic, the individual ions separate from each other, forming a solution that conducts electricity. Such solutions are called **electrolytes**. If the dissociation of ions is complete, the solution is a **strong electrolyte**. If the dissociation is only partial, the solution is a **weak electrolyte**. Solutions of molecules do not conduct electricity and are called **nonelectrolytes**.

Solutions have properties that differ from those of the pure solvent. Some of these are **colligative** properties, which are due to the number of solute particles dissolved, not the chemical identity of the solute. Colligative properties include **vapor pressure depression**, **boiling point elevation**, **freezing point depression**, and **osmotic pressure**. Osmotic pressure is particularly important in biological systems. It is caused by **osmosis**, the passage of solvents through certain membranes like cell walls. The **osmolarity** of a solution is the product of a solution's molarity and the number of particles a solute separates into when it dissolves. Osmosis can be reversed by the application of pressure; this reverse osmosis is used to make fresh water from saltwater in some parts of the world. Because of osmosis, red blood cells placed in hypotonic or hypertonic solutions lose function through either hemolysis or crenation. If they are placed in isotonic solutions, however, the cells are unaffected because osmotic pressure is equal on either side of the cell membrane.



11: CHEMICAL EQUILIBRIUM

So far in this text, when we present a chemical reaction, we have implicitly assumed that the reaction goes to completion. Indeed, our stoichiometric calculations were based on this; when we asked how much of a product is produced when so much of a reactant reacts, we are assuming that all of a reactant reacts. However, this is usually not the case; many reactions do not go to completion, and many chemists have to deal with that. In this chapter, we will study this phenomenon and see ways in whi

11.1: PRELUDE TO CHEMICAL EQUILIBRIUM

More chemical reactions come to an equilibrium. The actual position of the equilibrium-whether it favors the reactants or the productsis characteristic of a chemical reaction; it is difficult to see just by looking at the balanced chemical equation. But chemistry has tools to help you understand the equilibrium of chemical reactions-the focus of our study in this chapter.

11.2: CHEMICAL EQUILIBRIUM

Chemical reactions eventually reach equilibrium, a point at which forward and reverse reactions balance each other's progress. Chemical equilibria are dynamic: the chemical reactions are always occurring; they just cancel each other's progress.

11.3: THE EQUILIBRIUM CONSTANT

Every chemical equilibrium can be characterized by an equilibrium constant, known as Keq. The Keq and KP expressions are formulated as amounts of products divided by amounts of reactants; each amount (either a concentration or a pressure) is raised to the power of its coefficient in the balanced chemical equation. Solids and liquids do not appear in the expression for the equilibrium constant.

11.4: SHIFTING EQUILIBRIA - LE CHATELIER'S PRINCIPLE

Le Chatelier's principle addresses how an equilibrium shifts when the conditions of an equilibrium are changed. The direction of shift can be predicted for changes in concentrations, temperature, or pressure. Catalysts do not affect the position of an equilibrium; they help reactions achieve equilibrium faster.

11.5: CALCULATING EQUILIBRIUM CONSTANT VALUES

11.6: SOME SPECIAL TYPES OF EQUILIBRIA

In one sense, all chemical equilibria are treated the same. However, there are several classes of reactions that are noteworthy because of either the identities of the reactants and products or the form of the K expression.

11.E: CHEMICAL EQUILIBRIUM (EXERCISES)



11.1: PRELUDE TO CHEMICAL EQUILIBRIUM

Imagine you are stranded in a rowboat in the middle of the ocean. Suddenly, your boat springs a small leak, and you need to bail out water. You grab a bucket and begin to bail. After a few minutes, your efforts against the leak keep the water to only about half an inch, but any further bailing doesn't change the water level; the leak brings in as much water as you bail out.

You are at a dynamics *equilibrium*. Two opposing processes have reached the same speed, and there is no more overall change in the process.

Chemical reactions are like that as well. Most of them come to an equilibrium. The actual position of the equilibrium-whether it favors the reactants or the products-is characteristic of a chemical reaction; it is difficult to see just by looking at the balanced chemical equation. But chemistry has tools to help you understand the equilibrium of chemical reactions-the focus of our study in this chapter.



11.2: CHEMICAL EQUILIBRIUM

LEARNING OBJECTIVES

- Define *chemical equilibrium*.
- Recognize chemical equilibrium as a dynamic process.

Consider the following reaction occurring in a closed container (so that no material can go in or out):

 $H_2 + I_2 \rightarrow 2HI$

This is simply the reaction between elemental hydrogen and elemental iodine to make hydrogen iodide. The way the equation is written, we are led to believe that the reaction goes to completion, that all the H₂ and the I₂ react to make HI.

However, this is not the case. The reverse chemical reaction is also taking place:

 $\rm 2HI \, \rightarrow \, H2 + I2$

It acts to undo what the first reaction does. Eventually, the reverse reaction proceeds so quickly that it matches the speed of the forward reaction. When that happens, any continued overall reaction stops: the reaction has reached **chemical equilibrium** (sometimes just spoken as *equilibrium*; plural *equilibria*), the point at which the forward and reverse processes balance each other's progress.

Because two opposing processes are occurring at once, it is conventional to represent an equilibrium using a double arrow, like this:

$$H_2 + I_2 \rightleftharpoons 2HI$$
 (11.2.1)

The double arrow implies that the reaction is going in both directions. Note that the reaction must still be balanced.

Example 11.2.1:

Write the equilibrium equation that exists between calcium carbonate as a reactant and calcium oxide and carbon dioxide as products.

Solution

As this is an equilibrium situation, a double arrow is used. The equilibrium equation is written as follows:

$$CaCO_3 + \rightleftharpoons CaO + CO_2$$
 (11.2.2)

Exercise 11.2.1

Write the equilibrium equation between elemental hydrogen and elemental oxygen as reactants and water as the product.

Answer:

$$2H_2 + O_2 + \rightleftharpoons 2H_2O \tag{11.2.3}$$

One thing to note about equilibrium is that the reactions do not stop; both the forward reaction and the reverse reaction continue to occur. They both occur at the same rate, so any overall change by one reaction is cancelled by the reverse reaction. We say that chemical equilibrium is *dynamic*, rather than static. Also, because both reactions are occurring simultaneously, the equilibrium can be written backward. For example, representing an equilibrium as

$$H_2 + I_2 \rightleftharpoons 2HI \tag{11.2.4}$$

is the same thing as representing the same equilibrium as

$$2HI \rightleftharpoons H_2 + I_2 \tag{11.2.5}$$

The reaction must be at equilibrium for this to be the case, however.

KEY TAKEAWAYS

- Chemical reactions eventually reach equilibrium, a point at which forward and reverse reactions balance each other's progress.
- Chemical equilibria are dynamic: the chemical reactions are always occurring; they just cancel each other's progress.

Exercise 11.2.1

1. Define *chemical equilibrium*. Give an example.

2. Explain what is meant when it is said that chemical equilibrium is dynamic.



- 3. Write the equilibrium equation between elemental hydrogen and elemental chlorine as reactants and hydrochloric acid as the product.
- 4. Write the equilibrium equation between iron(III) sulfate as the reactant and iron(III) oxide and sulfur trioxide as the products.
- 5. Graphite and diamond are two forms of elemental carbon. Write the equilibrium equation between these two forms in two different ways.
- 6. At 1,500 K, iodine molecules break apart into iodine atoms. Write the equilibrium equation between these two species in two different ways.

Answers

3.

1. the situation when the forward and reverse chemical reactions occur, leading to no additional net change in the reaction position

$H_{2} \perp I_{2} \rightarrow 2HI$	(11 2 6)
$\Pi_2 + I_2 = 2\Pi I$	(11.2.0)

answers will vary

$$H_2 + Cl_2 \rightleftharpoons 2HCl \tag{11.2.7}$$

4.
5.
$$C(gra) \rightleftharpoons C(dia); C(dia) \rightleftharpoons C(gra)$$
 (11.2.8)



11.3: THE EQUILIBRIUM CONSTANT

LEARNING OBJECTIVES

- Explain the importance of the equilibrium constant.
- Construct an equilibrium constant expression for a chemical reaction.

In the mid 1860s, Norwegian scientists C. M. Guldberg and P. Waage noted a peculiar relationship between the amounts of reactants and products in an equilibrium. No matter how many reactants they started with, a certain ratio of reactants and products was achieved at equilibrium. Today, we call this observation the **law of mass action**. It relates the amounts of reactants and products at equilibrium for a chemical reaction. For a general chemical reaction occurring in solution,

$$aA + bB \rightleftharpoons cC + dD$$

the **equilibrium constant**, also known as K_{eq} , is defined by the following expression:

$$K_{eq} = rac{[C]^c [D]^d}{[A]^a [B]^b}$$

where [A] is the molar concentration of species A at equilibrium, and so forth. The coefficients *a*, *b*, *c*, and *d* in the chemical equation become exponents in the expression for K_{eq} . The K_{eq} is a characteristic numerical value for a given reaction at a given temperature; that is, each chemical reaction has its own characteristic K_{eq} . The concentration of each reactant and product in a chemical reaction at equilibrium is *related*; the concentrations cannot be random values, but they depend on each other. The numerator of the expression for K_{eq} has the concentrations of every product (however many products there are), while the denominator of the expression for K_{eq} has the concentrations of every reactant, leading to the common *products over reactants* definition for the K_{eq} .

Let us consider a simple example. Suppose we have this equilibrium:

$$A \rightleftharpoons B$$

There is one reactant, one product, and the coefficients on each are just 1 (assumed, not written). The K_{eq} expression for this equilibrium is

$$K_{eq} = rac{[B]}{[A]}$$

(Exponents of 1 on each concentration are understood.) Suppose the numerical value of K_{eq} for this chemical reaction is 2.0. If [B] = 4.0 M, then [A] must equal 2.0 M so that the value of the fraction equals 2.0:

$$K_{eq} = rac{[B]}{[A]} = rac{4.0}{2.0} = 2.0$$

By convention, the units are understood to be M and are omitted from the K_{eq} expression. Suppose [B] were 6.0 M. For the K_{eq} value to remain constant (it is, after all, called the equilibrium *constant*), then [A] would have to be 3.0 M at equilibrium:

$$K_{eq} = rac{[B]}{[A]} = rac{6.0}{3.0} = 2.0$$

If [A] were *not* equal to 3.0 M, the reaction would not be at equilibrium, and a net reaction would occur until that ratio was indeed 2.0. At that point, the reaction is at equilibrium, and any net change would cease. (Recall, however, that the forward and reverse reactions do not stop because chemical equilibrium is dynamic.)

The issue is the same with more complex expressions for the K_{eq} ; only the mathematics becomes more complex. Generally speaking, given a value for the K_{eq} and all but one concentration at equilibrium, the missing concentration can be calculated.

Example
$$11.3.1$$

Given the following reaction:

 $H_2 + I_2 \rightleftharpoons 2HI$

If the equilibrium [HI] is 0.75 M and the equilibrium [H₂] is 0.20 M, what is the equilibrium [I₂] if the K_{eq} is 0.40? **Solution**



We start by writing the Keq expression. Using the *products over reactants* approach, the Keq expression is as follows:

$$K_{eq} = rac{[HI]^2}{[H_2][I_2]}$$

Note that [HI] is squared because of the coefficient 2 in the balanced chemical equation. Substituting for the equilibrium [H₂] and [HI] and for the given value of K_{eq} :

$$0.40 = rac{(0.75)^2}{(0.20)[I_2]}$$

To solve for [I₂], we have to do some algebraic rearrangement: divide the 0.40 into both sides of the equation and multiply both sides of the equation by [I₂]. This brings [I₂] into the numerator of the left side and the 0.40 into the denominator of the right side:

$$[I_2] = \frac{(0.75)^2}{(0.20)(0.40)}$$

Solving,

[I₂] = 7.0 M

The concentration unit is assumed to be molarity. This value for [I2] can be easily verified by substituting 0.75, 0.20, and 7.0 into the expression for K_{eq} and evaluating: you should get 0.40, the numerical value of K_{eq} (and you do).

Exercise 11.3.1

Given the following reaction:

$$H_2 + I_2 \rightleftharpoons 2HI$$

If the equilibrium [HI] is 0.060 M and the equilibrium [I2] is 0.90 M, what is the equilibrium [H2] if the Keq is 0.40?

Answer:

0.010 M

In some types of equilibrium problems, square roots, cube roots, or even higher roots need to be analyzed to determine a final answer. Make sure you know how to perform such operations on your calculator; if you do not know, ask your instructor for assistance.

Example 11.3.2

The following reaction is at equilibrium:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

The K_{eq} at a particular temperature is 13.7. If the equilibrium [N2] is 1.88 M and the equilibrium [NH3] is 6.62 M, what is the equilibrium [H2]?

Solution

We start by writing the K_{eq} expression from the balanced chemical equation:

$$K_{eq} = rac{[NH_3]^2}{[N_2][H_2]^3}$$

Substituting for the known equilibrium concentrations and the K_{eq} , this becomes

$$13.7 = rac{(6.62)^2}{(1.88)[H_2]^3}$$

Rearranging algebraically and then evaluating the numerical expression, we get

$$[H_2]^3 = rac{(6.62)^2}{(1.88)(13.7)} = 1.7015219754$$

To solve for $[H_2]$, we need to take the cube root of the equation. Performing this operation, we get $[H_2] = 1.19 \text{ M}$



You should verify that this is correct using your own calculator to confirm that you know how to do a cube root correctly.

EXERCISE 11.3.2

The following reaction is at equilibrium:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

The K_{eq} at a particular temperature is 13.7. If the equilibrium [N₂] is 0.055 M and the equilibrium [H₂] is 1.62 M, what is the equilibrium [NH₃]?

Answer:

1.79 M

The K_{eq} was defined earlier in terms of concentrations. For gas-phase reactions, the K_{eq} can also be defined in terms of the partial pressures of the reactants and products, P_i . For the gas-phase reaction

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$

the pressure-based equilibrium constant, *K*p, is defined as follows:

$$K_P = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

where P_A is the partial pressure of substance A at equilibrium in atmospheres, and so forth. As with the concentration-based equilibrium constant, the units are omitted when substituting into the expression for K_P .

Example 11.3.3

What is the *K*p for this reaction, given the equilibrium partial pressures of 0.664 atm for NO₂ and 1.09 for N₂O₄?

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

Solution

Write the *K***p** expression for this reaction:

$$K_P = rac{P_{N_2O_4}}{P_{NO_2}^2}$$

Then substitute the equilibrium partial pressures into the expression and evaluate:

$$K_P = rac{(1.09)}{(0.664)^2} = 2.47$$

EXERCISE 11.3.3

What is the *K*p for this reaction, given the equilibrium partial pressures of 0.44 atm for H₂, 0.22 atm for Cl₂, and 2.98 atm for HCl?

$$H_2 + Cl_2 \rightleftharpoons 2HCl$$

Answer:

91.7

There is a simple relationship between *K*_{eq} (based on concentration units) and *K*p (based on pressure units):

$$K_P = K_{eq} \cdot (RT)^{\Delta r}$$

where *R* is the ideal gas law constant (in units of L·atm/mol·K), *T* is the absolute temperature, and Δn is the change in the number of moles of gas in the balanced chemical equation, defined as $n_{\text{gas,prods}} - n_{\text{gas,rcts}}$. Note that this equation implies that if the number of moles of gas are the same in reactants and products, $K_{\text{eq}} = K_{\text{P}}$.

Example 11.3.4

What is the *K***P** at 25°C for this reaction if the K_{eq} is 4.2×10^{-2} ?



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

Solution

Before we use the relevant equation, we need to do two things: convert the temperature to kelvins and determine Δn . Converting the temperature is easy:

T = 25 + 273 = 298 K

To determine the change in the number of moles of gas, take the number of moles of gaseous products and subtract the number of moles of gaseous reactants. There are 2 mol of gas as product and 4 mol of gas of reactant:

$\Delta n = 2 - 4 = -2 \text{ mol}$

Note that Δn is negative. Now we can substitute into our equation, using R = 0.08205 L·atm/mol·K. The units are omitted for clarity:

 $Kp = (4.2 \times 10^{-2})(0.08205)(298)^{-2}$ Solving, $Kp = 7.0 \times 10^{-5}$

Exercise 11.3.4

What is the K_{P} at 25°C for this reaction if the K_{eq} is 98.3?

$$I_2(g) \rightleftharpoons 2I(g)$$

Answer:

 2.40×10^{3}

Finally, we recognize that many chemical reactions involve substances in the solid or liquid phases. For example, a particular chemical reaction is represented as follows:

$$2NaHCO_3(s)
ightarrow Na_2CO_3(s) + CO_2(g) + H_2O(l)$$

This chemical equation includes all three phases of matter. This kind of equilibrium is called a **heterogeneous equilibrium** because there is more than one phase present.

The rule for heterogeneous equilibria is as follows: Do not include the concentrations of pure solids and pure liquids in K_{eq} expressions. Only partial pressures for gas-phase substances or concentrations in solutions are included in the expressions of equilibrium constants. As such, the equilibrium constant expression for this reaction would simply be

$$K_P = P_{CO_2}$$

because the two solids and one liquid would not appear in the expression.

KEY TAKEAWAYS

- Every chemical equilibrium can be characterized by an equilibrium constant, known as *K*eq.
- The *K*_{eq} and *K*p expressions are formulated as amounts of products divided by amounts of reactants; each amount (either a concentration or a pressure) is raised to the power of its coefficient in the balanced chemical equation.
- Solids and liquids do not appear in the expression for the equilibrium constant.

Exercise 11.3.1

1. Define the <i>law of mass action</i> .
2 What is an equilibrium constant for a ch

2. What is an equilibrium constant for a chemical reaction? How is it constructed?3. Write the *K*_{eq} expression for each reaction.

a.
$$H_2+Cl_2\rightleftharpoons 2HCl$$

b. $NO + NO_2 \rightleftharpoons N_2O_3$

4. Write the K_{eq} expression for each reaction.

a.
$$C_2H_5OH + NaI \rightleftharpoons C_2H_5I + NaOH$$

b.
$$PCl_3 + Cl_2 \rightleftharpoons PCl_5$$



5. Write the *K***p** expression for each reaction.

b.

 $2H_2O_2(g)
ightrightarrow 2H_2O(g)+O_2(g)$

6. Write the *K***p** expression for each reaction.

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

b. $CH_4(g) + 4Cl_2(g) \rightleftharpoons CCl_4(g) + 4HCl(g)$

7. The following reaction is at equilibrium:

$$PBr_3 + Br_2 \rightleftharpoons PBr_5$$

 $2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$

The equilibrium [Br2] and [PBr5] are 2.05 M and 0.55 M, respectively. If the K_{eq} is 1.65, what is the equilibrium [PBr3]? 8. The following reaction is at equilibrium:

$$CO + Cl_2 \rightleftharpoons CoCl_2$$

The equilibrium [CO] and [Cl₂] are 0.088 M and 0.103 M, respectively. If the K_{eq} is 0.225, what is the equilibrium [CoCl₂]? 9. The following reaction is at equilibrium:

$$CH_4 + 2Cl_2 \rightleftharpoons CH_2Cl_2 + 2HCl$$

If [CH4] is 0.250 M, [Cl2] is 0.150 M, and [CH₂Cl₂] is 0.175 M at equilibrium, what is [HCl] at equilibrium if the K_{eq} is 2.30? 10. The following reaction is at equilibrium:

$$4HBr + O_2 \rightleftharpoons 2H_2O + 2Br_2$$

If [HBr] is 0.100 M, [O₂] is 0.250 M, and [H₂O] is 0.0500 M at equilibrium, what is [Br₂] at equilibrium if the K_{eq} is 0.770? 11. Write the K_P expression for the following gas-phase reaction:

$$4NO_2(g) + O_2(g) \rightleftharpoons 2N_2O_5(g)$$

12. Write the *K***p** expression for the following gas-phase reaction:

$$CIO(g) + O_3(g) \rightleftharpoons CIO_2(g) + O_2(g)$$

13. What is the equilibrium partial pressure of COBr₂ if the equilibrium partial pressures of CO and Br₂ are 0.666 atm and 0.235 atm and the *K*p for this equilibrium is 4.08?

$$CO(g) + Br_2(g) \rightleftharpoons COBr_2(g)$$

14. What is the equilibrium partial pressure of O₃ if the equilibrium partial pressure of O₂ is 0.0044 atm and *K*p for this equilibrium is 0.00755?

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

15. Calculate the *K*p for this reaction at 298 K if the $K_{eq} = 1.76 \times 10^{-3}$.

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

16. Calculate the *K***p** for this reaction at 310 K if the $K_{eq} = 6.22 \times 10^3$.

$$4NO_2(g) + O_2(g) \rightleftharpoons 2N_2O_5(g)$$

17. Calculate the K_{eq} for this reaction if the $K_{p} = 5.205 \times 10^{-3}$ at 660°C.

$$CO(g) + F_2(g) \rightleftharpoons COF_2(g)$$

18. Calculate the K_{eq} for this reaction if the K_P = 78.3 at 100°C.

$$4HCl(g) + O_2(g) \rightleftharpoons 2H_2O(g) + 2Cl_2(g)$$



19. Write the correct K_{eq} expression for this reaction.

$$NaOh(aq) + HCl(aq) \rightleftharpoons NaCl(aq) + H_2O(l)$$

20. Write the correct K_{eq} expression for this reaction.

$$AgNO_3(aq) + NaCl(aq) \rightleftharpoons AgCl(s) + NaNO_3(aq)$$

21. Write the correct *K***p** expression for this reaction.

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

22. Write the correct *K***p** expression for this reaction.

$$C_2H_2(g) + 2I_2(s) \rightleftharpoons C_2H_2I_4(g)$$

Answers

1. 2	the relationship between the concentrations of reacta	ants and products of a chemical reaction at equilibrium
3.	a.	$K_{eq}=rac{[HCl]^2}{[H_2][Cl_2]}$
	b.	$K_{eq}=rac{[N_2O_3]}{[NO][NO_2]}$

5. a.
$$K_P = rac{P_{H_2O}^2}{P_{H_2}^2 P_{O_2}}$$

b.
$$K_P = rac{P_{H_2O}^2 P_{O_2}}{P_{H_2O_2}^2}$$

~

11.

$$K_P = rac{P_{N_2O_5}^2}{P_{NO_2}^4 P_{O_2}}$$

12. 13. 0.639 atm 14. 15. 7.20×10^{-5} 16. 17. $K_{eq} = 3.98 \times 10^{-1}$ 18. 19.

$$K_{eq} = rac{[NaCl]}{[NaOH][HCl]}$$

20. 21. *K***P** = *P***CO**₂



11.4: SHIFTING EQUILIBRIA - LE CHATELIER'S PRINCIPLE

LEARNING OBJECTIVES

- Define *Le Chatelier's principle*.
- Predict the direction of shift for an equilibrium under stress.

Once equilibrium is established, the reaction is over, right? Not exactly. An experimenter has some ability to affect the equilibrium.

Chemical equilibria can be shifted by changing the conditions that the system experiences. We say that we "stress" the equilibrium. When we stress the equilibrium, the chemical reaction is no longer at equilibrium, and the reaction starts to move back toward equilibrium in such a way as to decrease the stress. The formal statement is called **Le Chatelier's principle**: If an equilibrium is stressed, then the reaction shifts to reduce the stress.

There are several ways to stress an equilibrium. One way is to add or remove a product or a reactant in a chemical reaction at equilibrium. When additional reactant is added, the equilibrium shifts to reduce this stress: it makes more product. When additional product is added, the equilibrium shifts to reactants to reduce the stress. If reactant or product is removed, the equilibrium shifts to make more reactant or product, respectively, to make up for the loss.

Example 11.4.1:

Given this reaction at equilibrium:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

(11.4.1)

In which direction-toward reactants or toward products-does the reaction shift if the equilibrium is stressed by each change?

1. H₂ is added.

2. NH3 is added.

3. NH₃ is removed.

Solution

1. If H₂ is added, there is now more reactant, so the reaction will shift toward products to reduce the added H₂.

2. If NH3 is added, there is now more product, so the reaction will shift toward reactants to reduce the added NH3.

3. If NH3 is removed, there is now less product, so the reaction will shift toward products to replace the product removed.

Exercise 11.4.1

Given this reaction at equilibrium:

$$CO(g) + Br_2(g) \rightleftharpoons COBr_2(g)$$
 (11.4.2)

In which direction-toward reactants or toward products-does the reaction shift if the equilibrium is stressed by each change?

1. Br2 is removed.

2. COBr2 is added.

Answers

1. toward reactants

2. toward reactants

It is worth noting that when reactants or products are added or removed, *the value of the* K_{eq} *does not change*. The chemical reaction simply shifts, in a predictable fashion, to reestablish concentrations so that the K_{eq} expression reverts to the correct value.

How does an equilibrium react to a change in pressure? Pressure changes do not markedly affect the solid or liquid phases. However, pressure strongly impacts the gas phase. Le Chatelier's principle implies that a pressure increase shifts an equilibrium to the side of the reaction with the fewer number of moles of gas, while a pressure decrease shifts an equilibrium to the side of the reaction with the greater number of moles of gas. If the number of moles of gas is the same on both sides of the reaction, pressure has no effect.

Example 11.4.2:		
What is the effect on this equilibrium if pressure	e is increased?	
	$N_2(g) + 3H_2(g) ightrightarrow 2NH_3(g)$	(11.4.3)
Solution		



According to Le Chatelier's principle, if pressure is increased, then the equilibrium shifts to the side with the fewer number of moles of gas. This particular reaction shows a total of 4 mol of gas as reactants and 2 mol of gas as products, so the reaction shifts toward the products side.

Exercise 11.4.2

What is the effect on this equilibrium if pressure is decreased?

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

(11.4.4)

Answer:

Reaction shifts toward reactants.

What is the effect of temperature changes on an equilibrium? It depends on whether the reaction is endothermic or exothermic. Recall that *endothermic* means that energy is absorbed by a chemical reaction, while *exothermic* means that energy is given off by the reaction. As such, energy can be thought of as a reactant or a product, respectively, of a reaction:

endothermic: energy + reactants \rightarrow products exothermic: reactants \rightarrow products + energy

Because temperature is a measure of the energy of the system, increasing temperature can be thought of as adding energy. The reaction will react as if a reactant or a product is being added and will act accordingly by shifting to the other side. For example, if the temperature is increased for an endothermic reaction, essentially a reactant is being added, so the equilibrium shifts toward products. Decreasing the temperature is equivalent to decreasing a reactant (for endothermic reactions) or a product (for exothermic reactions), and the equilibrium shifts accordingly.

Example 11.4.3:

Predict the effect of increasing the temperature on this equilibrium.

$$PCl_3 + Cl_2 \rightleftharpoons PCl_5 + 60kJ \tag{11.4.5}$$

Solution

Because energy is listed as a product, it is being produced, so the reaction is exothermic. If the temperature is increasing, a product is being added to the equilibrium, so the equilibrium shifts to minimize the addition of extra product: it shifts back toward reactants.

Exercise 11.4.3

Predict the effect of decreasing the temperature on this equilibrium.

$$N_2O_4 + 57kJ \rightleftharpoons 2NO_2 \tag{11.4.6}$$

Answer:

Equilibrium shifts toward reactants.

In the case of temperature, the value of the equilibrium has changed because the K_{eq} is dependent on temperature. That is why equilibria shift with changes in temperature.

A **catalyst** is a substance that increases the speed of a reaction. Overall, a catalyst is not a reactant and is not used up, but it still affects how fast a reaction proceeds. However, a catalyst does not affect the extent or position of a reaction at equilibrium. It helps a reaction achieve equilibrium faster.

CHEMISTRY IS EVERYWHERE: EQUILIBRIA IN THE GARDEN

Hydrangeas are common flowering plants around the world. Although many hydrangeas are white, there is one common species (*Hydrangea macrophylla*) whose flowers can be either red or blue, as shown in the accompanying figure. How is it that a plant can have different colored flowers like this?





Fig. 13.4.1 Garden Equilibria © Thinkstock This species of hydrangea has flowers that can be either red or blue. Why the color difference?

Interestingly, the color of the flowers is due to the acidity of the soil that the hydrangea is planted in. An astute gardener can adjust the pH of the soil and actually change the color of the flowers. However, it is not the H^+ or OH^- ions that affect the color of the flowers. Rather, it is the presence of aluminum that causes the color change.

The solubility of aluminum in soil-and thus the ability of plants to absorb it-is dependent on the acidity of the soil. If the soil is relatively acidic, the aluminum is more soluble, and plants can absorb it more easily. Under these conditions, hydrangea flowers are blue as Al ions interact with anthocyanin pigments in the plant. In more basic soils, aluminum is less soluble, and under these conditions the hydrangea flowers are red. Gardeners who change the pH of their soils to change the color of their hydrangea flowers are therefore employing Le Chatelier's principle: the amount of acid in the soil changes the equilibrium of aluminum solubility, which in turn affects the color of the flowers.

KEY TAKEAWAYS

- Le Chatelier's principle addresses how an equilibrium shifts when the conditions of an equilibrium are changed.
- The direction of shift can be predicted for changes in concentrations, temperature, or pressure.
- Catalysts do not affect the position of an equilibrium; they help reactions achieve equilibrium faster.

Exercise 11.4.1

- 1. Define *Le Chatelier's principle*.
- 2. What is meant by a stress? What are some of the ways an equilibrium can be stressed?
- 3. Given this equilibrium, predict the direction of shift for each stress.

$$H_2(g) + I_2(s) + 53kJ \rightleftharpoons 2HI(g) \tag{11.4.7}$$

a. decreased temperature

b. increased pressure

c. removal of HI

4. Given this equilibrium, predict the direction of shift for each stress.

$$H_2(g) + F_2(g) \rightleftharpoons 2HF(g) + 546kJ \tag{11.4.8}$$

a. increased temperature

b. addition of H₂

c. decreased pressure

5. Given this equilibrium, predict the direction of shift for each stress.

11.4.3



CHEMISTRY

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) + 196kJ \tag{11.4.9}$$

a. removal of SO3

b. addition of O₂

c. decreased temperature

6. Given this equilibrium, predict the direction of shift for each stress.

$$CO_2(g) + C(s) + 171kJ \rightleftharpoons 2CO(g) \tag{11.4.10}$$

a. addition of CO

b. increased pressure

c. addition of a catalyst

7. The synthesis of NH3 uses this chemical reaction.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 92kJ$$
 (11.4.11)

Identify three stresses that can be imposed on the equilibrium to maximize the amount of NH3. 8. The synthesis of CaCO3 uses this chemical reaction.

$$CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s) + 180kJ \tag{11.4.12}$$

Identify three stresses that can be imposed on the equilibrium to maximize the amount of CaCO3.

Answers

1. When an equilibrium is stressed, the equilibrium shifts to minimize that stress.

2.

- 3. a. toward reactants
 - b. toward reactants
 - c. toward products

4.

5. a. toward products b. toward products c. toward products

6.

7. increased pressure, decreased temperature, removal of NH3



11.5: CALCULATING EQUILIBRIUM CONSTANT VALUES

LEARNING OBJECTIVE

• Calculate equilibrium concentrations from the values of the initial amounts and the *K*_{eq}.

There are some circumstances in which, given some initial amounts and the K_{eq} , you will have to determine the concentrations of all species when equilibrium is achieved. Such calculations are not difficult to do, especially if a consistent approach is applied. We will consider such an approach here.

Suppose we have this simple equilibrium. Its associated K_{eq} is 4.0, and the initial concentration of each reactant is 1.0 M:

$$\begin{array}{cc} H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g) & K_{eq} = 4.0 \\ & & 1.0M & 1.0M \end{array}$$
(11.5.1)

Because we have concentrations for the reactants but not the products, we presume that the reaction will proceed in the forward direction to make products. But by how much will it proceed? We do not know, so let us assign it a variable. Let us assume that *x* M H₂ reacts as the reaction goes to equilibrium. This means that at equilibrium, we have (1.0 - x) M H₂ left over.

According to the balanced chemical equation, H₂ and Cl₂ react in a 1:1 ratio. How do we know that? The coefficients of these two species in the balanced chemical equation are 1 (unwritten, of course). This means that if x M H₂ reacts, x M Cl₂ reacts as well. If we start with 1.0 M Cl₂ at the beginning and we react x M, we have (1.0 - x) M Cl₂ left at equilibrium.

How much HCl is made? We start with zero, but we also see that 2 mol of HCl are made for every mole of H₂ (or Cl₂) that reacts (from the coefficients in the balanced chemical equation), so if we lose x M H₂, we gain 2x M HCl. So now we know the equilibrium concentrations of our species:

$$\begin{array}{l} H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g) \\ (1.0-x)M & (1.0-x)M & 2xM \end{array} \tag{11.5.2}$$

We can substitute these concentrations into the K_{eq} expression for this reaction and combine it with the known value of K_{eq} :

$$K_{eq} = \frac{[HCl]^2}{[H_2][Cl_2]} = \frac{(2x)^2}{(1-x)(1-x)} = 4.0$$
(11.5.3)

This is an equation in one variable, so we should be able to solve for the unknown value. This expression may look formidable, but first we can simplify the denominator and write it as a perfect square as well:

$$\frac{(2x)^2}{(1-x)^2} = 4.0\tag{11.5.4}$$

The fraction is a perfect square, as is the 4.0 on the right. So we can take the square root of both sides:

$$\frac{(2x)}{(1-x)} = 2.0\tag{11.5.5}$$

Now we rearrange and solve (be sure you can follow each step):

$$2x = 2.0 - 2.0x$$
(11.5.6)

$$4x = 2.0
x = 0.50$$

Now we have to remind ourselves what *x* is-the amount of H₂ and Cl₂ that reacted-and 2*x* is the equilibrium [HCl]. To determine the equilibrium concentrations, we need to go back and evaluate the expressions 1 - x and 2x to get the equilibrium concentrations of our species:

$$1.0 - x = 1.0 - 0.50 = 0.50 \text{ M} = [\text{H}_2] = [\text{Cl}_2]2x = 2(0.50) = 1.0 \text{ M} = [\text{HCl}]$$

The units are assumed to be molarity. To check, we simply substitute these concentrations and verify that we get the numerical value of the K_{eq} , in this case 4.0:

$$\frac{(1.0)^2}{(0.50)(0.50)} = 4.0\tag{11.5.7}$$

We formalize this process by introducing the ICE chart, where ICE stands for initial, change, and equilibrium. The initial values go in the first row of the chart. The change values, usually algebraic expressions because we do not yet know their exact numerical values,



go in the next row. However, the change values *must* be in the proper stoichiometric ratio as indicated by the balanced chemical equation. Finally, the equilibrium expressions in the last row are a combination of the initial value and the change value for each species. The expressions in the equilibrium row are substituted into the K_{eq} expression, which yields an algebraic equation that we try to solve.

The ICE chart for the above example would look like this:

	H2(g) +	- Cl2(g)	⇄" id="MathJax-Element-85-Frame" role="presentation" style="position:relative;" tabindex="0">	2HCl(g)	<i>K</i> eq = 4.0
Ι	1.0	1.0		0	
С	-x	-x		+2 <i>x</i>	
Е	1.0 <i>- x</i>	1.0 <i>- x</i>		+2x	

Substituting the last row into the expression for the K_{eq} yields

$$K_{eq} = \frac{[HCl]^2}{[H_2][Cl_2]} = \frac{(2x)^2}{(1-x)(1-x)} = 4.0$$
(11.5.8)

which, of course, is the same expression we have already solved and yields the same answers for the equilibrium concentrations. The ICE chart is a more formalized way to do these types of problems. The + sign is included explicitly in the change row of the ICE chart to avoid any confusion.

Sometimes when an ICE chart is set up and the K_{eq} expression is constructed, a more complex algebraic equation will result. One of the more common equations has an x^2 term in it and is called a *quadratic equation*. There will be two values possible for the unknown x, and for a quadratic equation with the general formula $ax^2 + bx + c = 0$ (where a, b, and c are the *coefficients* of the quadratic equation), the two possible values are as follows:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$
(11.5.9)

One value of x is the + sign used in the numerator, and the other value of x is the – sign used in the numerator. In this case, one value of x typically makes no sense as an answer and can be discarded as physically impossible, leaving only one possible value and the resulting set of concentrations. Example 9 illustrates this.

Set	up an IC	E chart and solve for the equilibrium concentrations in this chemical reaction.			
		$COI_{2}(g) \rightleftharpoons CO(g) + I_{2}(g) \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \$	(11.	5.10)
Sol	ution				
The	e ICE cha	rt is set up like this. First, the initial values:			
	COI2(g)	⇄" id="MathJax-Element-89-Frame" role="presentation" style="position:relative;" tabindex="0">	CO(g)	+	I2(g)
Ι	0.55		0		0
С					
Е					
Son for	ne of the each CO	COI2 will be lost, but how much? We do not know, so we represent it by the variable x . So x M COI I2 that is lost, x M CO and x M I2 will be produced. These expressions go into the change row:	2 will be	lo	st, and
	COI2(g)		CO(g)	+	I2(g)
Ι	0.55		0		0
C	-x		$+\chi$		$+\chi$
At e	equilibriu	um, the resulting concentrations will be a combination of the initial amount and the changes:			
	COI2(g)	⇄" id="MathJax-Element-91-Frame" role="presentation" style="position:relative;" tabindex="0">	CO(g)	+	I <u>2(g</u>)
Ι	0.55		0		0
С	-x		$+\chi$		$+\chi$
E	0.55 – <i>x</i>		+x		+χ
The	e expressi	ions in the equilibrium row go into the K _{eq} expression:			



We rearrange this into a quadratic equation that equals 0:

 $0.000484 - 0.00088x = x^2x^2 + 0.00088x - 0.000484 = 0$

Now we use the quadratic equation to solve for the two possible values of *x*:

$$x = \frac{-0.00088 \pm \sqrt{(0.00088)^2 - 4(1)(-0.000484)}}{2(1)}$$
(11.5.12)

Evaluate for both signs in the numerator-first the + sign and then the – sign:

x = 0.0216 or x = -0.0224

Because *x* is the final concentration of both CO and I₂, it cannot be negative, so we discount the second numerical answer as impossible. Thus x = 0.0216.

Going back to determine the final concentrations using the expressions in the E row of our ICE chart, we have

 $[COI_2] = 0.55 - x = 0.55 - 0.0216 = 0.53 M[CO] = x = 0.0216 M[I_2] = x = 0.0216 M$

You can verify that these numbers are correct by substituting them into the K_{eq} expression and evaluating and comparing to the known K_{eq} value.

Exercise 11.5.1

Set up an ICE chart and solve for the equilibrium concentrations in this chemical reaction.

$$N_2 H_2(g) \rightleftharpoons N_2(g) + H_2(g) \qquad K_{eq} = 0.052 \tag{11.5.13}$$

Answer

The completed ICE chart is as follows:

	N2H2(g)	₽" id="MathJax-Element-95-Frame" role="presentation" style="position:relative;" tabindex="0">	N2(g)	+ H2(g)
Ι	0.075		0	0
С	-x		$+\chi$	$+\chi$
Е	0.075 <i>- x</i>		$+\chi$	$+\chi$

Solving for *x* gives the equilibrium concentrations as $[N_2H_2] = 0.033$ M; $[N_2] = 0.042$ M; and $[H_2] = 0.042$ M

KEY TAKEAWAY

• An ICE chart is a convenient way to determine equilibrium concentrations from starting amounts.

Exercise 11.5.1

- 1. Describe the three parts of an ICE chart.
- 2. What is the relationship between the equilibrium row in an ICE chart and the other two rows?
- 3. Set up (but do not solve) an ICE chart for this reaction, given the initial conditions.

$$3O_2(g) \rightleftharpoons 2O_3(g) = 0.075M$$
 (11.5.14)

4. Set up (but do not solve) an ICE chart for this reaction, given the initial conditions.

$$CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(g)$$
(11.5.15)

5. Given that pure solids and liquids do not appear in K_{eq} expressions, set up the ICE chart for this reaction, given the initial conditions.

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

$$(11.5.16)$$

6. Given that pure solids and liquids do not appear in K_{eq} expressions, set up the ICE chart for this reaction, given the initial conditions.

$$N_2 H_4(l) + O_2(g) \rightleftharpoons N_2(g) + 2H_2 O(l)$$
(11.5.17)

7. Determine the equilibrium concentrations for this chemical reaction with the given K_{eq} .



$$\begin{array}{ll} HCN(g) \rightleftharpoons HCN(g) & K_{eq} = 4.50 \end{array} \tag{11.5.18}$$

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8. Determine the equilibrium concentrations for this chemical reaction with the given K_{eq} .

$$IF_{3}(g) + F_{2}(g) \rightleftharpoons IF_{5}(g) \qquad K_{eq} = 7.59$$
(11.5.19)

9. Determine the equilibrium concentrations for this chemical reaction with the given K_{eq} .

$$N_2O_3(g) \rightleftharpoons NO(g) + NO_2(g) \qquad K_{eq} = 2.50 \tag{11.5.20}$$

10. Determine the equilibrium concentrations for this chemical reaction with the given K_{eq} .

$$\begin{array}{c} CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) \quad K_{eq} = 16.0 \\ _{0.750M} \quad _{0.750M} \quad _{0.750M} \end{array} \tag{11.5.21}$$

11. Determine the equilibrium concentrations for this chemical reaction with the given K_{eq} .

$$\begin{array}{ll} H_2S(g) \rightleftharpoons H_2(g) + S(s) & K_{eq} = 0.055 \\ & 0.882M \end{array} \tag{11.5.22}$$

12. Determine the equilibrium concentrations for this chemical reaction with the given K_{eq} .

$$2AgCl(s) + F_2(g) \rightleftharpoons 2AgF(s) + Cl_2(g) \qquad K_{eq} = 1.2 \times 10^2$$
(11.5.23)

Answers

1. I = initial concentrations; C = change in concentrations; E = equilibrium concentrations

2.											
3.		302		æ" id="MathJax-Element-106-Frame" role="presentation" style="position:relative;" tabindex="0">		203					
	Ι	0.075				0					
	С	-3x				+2x					
	Е	0.075 - 3x				+2x					
4.											
5.		CH4 +	202	⇄" id="MathJax-Element-107-Frame" role="presentation" style="position:relative;" tabindex="0">	CO2 +	2H 2 O					
	Ι	0.0060	0.055		0	0					
	С	-x	-2x		$+\chi$	-					
	Е	0.0060 – <i>x</i>	0.055 - 2x		$+\chi$	-					
6.											
7. [HCN] = 0.364 M; [HNC] = 1.64 M											
8.											
9. [N2O3] = 0.0017 M; [NO] = [NO2] = 0.0646 M											
10.											
11. [H ₂ S] = 0.836 M; [H ₂] = 0.046 M											



11.6: SOME SPECIAL TYPES OF EQUILIBRIA

LEARNING OBJECTIVE

• Identify several special chemical equilibria and construct their *K*_a expressions.

In one sense, all chemical equilibria are treated the same. However, there are several classes of reactions that are noteworthy because of either the identities of the reactants and products or the form of the K_{eq} expression.

WEAK ACIDS AND BASES

In Chapter 12 - Acids and Bases, we noted how some acids and bases are strong and some are weak. If an acid or base is strong, it is ionized 100% in H₂O. HCl(aq) is an example of a strong acid:

$$HCl(aq) = \stackrel{100\%}{\rightarrow} H^+(aq) + Cl^-(aq)$$
 (11.6.1)

However, if an acid or base is weak, it may dissolve in H₂O but does not ionize completely. This means that there is an equilibrium between the unionized acid or base and the ionized form. HC₂H₃O₂ is an example of a weak acid:

$$HC_2H_3O_2(aq) \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq)$$
 (11.6.2)

HC₂H₃O₂ is soluble in H₂O (in fact, it is the acid in vinegar), so the reactant concentration will appear in the equilibrium constant expression. But not all the molecules separate into ions. This is the case for all weak acids and bases.

An **acid dissociation constant**, K_a , is the equilibrium constant for the dissociation of a weak acid into ions. Note the *a* subscript on the *K*; it implies that the substance is acting as an acid. The larger K_a is, the stronger the acid is. Table 13.6.1 - Acid Dissociation Constants for Some Weak Acids, lists several acid dissociation constants. Keep in mind that they are just equilibrium constants.

Acid	Ka
нс2н302	1.8×10^{-5}
HClO2	1.1×10^{-2}
H2PO4	6.2×10^{-8}
HCN	$_{6.2 \times 10}$ -10
HF	6.3×10^{-4}
HNO2	5.6×10^{-4}
нзро4	$_{7.5 \times 10} - 3$

Table 13.6.1 Acid Dissociation Constants for Some Weak Acids

Note also that the acid dissociation constant refers to *one* H^+ ion coming off the initial reactant. Thus the acid dissociation constant for H3PO4 refers to this equilibrium:

$$H_3PO_4(aq) \rightleftharpoons H^+(aq) + H_2PO_4^-(aq) \quad K_a = 7.5 \times 10^{-3}$$
 (11.6.3)

The H₂PO₄⁻ ion, called the dihydrogen phosphate ion, is also a weak acid with its own acid dissociation constant:

$$H_2 PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq) \qquad K_a = 6.2 \times 10^{-8}$$
 (11.6.4)

Thus for so-called *polyprotic* acids, each H^+ ion comes off in sequence, and each H^+ ion that ionizes does so with its own characteristic K_a .

Example 11.6.1:

Write the equilibrium equation and the *K*_a expression for HSO4[–] acting as a weak acid.

Solution

 $HSO4^{-}$ acts as a weak acid by separating into an H^{+} ion and an $SO4^{2-}$ ion:

$$HSO_4^-(aq) \rightleftharpoons H^+(aq) + SO_4^{2-}(aq) \tag{11.6.5}$$

The K_{a} is written just like any other equilibrium constant, in terms of the concentrations of products divided by concentrations of reactants:

$$K_a = \frac{[H^+][SO_4^2 -]}{[HSO_4^-]} \tag{11.6.6}$$



Exercise 11.6.1

Write the equilibrium equation and the K_a expression for HPO4²⁻ acting as a weak acid.

Answer:

$$HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq) \qquad K_a = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]}$$
(11.6.7)

The K_a is used in equilibrium constant problems just like other equilibrium constants are. However, in some cases, we can simplify the mathematics if the numerical value of the K_a is small, much smaller than the concentration of the acid itself. Example 11 illustrates this.

Example 11.6.1:

What is the pH of a 1.00 M solution of HC2H3O2? The K_a of HC2H3O2 is 1.8×10^{-5} .

Solution

This is a two-part problem. We need to determine $[H^+]$ and then use the definition of pH to determine the pH of the solution. For the first part, we can use an ICE chart:

	HC2H3O2(aq)	₽" id="MathJax-Element-115-Frame" role="presentation" style="position:relative;" tabindex="0">	H ⁺ (g) +	C2H3O2 ⁻ (g)
Ι	1.00		0	0
С	-x		+x	$+\chi$
Е	1.00 - x		$+\chi$	$+\chi$

We now construct the K_a expression, substituting the concentrations from the equilibrium row in the ICE chart:

$$K_a = rac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = rac{(x)(x)}{(1.00-x)} = 1.8 imes 10^{-5}$$
 $(11.6.8)$

Here is where a useful approximation comes in: at 1.8×10^{-5} , HC₂H₃O₂ will not ionize very much, so we expect that the value of *x* will be small. It should be so small that in the denominator of the fraction, the term (1.00 - x) will likely be very close to 1.00. As such, we would introduce very little error if we simply neglect the *x* in that term, making it equal to 1.00:

 $(1.00 - x) \approx 1.00$ for small values of x

This simplifies the mathematical expression we need to solve:

$$\frac{(x)(x)}{1.00} = 1.8 \times 10^{-5} \tag{11.6.9}$$

This is much easier to solve than a more complete quadratic equation. The new equation to solve becomes $x^2 = 1.8 \times 10^{-5}$

Taking the square root of both sides,

$$x = 4.2 \times 10^{-3}$$

Because *x* is the equilibrium concentrations of H^+ and $C_2H_3O_2^-$, we thus have

$$[\text{H}^+] = 4.2 \times 10^{-3} \text{ M}$$

Notice that we are justified by neglecting the *x* in the denominator; it truly is small compared to 1.00. Now we can determine the pH of the solution:

$$pH = -log[H^+] = -log(4.2 \times 10^{-3}) = 2.38$$

Exercise 11.6.1

What is the pH of a 0.500 M solution of HCN? The K_a of HCN is 6.2×10^{-10} .

Answer:

4.75

Weak bases also have dissociation constants, labeled K_b (the *b* subscript stands for base). However, values of K_b are rarely tabulated because there is a simple relationship between the K_b of a base and the K_a of its conjugate acid:

 $K_a \times K_b = 1.0 \times 10^{-14}$



Thus it is simple to calculate the $K_{\rm b}$ of a base from the $K_{\rm a}$ of its conjugate acid.

Example 11.6.1:

What is the value of *K*_b for C₂H₃O₂⁻, which can accept a proton and act as a base?

Solution

To determine the *K*_b for C₂H₃O₂⁻, we need to know the *K*_a of its conjugate acid. The conjugate acid of C₂H₃O₂⁻ is HC₂H₃O₂. The *K*_a for HC₂H₃O₂ is in Table 13.6.1 "Acid Dissociation Constants for Some Weak Acids" and is 1.8×10^{-5} . Using the mathematical relationship between *K*_a and *K*_b:

 $(1.8 \times 10^{-5})K_{\rm b} = 1.0 \times 10^{-14}$

Solving,

$$K_b = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} \tag{11.6.10}$$

Exercise 11.6.1

What is the value of $K_{\rm b}$ for PO₄³⁻, which can accept a proton and act as a base? The $K_{\rm a}$ for HPO₄²⁻ is 2.2 × 10⁻¹³.

Answer:

 4.5×10^{-2}

AUTOIONIZATION OF WATER

In Chapter 12 -Acids and Bases, we introduced the autoionization of water-the idea that water can act as a proton donor and proton acceptor simultaneously. Because water is not a strong acid (Table - 12.5.1 - Strong Acids and Bases), it must be a weak acid, which means that its behavior as an acid must be described as an equilibrium. That equilibrium is as follows:

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$
 (11.6.11)

The equilibrium constant includes $[H_{3O}^+]$ and $[OH^-]$ but not $[H_{2O}(\ell)]$ because it is a pure liquid. Hence the expression *does not have any terms in its denominator*:

$$K = [H_{3O}^{+}][OH^{-}] \equiv K_{W} = 1.0 \times 10^{-14}$$

This is the same K_W that was introduced in Chapter 12 "Acids and Bases" and the same 1.0×10^{-14} that appears in the relationship between the K_a and the K_b of a conjugate acid-base pair. In fact, we can rewrite this relationship as follows:

$K_a \times K_b = K_W$

INSOLUBLE COMPOUNDS

In Chapter4, 4.3: Types of Chemical Reactions - Single and Double Displacement Reactions, on chemical reactions, the concept of soluble and insoluble compounds was introduced. Solubility rules were presented that allow a person to predict whether certain simple ionic compounds will or will not dissolve.

Describing a substance as soluble or insoluble is a bit misleading because virtually all substances are soluble; they are just soluble to different extents. In particular for ionic compounds, what we typically describe as an *insoluble* compound can actually be ever so slightly soluble; an equilibrium is quickly established between the solid compound and the ions that do form in solution. Thus the hypothetical compound MX does in fact dissolve but only very slightly. That means we can write an equilibrium for it:

$$MX(s) \rightleftharpoons M^+(aq) + X^-(aq)$$
 (11.6.12)

The equilibrium constant for a compound normally considered insoluble is called a **solubility product constant** and is labeled K_{sp} (with the subscript *sp*, meaning "solubility product"). Because the reactant is a solid, its concentration does not appear in the K_{sp} expression, so like K_w , expressions for K_{sp} do not have denominators. For example, the chemical equation and the expression for the K_{sp} for AgCl, normally considered insoluble, are as follows:

$$AgCl(s) \rightleftharpoons Ag^{+}(aq) + Cl^{-}(aq) \qquad K_{sp} = [Ag^{+}][Cl^{-}]$$
(11.6.13)

Table 13.6.2 - Solubility Product Constants for Slightly Soluble Ionic Compounds, lists some values of the K_{SP} for slightly soluble ionic compounds.


Compound	K _S p
BaSO4	1.1×10^{-10}
Ca(OH)2	5.0×10^{-6}
Ca3(PO4)2	2.1×10^{-33}
Mg(OH)2	5.6×10^{-12}
HgI2	2.9×10^{-29}
AgCl	1.8×10^{-10}
AgI	8.5×10^{-17}
Ag2SO4	1.5×10^{-5}

Table 13.6.2 Solubility Product Constants for Slightly Soluble Ionic Compounds

Example 11.6.1:

Write the K_{SP} expression for Ca3(PO4)2.

Solution

Recall that when an ionic compound dissolves, it separates into its individual ions. For Ca₃(PO₄)₂, the ionization reaction is as follows:

$$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$$
 (11.6.14)

Hence the K_{sp} expression is $K_{sp} = [Ca^{2+}]^3 [PO4^{3-}]^2$

Exercise 11.6.1

Write the K_{SP} expression Ag₂SO₄.

Answer:

$$K_{\rm Sp} = [{\rm Ag}^+]^2 [{\rm SO4}^{2-}]$$

Equilibrium problems involving the K_{SP} can also be done, and they are usually more straightforward than other equilibrium problems because there is no denominator in the K_{SP} expression. Care must be taken, however, in completing the ICE chart and evaluating exponential expressions.

Example 11.6.1:			
What are [Ag ⁺] and [Cl ⁻] in a saturated solution of AgCl? The K_{sp} of AgCl is 1.8 × 10 ⁻¹⁰ .			
Solution			
The chemical equation for the dissolving of AgCl is			
$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$ (11.6.1)	.5)		
The K _{sp} expression is as follows:			
$K_{\rm Sp} = [{\rm Ag}^+][{\rm Cl}^-]$			
So the ICE chart for the equilibrium is as follows:			
AgCl(s) #" id="MathJax-Element-124-Frame" role="presentation" style="position:relative;" tabindex="0"> Ag ⁺ (aq) + Cl ⁻ (a	q)		
I 0 0			
C -x +x +x			
E +x +x			
Notice that we have little in the column under AgCl except the stoichiometry of the change; we do not need to know its initial equilibrium concentrations because its concentration does not appear in the K_{sp} expression. Substituting the equilibrium values in the expression:	or nto		

(x)(x) = 1.8×10^{-10} Solving, $x^2 = 1.8 \times 10^{-10} x = 1.3 \times 10^{-5}$ Thus [Ag⁺] and [Cl⁻] are both 1.3×10^{-5} M.

Exercise 11.6.1



What are $[Ba^{2+}]$ and $[SO4^{2-}]$ in a saturated solution of BaSO4? The K_{SD} of BaSO4 is 1.1×10^{-10} .

Answer:

 $1.0 \times 10^{-5} \,\mathrm{M}$

EXAMPLE 11.6.1:

What are $[Ca^{2+}]$ and $[PO4^{3-}]$ in a saturated solution of Ca₃(PO4)₂? The K_{SD} of Ca₃(PO4)₂ is 2.1 × 10⁻³³.

Solution

This is similar to Example 14, but the ICE chart is much different because of the number of ions formed.

	Ca3(PO4)2(s)	₽ id="MathJax-Element-125-Frame" role="presentation" style="position:relative;" tabindex="0">	3Ca ²⁺ (aq) +	- 2PO4 ³⁻ (aq)
Ι			0	0
C	-x		+3x	+2x
E			+3 <i>x</i>	+2x

For every unit of Ca₃(PO₄)₂ that dissolves, three Ca²⁺ ions and two PO₄³⁻ ions are formed. The expression for the K_{SD} is also different:

 $K_{\rm Sp} = [{\rm Ca}^{2+}]^3 [{\rm PO4}^{3-}]^2 = 2.1 \times 10^{-33}$

Now when we substitute the unknown concentrations into the expression, we get

 $(3x)^3(2x)^2 = 2.1 \times 10^{-33}$

When we raise each expression inside parentheses to the proper power, remember that the power affects everything inside the parentheses, including the number. So

 $(27x^3)(4x^2) = 2.1 \times 10^{-33}$ Simplifying, $108x^5 = 2.1 \times 10^{-33}$

Dividing both sides of the equation by 108, we get

 $x^5 = 1.9 \times 10^{-35}$

Now we take the fifth root of both sides of the equation (be sure you know how to do this on your calculator):

 $x = 1.1 \times 10^{-7}$

We are not done yet. We still need to determine the concentrations of the ions. According to the ICE chart, $[Ca^{2+}]$ is 3*x*, not *x*. So $[Ca^{2+}] = 3x = 3 \times 1.1 \times 10^{-7} = 3.3 \times 10^{-7} M$ $[PO4^{3^{-}}]$ is 2x, so

 $[PO_4^{3^-}] = 2x = 2 \times 1.1 \times 10^{-7} = 2.2 \times 10^{-7} M$

EXERCISE 11.6.1

EXERCISE 11.0.1 What are $[Mg^{2+}]$ and $[OH^{-}]$ in a saturated solution of Mg(OH)₂? The *K*_{SP} of Mg(OH)₂ is 5.6 × 10⁻¹².

Answer:

 $[Mg^{2+}] = 1.1 \times 10^{-4} \text{ M}; [OH^{-}] = 2.2 \times 10^{-4} \text{ M}$

FOOD AND DRINK APP: SOLIDS IN YOUR WINE BOTTLE

People who drink wine from bottles (as opposed to boxes) will occasionally notice some insoluble materials in the wine, either crusting the bottle, stuck to the cork, or suspended in the liquid wine itself. The accompanying figure shows a cork encrusted with colored crystals. What are these crystals?







Fig. 13.6.1 Wine Cork

The red crystals on the top of the wine cork are from insoluble compounds that are not soluble in the wine.

Source: Photo courtesy of Paul A. Hernandez, flickr.

One of the acids in wine is tartaric acid (H₂C₄H₄O₆). Like the other acids in wine (citric and malic acids, among others), tartaric acid imparts a slight tartness to the wine. Tartaric acid is rather soluble in H₂O, dissolving over 130 g of the acid in only 100 g of H₂O. However, the potassium salt of singly ionized tartaric acid, potassium hydrogen tartrate (KHC₄H₄O₆; also known as potassium bitartrate and better known in the kitchen as cream of tartar), has a solubility of only 6 g per 100 g of H₂O. Thus, over time, wine stored at cool temperatures will slowly precipitate potassium hydrogen tartrate. The crystals precipitate in the wine or grow on the insides of the wine bottle and, if the bottle is stored on its side, on the bottom of the cork. The color of the crystals comes from pigments in the wine; pure potassium hydrogen tartrate is clear in its crystalline form, but in powder form it is white.

The crystals are harmless to ingest; indeed, cream of tartar is used as an ingredient in cooking. However, most wine drinkers do not like to chew their wine, so if tartrate crystals are present in a wine, the wine is usually filtered or decanted to remove the crystals. Tartrate crystals are almost exclusively in red wines; white and rose wines do not have as much tartaric acid in them.

KEY TAKEAWAY

• Equilibrium constants exist for certain groups of equilibria, such as weak acids, weak bases, the autoionization of water, and slightly soluble salts.

Exercise 11.6.1

- 1. Explain the difference between the K_{eq} and the K_{sp} .
- 2. Explain the difference between the K_a and the K_b .
- 3. Write the balanced chemical equation that represents the equilibrium between HF(aq) as reactants and H⁺(aq) and F⁻(aq) as products.
- 4. Write the balanced chemical equation that represents the equilibrium between $CaF_2(s)$ as reactants and $Ca^{2+}(aq)$ and $F^{-}(aq)$ as products.
- 5. Assuming that all species are dissolved in solution, write the K_{eq} expression for the chemical equation in Exercise 3.
- 6. Noting the phase labels, write the K_{SD} expression for the chemical equation in Exercise 4.
- 7. Determine the concentrations of all species in the ionization of 0.100 M HClO₂ in H₂O. The K_a for HClO₂ is 1.1×10^{-2} .
- 8. Determine the concentrations of all species in the ionization of 0.0800 M HCN in H₂O. The K_a for HCN is 6.2×10^{-10} .
- 9. Determine the pH of a 1.00 M solution of HNO₂. The K_a for HNO₂ is 5.6 × 10⁻⁴.
- 10. Determine the pH of a 3.35 M solution of HC₂H₃O₂. The K_a for HC₂H₃O₂ is 1.8 × 10⁻⁵.
- 11. Write the chemical equations and K_a expressions for the stepwise dissociation of H3PO4.
- 12. Write the chemical equations and K_a expressions for the stepwise dissociation of H3C6H5O7.
- 13. If the K_a for HNO₂ is 5.6 × 10⁻⁴, what is the K_b for NO₂^{-(aq)}?
- 14. If the K_a for HCN is 6.2×10^{-10} , what is the K_b for CN⁻(aq)?



CHEMISTRY

15. What is $[OH^-]$ in a solution whose $[H^+]$ is 3.23×10^{-6} M? 16. What is $[OH^-]$ in a solution whose $[H^+]$ is 9.44×10^{-11} M? 17. What is $[H^+]$ in a solution whose $[OH^-]$ is 2.09×10^{-2} M? 18. What is $[H^+]$ in a solution whose $[OH^-]$ is 4.07×10^{-7} M? 19. Write the balanced chemical equation and the K_{SD} expression for the slight solubility of Mg(OH)₂(s). 20. Write the balanced chemical equation and the K_{SD} expression for the slight solubility of Fe₂(SO₄)₃(s). 21. What are $[Sr^{2+}]$ and $[SO4^{2-}]$ in a saturated solution of SrSO4(s)? The K_{SD} of SrSO4(s) is 3.8×10^{-4} . 22. What are [Ba²⁺] and [F⁻] in a saturated solution of BaF₂(s)? The K_{SD} of BaF₂(s) is 1.8 × 10⁻⁷. 23. What are $[Ca_{-}^{2+}]$ and $[OH^{-}]$ in a saturated solution of Ca(OH)₂(s)? The K_{sp} of Ca(OH)₂(s) is 5.0 × 10⁻⁶. 24. What are [Pb²⁺] and [I⁻] in a saturated solution of PbI₂? The K_{SP} for PbI₂ is 9.8 × 10⁻⁹. Answers 1. The K_{SP} is a special type of the K_{eq} and applies to compounds that are only slightly soluble. 2. 3. $HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$ (11.6.16)4. $K_{eq} = \frac{[H^+][F^-]}{[HF]}$ 5. (11.6.17)6. 7. $[HClO_2] = 0.0719 \text{ M}; [H^+] = [ClO_2^-] = 0.0281 \text{ M}$ 8. 9.1.63 10. $H_3PO_4(aq) \rightleftharpoons H^+(aq) + H_2PO_4^-(aq); \quad K_a = rac{[H^+][H_2PO_4^-]}{[H_3PO_4]}$ (11.6.18) $H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq); \quad K_a = rac{[H^+][H_2PO_4^{2-}]}{[H_2PO_4]}$ 11. $HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq); \quad K_a = rac{[H^+][PO_4^{3-}]}{[H_3PO_4^{2-}]}$ 12. 13. 1.8×10^{-11} 14 15. 3.10×10^{-9} M 16. 17. 4.78×10^{-13} M 18. 19. $MgOH_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq); \quad K_{sp} = [Mg^{2+}][OH^-]^2$ (11.6.19)20. 21. $[Sr^{2+}] = [SO_4^{2-}] = 1.9 \times 10^{-2} M$ 22 23. $[Ca^{2+}] = 0.011 \text{ M}; [OH^{-}] = 0.022 \text{ M}$



11.E: CHEMICAL EQUILIBRIUM (EXERCISES)

Additional Exercises

- 1. What is the relationship between the K_{SD} expressions for a chemical reaction and its reverse chemical reaction?
- 2. What is the relationship between the K_W value for H₂O and its reverse chemical reaction?
- 3. For the equilibrium

$$PCl_3(g) + Cl^{2+}(g) \rightleftharpoons PCl_5(g) + 60kJ$$
(11.E.1)

list four stresses that serve to increase the amount of PCl₅.

4. For the equilibrium

$$N_2O_4 + 57kJ \rightleftharpoons 2NO_2 \tag{11.E.2}$$

list four stresses that serve to increase the amount of NO₂.

- 5. Does a very large K_{eq} favor the reactants or the products? Explain your answer.
- 6. Is the K_{eq} for reactions that favor reactants large or small? Explain your answer.
- 7. Show that $K_a \times K_b = K_W$ by determining the expressions for these two reactions and multiplying them together.

$$\begin{aligned} HX(aq) &\rightleftharpoons H^+(aq) + X^-(aq) \\ X^+(aq) + H_2O(l) &\rightleftharpoons HX(aq) + OH^-(aq) \end{aligned} \tag{11.E.3}$$

- 8. Is the conjugate base of a strong acid weak or strong? Explain your answer.
- 9. What is the solubility in moles per liter of AgCl? Use data from Table 13.6.2 Solubility Product Constants for Slightly Soluble Ionic Compounds.
- 10. What is the solubility in moles per liter of Ca(OH)₂? Use data from Table 13.6.2 Solubility Product Constants for Slightly Soluble Ionic Compounds.
- 11. Under what conditions is $K_{eq} = Kp$?
- 12. Under what conditions is $K_{eq} > K_P$ when the temperature is 298 K?
- 13. What is the pH of a saturated solution of Mg(OH)₂? Use data from Table 13.6.2 Solubility Product Constants for Slightly Soluble Ionic Compounds.
- 14. What are the pH and the pOH of a saturated solution of Fe(OH)3? The K_{sp} of Fe(OH)3 is 2.8 × 10⁻³⁹.
- 15. For a salt that has the general formula MX, an ICE chart shows that the K_{SP} is equal to x^2 , where *x* is the concentration of the cation. What is the appropriate formula for the K_{SD} of a salt that has a general formula of MX2?
- 16. Referring to Exercise 15, what is the appropriate formula for the K_{SP} of a salt that has a general formula of M2X3 if the concentration of the cation is defined as 2x, rather than x?
- 17. Consider a saturated solution of PbBr₂(s). If $[Pb^{2+}]$ is 1.33×10^{-5} M, find each of the following.
 - a. [Br⁻]
 - b. the K_{SD} of PbBr₂(s)

18. Consider a saturated solution of Pb3(PO4)2(s). If $[Pb^{2+}]$ is 7.34×10^{-14} M, find each of the following.

a. [PO⊿^{3−}]

```
b. the K<sub>SD</sub> of Pb3(PO4)2(s)
```

ANSWERS

1. They are reciprocals of each other.

2.

3. increase the pressure; decrease the temperature; add PCl₃; add Cl₂; remove PCl₅

4.

5. favor products because the numerator of the ratio for the K_{eq} is larger than the denominator

6.

7.

$$K_a imes K_b = rac{[H^+][X]}{[HX]} imes rac{[HX][OH]}{[X]} = [H^+][OH^-] = K_W$$
(11.E.4)



```
8.

9. 1.3 \times 10^{-5} mol/L

10.

11. K_{eq} = K_{P} when the number of moles of gas on both sides of the reaction is the same.

12.

13. 10.35

14.

15. 4x^{3}

16.

17.

a. 2.66 \times 10^{-5} M

b. 9.41 \times 10^{-15}
```



12: ACIDS AND BASES

Acids and bases are important classes of chemical compounds. They are part of the foods and beverages we ingest, they are present in medicines and other consumer products, and they are prevalent in the world around us. In this chapter, we will focus on acids and bases and their chemistry.

12.1: INTRODUCTION

Certain household chemicals, such as some brands of cleanser, can be very concentrated bases, which makes them among the most potentially hazardous substances found around the home; if spilled on the skin, the strong caustic compound can immediately remove H+ ions from the flesh, resulting in chemical burns. Compare that to the fact that we occasionally purposefully ingest substances such as citrus fruits, vinegar, and wine-all of which contain acids.

12.2: ARRHENIUS ACIDS AND BASES

An Arrhenius acid is a compound that increases the H^+ ion concentration in aqueous solution. An Arrhenius base is a compound that increases the OH^- ion concentration in aqueous solution. The reaction between an Arrhenius acid and an Arrhenius base is called neutralization and results in the formation of water and a salt.

12.3: BRØNSTED-LOWRY ACIDS AND BASES

A Brønsted-Lowry acid is a proton donor; a Brønsted-Lowry base is a proton acceptor. Acid-base reactions include two sets of conjugate acid-base pairs.

12.4: AUTOIONIZATION OF WATER

In any aqueous solution at room temperature, the product of $[H^+]$ and $[OH^-]$ equals 1.0×10^{-14} .

12.5: THE PH SCALE

pH is a logarithmic function of [H+]. [H+] can be calculated directly from pH. pOH is related to pH and can be easily calculated from pH.

12.6: ACID-BASE TITRATIONS

A titration is the quantitative reaction of an acid and a base. Indicators are used to show that all the analyte has reacted with the titrant.

12.7: STRONG AND WEAK ACIDS AND BASES AND THEIR SALTS

Strong acids and bases are 100% ionized in aqueous solution. Weak acids and bases are less than 100% ionized in aqueous solution. Salts of weak acids or bases can affect the acidity or basicity of their aqueous solutions.

12.8: BUFFERS

A buffer is a solution that resists sudden changes in pH.

12.9: ACIDS AND BASES (EXERCISES)



12.1: INTRODUCTION

Formerly there were rather campy science-fiction television shows in which the hero was always being threatened with death by being plunged into a vat of boiling acid: "Mwa ha ha, Buck Rogers [or whatever the hero's name was], prepare to meet your doom by being dropped into a vat of boiling acid!" (The hero always escapes, of course.) This may have been interesting drama but not very good chemistry. If the villain knew his/her/its science, the hero would have been dropped into a vat of boiling base.

Recall that the active component of a classic acid is the H^+ ion, while the active part of a classic base is the OH^- ion. Both ions are related to water in that all H^+ ion needs to become a water molecule is an OH^- ion, while all an OH^- ion needs to become water is an H^+ ion. Consider the relative masses involved: an ion of mass 1 needs an ion of mass 17 to make water, while an ion of mass 17 needs an ion of mass 1 to make water. Which process do you think will be easier?

In fact, bases are more potentially dangerous than acids because it is much easier for an OH^- ion to rip off an H^+ ion from surrounding matter than it is for an H^+ ion to rip off an OH^- ion. Certain household chemicals, such as some brands of cleanser, can be very concentrated bases, which makes them among the most potentially hazardous substances found around the home; if spilled on the skin, the strong caustic compound can immediately remove H^+ ions from the flesh, resulting in chemical burns. Compare that to the fact that we occasionally purposefully ingest substances such as citrus fruits, vinegar, and wine-all of which contain acids. (Of course, some parts of the body, such as the eyes, are extremely sensitive to acids as well as bases.) It seems that our bodies are more capable of dealing with acids than with bases.



Fig. 12.1.1 Household chemicals © Thinkstock On the left is a common acid, and on the right is a common base. Which one is more potentially hazardous?

So a note to all the villains out there: get your chemistry right if you want to be successful!



12.2: ARRHENIUS ACIDS AND BASES

LEARNING OBJECTIVE

- Identify an Arrhenius acid and an Arrhenius base.
- Write the chemical reaction between an Arrhenius acid and an Arrhenius base.

Historically, the first chemical definition of an acid and a base was put forward by Svante Arrhenius, a Swedish chemist, in 1884. An **Arrhenius acid** is a compound that increases the H^+ ion concentration in aqueous solution. The H^+ ion is just a bare proton, and it is rather clear that bare protons are not floating around in an aqueous solution. Instead, chemistry has defined the **hydronium ion** (H₃O⁺) as the actual chemical species that represents an H^+ ion. H^+ ions and H₃O⁺ ions are often considered interchangeable when writing chemical equations (although a properly balanced chemical equation should also include the additional H₂O). Classic Arrhenius acids can be considered ionic compounds in which H^+ is the cation. Table 12.2.1 lists some Arrhenius acids and their names.

Formula	Name
HC2H3O2 (also written CH3COOH)	acetic acid
HClO3	chloric acid
HCl	hydrochloric acid
HBr	hydrobromic acid
HI	hydriodic acid
HF	hydrofluoric acid
HNO3	nitric acid
H2C2O4	oxalic acid
HClO4	perchloric acid
НЗРО4	phosphoric acid
H <u>2</u> SO4	sulfuric acid
H2SO3	sulfurous acid

An **Arrhenius base** is a compound that increases the OH⁻ ion concentration in aqueous solution. Ionic compounds of the OH⁻ ion are classic Arrhenius bases.

Example 12.2.1:

Identify each compound as an Arrhenius acid, an Arrhenius base, or neither.

- a. HNO3
- b. CH3OH

c. Mg(OH)2

Solution

- a. This compound is an ionic compound between H⁺ ions and NO3⁻ ions, so it is an Arrhenius acid.
- b. Although this formula has an OH in it, we do not recognize the remaining part of the molecule as a cation. It is neither an acid nor a base. (In fact, it is the formula for methanol, an organic compound.)
- c. This formula also has an OH in it, but this time we recognize that the magnesium is present as Mg^{2+} cations. As such, this is an ionic compound of the OH⁻ ion and is an Arrhenius base.

Exercise 12.2.1

Identify each compound as an Arrhenius acid, an Arrhenius base, or neither.

1. KOH

2. H2SO4

3. C2H6

Answer

- 1. Arrhenius base
- 2. Arrhenius acid
- 3. neither



Acids have some properties in common. They turn litmus, a plant extract, red. They react with some metals to give off H2 gas. They react with carbonate and hydrogen carbonate salts to give off CO2 gas. Acids that are ingested typically have a sour, sharp taste. (The name *acid* comes from the Latin word *acidus*, meaning "sour.") Bases also have some properties in common. They are slippery to the touch, turn litmus blue, and have a bitter flavor if ingested.

Acids and bases have another property: they react with each other to make water and an ionic compound called a salt. A **salt**, in chemistry, is any ionic compound made by combining an acid with a base. A reaction between an acid and a base is called a **neutralization reaction** and can be represented as follows:acid + base \rightarrow H₂O + salt

The stoichiometry of the balanced chemical equation depends on the number of H^+ ions in the acid and the number of OH^- ions in the base.

Example 12.2.1:

Write the balanced chemical equation for the neutralization reaction between H₂SO₄ and KOH. What is the name of the salt that is formed?

Solution

The general reaction is as follows:

 $H_2SO_4 + KOH \rightarrow H_2O + salt$

Because the acid has two H⁺ ions in its formula, we need two OH⁻ ions to react with it, making two H₂O molecules as product. The remaining ions, K⁺ and SO4²⁻, make the salt potassium sulfate (K₂SO4). The balanced chemical reaction is as follows: H₂SO4 + 2KOH \rightarrow 2H₂O + K₂SO4

Exercise 12.2.1

Write the balanced chemical equation for the neutralization reaction between HCl and Mg(OH)₂. What is the name of the salt that is formed?

Answer:

 $2HCl + Mg(OH)_2 \rightarrow 2H_2O + MgCl_2$; magnesium chloride

KEY TAKEAWAYS

- An Arrhenius acid is a compound that increases the H⁺ ion concentration in aqueous solution.
- An Arrhenius base is a compound that increases the OH⁻ ion concentration in aqueous solution.
- The reaction between an Arrhenius acid and an Arrhenius base is called neutralization and results in the formation of water and a salt.



12.3: BRØNSTED-LOWRY ACIDS AND BASES

LEARNING OBJECTIVES

- Identify a Brønsted-Lowry acid and a Brønsted-Lowry base.
- Identify conjugate acid-base pairs in an acid-base reaction.

The Arrhenius definition of acid and base is limited to aqueous (that is, water) solutions. Although this is useful because water is a common solvent, it is limited to the relationship between the H^+ ion and the OH^- ion. What would be useful is a more general definition that would be more applicable to other chemical reactions and, importantly, independent of H₂O.

In 1923, Danish chemist Johannes Brønsted and English chemist Thomas Lowry independently proposed new definitions for acids and bases, ones that focus on proton transfer. A **Brønsted-Lowry acid** is any species that can donate a proton (H⁺) to another molecule. A **Brønsted-Lowry base** is any species that can accept a proton from another molecule. In short, a Brønsted-Lowry acid is a proton donor (PD), while a Brønsted-Lowry base is a proton acceptor (PA).

It is easy to see that the Brønsted-Lowry definition covers the Arrhenius definition of acids and bases. Consider the prototypical Arrhenius acid-base reaction:

$$\begin{array}{c} H^{+}(aq) + OH^{-}(aq) \rightarrow H_{2}O\left(l\right) \\ acid & base \end{array}$$
(12.3.1)

acid species and base species are marked. The proton, however, is (by definition) a proton donor (labeled PD), while the OH⁻ ion is acting as the proton acceptor (labeled PA):

$$H^{+}_{PD}(aq) + OH^{-}_{PA}(aq) \to H_2O(l)$$
(12.3.2)

The proton donor is a Brønsted-Lowry acid, and the proton acceptor is the Brønsted-Lowry base:

$$\begin{array}{l} H^{+}(aq) + OH^{-}(aq) \rightarrow H_{2}O\left(l\right) \\ BL \ acid \qquad BL \ base \end{array}$$
(12.3.3)

Thus H⁺ is an acid by both definitions, and OH⁻ is a base by both definitions.

Ammonia (NH3) is a base even though it does not contain OH⁻ ions in its formula. Instead, it generates OH⁻ ions as the product of a proton-transfer reaction with H2O molecules; NH3 acts like a Brønsted-Lowry base, and H2O acts like a Brønsted-Lowry acid:



A reaction with water is called **hydrolysis**; we say that NH3 hydrolyzes to make NH4⁺ ions and OH⁻ ions.

Even the dissolving of an Arrhenius acid in water can be considered a Brønsted-Lowry acid-base reaction. Consider the process of dissolving HCl(g) in water to make an aqueous solution of hydrochloric acid. The process can be written as follows:

$$\mathrm{HCl}(\mathbf{g}) + \mathrm{H}_{2}\mathrm{O}(\ell) \rightarrow \mathrm{H}_{3}\mathrm{O}^{+}(\mathrm{aq}) + \mathrm{Cl}^{-}(\mathrm{aq})$$

HCl(g) is the proton donor and therefore a Brønsted-Lowry acid, while H₂O is the proton acceptor and a Brønsted-Lowry base. These two examples show that H₂O can act as both a proton donor and a proton acceptor, depending on what other substance is in the chemical reaction. A substance that can act as a proton donor or a proton acceptor is called **amphiprotic**. Water is probably the most common amphiprotic substance we will encounter, but other substances are also amphiprotic.

Example 12.3.1

Identify the Brønsted-Lowry acid and the Brønsted-Lowry base in this chemical equation.

$$C_6H_5OH + NH_2^- \longrightarrow C_6H_5O^- + NH_3$$

Solution

The C₆H₅OH molecule is losing an H^+ ; it is the proton donor and the Brønsted-Lowry acid. The NH₂⁻ ion (called the amide ion) is accepting the H^+ ion to become NH₃, so it is the Brønsted-Lowry base.



Exercise 12.3.1: Aluminum Ions in Solution

Identify the Brønsted-Lowry acid and the Brønsted-Lowry base in this chemical equation.

$$\mathrm{Al}(\mathrm{H}_2\mathrm{O})_6^{3\,+}+\mathrm{H}_2\mathrm{O}\longrightarrow\mathrm{Al}(\mathrm{H}_2\mathrm{O})_5(\mathrm{OH})^{2\,+}+\mathrm{H}_3\mathrm{O}$$

Answer

Brønsted-Lowry acid: Al(H₂O)₆³⁺; Brønsted-Lowry base: H₂O

In the reaction between NH₃ and H₂O,



the chemical reaction does not go to completion; rather, the reverse process occurs as well, and eventually the two processes cancel out any additional change. At this point, we say the chemical reaction is at *equilibrium*. Both processes still occur, but any net change by one process is countered by the same net change by the other process; it is a *dynamic*, rather than a *static*, equilibrium. Because both reactions are occurring, it makes sense to use a double arrow instead of a single arrow:

$$H \xrightarrow{H} H + H \xrightarrow{O} H \iff H \xrightarrow{H} H + O \xrightarrow{H} H$$

What do you notice about the reverse reaction? The NH_4^+ ion is donating a proton to the OH^- ion, which is accepting it. This means that the NH_4^+ ion is acting as the proton donor, or Brønsted-Lowry acid, while OH^- ion, the proton acceptor, is acting as a Brønsted-Lowry base. The reverse reaction is also a Brønsted-Lowry acid base reaction:



This means that both reactions are acid-base reactions by the Brønsted-Lowry definition. If you consider the species in this chemical reaction, two sets of similar species exist on both sides. Within each set, the two species differ by a proton in their formulas, and one member of the set is a Brønsted-Lowry acid, while the other member is a Brønsted-Lowry base. These sets are marked here:



The two sets-NH3/NH4⁺ and H2O/OH⁻-are called **conjugate acid-base pairs**. We say that NH4⁺ is the conjugate acid of NH3, OH⁻ is the conjugate base of H2O, and so forth. Every Brønsted-Lowry acid-base reaction can be labeled with two conjugate acid-base pairs.

Example 12.3.2

Identify the conjugate acid-base pairs in this equilibrium.

12.3.2



$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$

Solution

One pair is H₂O and OH⁻, where H₂O has one more H⁺ and is the conjugate acid, while OH⁻ has one less H⁺ and is the conjugate base. The other pair consists of (CH₃)₃N and (CH₃)₃NH⁺, where (CH₃)₃NH⁺ is the conjugate acid (it has an additional proton) and (CH₃)₃N is the conjugate base.

Exercise 12.3.2

Identify the conjugate acid-base pairs in this equilibrium.

$$NH_2^- + H_2O \rightleftharpoons NH_3 + OH^-$$

Answer

H₂O (acid) and OH⁻ (base); NH₂⁻ (base) and NH₃ (acid)

CHEMISTRY IS EVERYWHERE: HOUSEHOLD ACIDS AND BASES

Many household products are acids or bases. For example, the owner of a swimming pool may use muriatic acid to clean the pool. Muriatic acid is another name for HCl(aq). In Section 4.6, vinegar was mentioned as a dilute solution of acetic acid [HC2H3O2(aq)]. In a medicine chest, one may find a bottle of vitamin C tablets; the chemical name of vitamin C is ascorbic acid (HC6H7O6).

One of the more familiar household bases is NH₃, which is found in numerous cleaning products. NH₃ is a base because it increases the OH^- ion concentration by reacting with H₂O:

 $NH_3(aq) + H_2O(\ell) \rightarrow NH_4^+(aq) + OH^-(aq)$

Many soaps are also slightly basic because they contain compounds that act as Brønsted-Lowry bases, accepting protons from H₂O and forming excess OH⁻ ions. This is one explanation for why soap solutions are slippery.

Perhaps the most dangerous household chemical is the lye-based drain cleaner. Lye is a common name for NaOH, although it is also used as a synonym for KOH. Lye is an extremely caustic chemical that can react with grease, hair, food particles, and other substances that may build up and clog a water pipe. Unfortunately, lye can also attack body tissues and other substances in our bodies. Thus when we use lye-based drain cleaners, we must be very careful not to touch any of the solid drain cleaner or spill the water it was poured into. Safer, nonlye drain cleaners (like the one in the accompanying figure) use peroxide compounds to react on the materials in the clog and clear the drain.



Fig. 12.3.1 Drain Cleaners. Drain cleaners can be made from a reactive material that is less caustic than a base. Source: Photo used by permission of Citrasolv, LLC.

KEY TAKEAWAYS

- A Brønsted-Lowry acid is a proton donor; a Brønsted-Lowry base is a proton acceptor.
- Acid-base reactions include two sets of conjugate acid-base pairs.



12.4: AUTOIONIZATION OF WATER

LEARNING OBJECTIVES

- Describe the autoionization of water.
- Calculate the concentrations of H⁺ and OH⁻ in solutions, knowing the other concentration.

We have already seen that H₂O can act as an acid or a base:

 $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$ (H₂O acts as an acid)

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$
 (H₂O acts as a base)

It may not surprise you to learn, then, that within any given sample of water, some H₂O molecules are acting as acids, and other H₂O molecules are acting as bases. The chemical equation is as follows:

$$H_2O + H_2O \rightarrow H_3O^+ + OH^-$$

This occurs only to a very small degree: only about 6 in 10^8 H₂O molecules are participating in this process, which is called the **autoionization of water**. At this level, the concentration of both H⁺(aq) and OH⁻(aq) in a sample of pure H₂O is about 1.0×10^{-7} M. If we use square brackets-[]-around a dissolved species to imply the molar concentration of that species, we have[H⁺] = [OH⁻] = 1.0 $\times 10^{-7}$ M

for *any* sample of pure water because H₂O can act as both an acid and a base. The product of these two concentrations is 1.0×10^{-14} : [H⁺] × [OH⁻] = $(1.0 \times 10^{-7})(1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$

In acids, the concentration of $H^+(aq)-[H^+]$ -is greater than 1.0×10^{-7} M, while for bases the concentration of $OH^-(aq)-[OH^-]$ -is greater than 1.0×10^{-7} M. However, the *product* of the two concentrations- $[H^+][OH^-]$ -is *always* equal to 1.0×10^{-14} , no matter whether the aqueous solution is an acid, a base, or neutral:

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

This value of the product of concentrations is so important for aqueous solutions that it is called the **autoionization constant of water** and is denoted K_W :

$$K_{\rm W} = [{\rm H}^+][{\rm OH}^-] = 1.0 \times 10^{-14}$$

This means that if you know $[H^+]$ for a solution, you can calculate what $[OH^-]$ has to be for the product to equal 1.0×10^{-14} , or if you know $[OH^-]$, you can calculate $[H^+]$. This also implies that as one concentration goes up, the other must go down to compensate so that their product always equals the value of K_W .

Example 12.4.1:

What is $[OH^{-}]$ of an aqueous solution if $[H^{+}]$ is 1.0×10^{-4} M?

Solution

Using the expression and known value for K_{W} ,

 $K_{\rm W} = [{\rm H}^+][{\rm OH}^-] = 1.0 \times 10^{-14} = (1.0 \times 10^{-4})[{\rm OH}^-]$

We solve by dividing both sides of the equation by 1.0×10^{-4} :

$$\left[OH^{-}\right] = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-4}} = 1.0 \times 10^{-10} M \tag{12.4.1}$$

It is assumed that the concentration unit is molarity, so $[OH^-]$ is 1.0×10^{-10} M.

Exercise 12.4.1

What is $[H^+]$ of an aqueous solution if $[OH^-]$ is 1.0×10^{-9} M?

Answer:

 $1.0 \times 10^{-5} \text{ M}$

When you have a solution of a particular acid or base, you need to look at the formula of the acid or base to determine the number of H^+ or OH^- ions in the formula unit because $[H^+]$ or $[OH^-]$ may not be the same as the concentration of the acid or base itself.

Example 12.4.2:

What is [H⁺] in a 0.0044 M solution of Ca(OH)₂?

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12.4.1



Solution

We begin by determining [OH⁻]. The concentration of the solute is 0.0044 M, but because Ca(OH)₂ is a strong base, there are two OH⁻ ions in solution for every formula unit dissolved, so the actual [OH⁻] is two times this, or 2×0.0044 M = 0.0088 M. Now we can use the K_W expression:

$$[H^+][OH^-] = 1.0 \times 10^{-14} = [H^+](0.0088 \text{ M})$$

Dividing both sides by 0.0088:

$$ig[H^+ig] = rac{1.0 imes 10^{-14}}{(0.0088)} = 1.1 imes 10^{-12} M ~~(12.4.2)$$

[H⁺] has decreased significantly in this basic solution.

Exercise 12.4.2

What is [OH⁻] in a 0.00032 M solution of H₂SO₄? (Hint: assume both H⁺ ions ionize.)

Answer

 $1.6 \times 10^{-11} \text{ M}$

For strong acids and bases, $[H^+]$ and $[OH^-]$ can be determined directly from the concentration of the acid or base itself because these ions are 100% ionized by definition. However, for weak acids and bases, this is not so. The degree, or percentage, of ionization would need to be known before we can determine $[H^+]$ and $[OH^-]$.

Example 12.4.3:

A 0.0788 M solution of HC₂H₃O₂ is 3.0% ionized into H^+ ions and C₂H₃O₂⁻ ions. What are [H⁺] and [OH⁻] for this solution?

Solution

Because the acid is only 3.0% ionized, we can determine [H⁺] from the concentration of the acid. Recall that 3.0% is 0.030 in decimal form:

 $[\text{H}^+] = 0.030 \times 0.0788 = 0.00236 \text{ M}$

With this [H⁺], then [OH⁻] can be calculated as follows:

$$[OH^{-}] = \frac{1.0 \times 10^{-14}}{0.00236} = 4.2 \times 10^{-12} M$$
(12.4.3)

This is about 30 times higher than would be expected for a strong acid of the same concentration.

Exercise 12.4.3

A 0.0222 M solution of pyridine (C₅H₅N) is 0.44% ionized into pyridinium ions (C₅H₅NH⁺) and OH⁻ ions. What are [OH⁻] and [H⁺] for this solution?

Answer:

 $[OH^{-}] = 9.77 \times 10^{-5} \text{ M}; [H^{+}] = 1.02 \times 10^{-10} \text{ M}$

SUMMARY

In any aqueous solution, the product of [H+] and [OH–] equals 1.0×10^{-14} (at room temperature).



12.5: THE PH SCALE

LEARNING OBJECTIVES

- Define *pH*.
- Determine the pH of acidic and basic solutions.

As we have seen, $[H^+]$ and $[OH^-]$ values can be markedly different from one aqueous solution to another. So chemists defined a new scale that succinctly indicates the concentrations of either of these two ions.

pH is a logarithmic function of [H⁺]:

 $pH = -log[H^+]$

pH is usually (but not always) between 0 and 14. Knowing the dependence of pH on [H⁺], we can summarize as follows:

- If pH < 7, then the solution is acidic.
- If pH = 7, then the solution is neutral.
- If pH > 7, then the solution is basic.

This is known as the pH scaleThe range of values from 0 to 14 that describes the acidity or basicity of a solution. You can use pH to make a quick determination whether a given aqueous solution is acidic, basic, or neutral.

Example 12.5.1:

Label each solution as acidic, basic, or neutral based only on the stated pH.

a. milk of magnesia, pH = 10.5

- b. pure water, pH = 7
- c. wine, pH = 3.0

Solution

- a. With a pH greater than 7, milk of magnesia is basic. (Milk of magnesia is largely Mg(OH)2.)
- b. Pure water, with a pH of 7, is neutral.
- c. With a pH of less than 7, wine is acidic.

Exercise 12.5.1

Identify each substance as acidic, basic, or neutral based only on the stated pH.

```
1. human blood, pH = 7.4
```

```
2. household ammonia, pH = 11.0
```

```
3. cherries, pH = 3.6
```

Answers

- 1. basic
- 2. basic
- 3. acidic

Table 12.7.1 gives the typical pH values of some common substances. Note that several food items are on the list, and most of them are acidic.



Table 12.7.1 Typical pH Values of Various Substances*		
Substance	pH	
stomach acid	1.7	
lemon juice	2.2	
vinegar	2.9	
soda	3.0	
wine	3.5	
coffee, black	5.0	
milk	6.9	
pure water	7.0	
blood	7.4	
seawater	8.5	
milk of magnesia	10.5	
ammonia solution	12.5	
1.0 M NaOH	14.0	
*Actual values may vary depen	ding on conditions	

pH is a *logarithmic* scale. A solution that has a pH of 1.0 has 10 times the $[H^+]$ as a solution with a pH of 2.0, which in turn has 10 times the $[H^+]$ as a solution with a pH of 3.0 and so forth.

Using the definition of pH, it is also possible to calculate $[H^+]$ (and $[OH^-]$) from pH and vice versa. The general formula for determining $[H^+]$ from pH is as follows:

 $[H^+] = 10^{-pH}$

You need to determine how to evaluate the above expression on your calculator. Ask your instructor if you have any questions. The other issue that concerns us here is significant figures. Because the number(s) before the decimal point in a logarithm relate to the power on 10, the number of digits *after* the decimal point is what determines the number of significant figures in the final answer:



Example 12.5.1:

What are [H⁺] and [OH⁻] for an aqueous solution whose pH is 4.88?

Solution

We need to evaluate the expression

 $[H^+] = 10^{-4.88}$

Depending on the calculator you use, the method for solving this problem will vary. In some cases, the "-4.88" is entered and a " 10^{X} " key is pressed; for other calculators, the sequence of keystrokes is reversed. In any case, the correct numerical answer is as follows:

$$[H^+] = 1.3 \times 10^{-5} M$$

Because 4.88 has two digits after the decimal point, [H⁺] is limited to two significant figures. From this, [OH⁻] can be determined:

$$\left[OH^{-}\right] = \frac{1 \times 10^{-14}}{1.3 \times 10^{-5}} = 7.7 \times 10^{-10} M \tag{12.5.1}$$

Exercise 12.5.1

What are [H⁺] and [OH⁻] for an aqueous solution whose pH is 10.36?

Answer

 $[\text{H}^+] = 4.4 \times 10^{-11} \text{ M}; [\text{OH}^-] = 2.3 \times 10^{-4} \text{ M}$

There is an easier way to relate $[H^+]$ and $[OH^-]$. We can also define **pOH** similar to pH:pOH = $-\log[OH^-]$

(In fact, p"anything" is defined as the negative logarithm of that anything.) This also implies that

$$[OH^{-}] = 10^{-}pOH$$

A simple and useful relationship is that for any aqueous solution,

pH + pOH = 14



This relationship makes it simple to determine pH from pOH or pOH from pH and then calculate the resulting ion concentration.

EXAMPLE 12.5.1: SOLUTIN PH The pH of a solution is 8.22. What are pOH, [H⁺], and [OH⁻]? Solution Because the sum of pH and pOH equals 14, we have 8.22 + pOH = 14Subtracting 8.22 from 14, we get pOH = 5.78Now we evaluate the following two expressions: $[H^+] = 10^{-8.22}[OH^-] = 10^{-5.78}$ So $[H^+] = 6.0 \times 10^{-9} M[OH^-] = 1.7 \times 10^{-6} M$

KEY TAKEAWAYS

- pH is a logarithmic function of [H⁺].
- [H⁺] can be calculated directly from pH.
- pOH is related to pH and can be easily calculated from pH.



12.6: ACID-BASE TITRATIONS

LEARNING OBJECTIVES

- Describe a titration experiment.
- Explain what an indicator does.
- Perform a titration calculation correctly.

The reaction of an acid with a base to make a salt and water is a common reaction in the laboratory, partly because so many compounds can act as acids or bases. Another reason that acid-base reactions are so prevalent is because they are often used to determine quantitative amounts of one or the other. Performing chemical reactions quantitatively to determine the exact amount of a reagent is called a **titration**. A titration can be performed with almost any chemical reaction for which the balanced chemical equation is known. Here, we will consider titrations that involve acid-base reactions.

In a titration, one reagent has a known concentration or amount, while the other reagent has an unknown concentration or amount. Typically, the known reagent (the **titrant**) is added to the unknown quantity and is dissolved in solution. The unknown amount of substance (the **analyte**) may or may not be dissolved in solution (but usually is). The titrant is added to the analyte using a precisely calibrated volumetric delivery tube called a burette (also spelled buret; see Fig. 12.4.1). The burette has markings to determine how much volume of solution has been added to the analyte. When the reaction is complete, it is said to be at the **equivalence point**; the number of moles of titrant can be calculated from the concentration and the volume, and the balanced chemical equation can be used to determine the number of moles (and then concentration or mass) of the unknown reactant.



Fig. 12.4.1 Equipment for Titrations. A burette is a type of liquid dispensing system that can accurately indicate the volume of liquid dispensed

For example, suppose 25.66 mL (or 0.02566 L) of 0.1078 M HCl was used to titrate an unknown sample of NaOH. What mass of NaOH was in the sample? We can calculate the number of moles of HCl reacted:

mol HCl = (0.02566 L)(0.1078 M) = 0.002766 mol HCl

We also have the balanced chemical reaction between HCl and NaOH:

$$HCl + NaOH \rightarrow NaCl + H_2O$$

So we can construct a conversion factor to convert to number of moles of NaOH reacted:

$$0.002766 \ \text{mol} \ HCl \times \frac{1 \ mol \ NaOH}{1 \ \text{mol} \ HCl} = 0.002766 \ mol \ NaOH$$
(12.6.1)

Then we convert this amount to mass, using the molar mass of NaOH (40.00 g/mol):

$$0.002766 \ \text{mol}\ HCl \times \frac{40.00 \ g \, NaOH}{1 \ \text{mol}\ HCl} = 0.1106 \ g \, NaOH \tag{12.6.2}$$

This is type of calculation is performed as part of a titration.

Example 12.6.1:

What mass of Ca(OH)₂ is present in a sample if it is titrated to its equivalence point with 44.02 mL of 0.0885 M HNO₃? The balanced chemical equation is as follows:

 $2HNO_3 + Ca(OH)_2 \rightarrow Ca(NO_3)_2 + 2H_2O$

Solution

In liters, the volume is 0.04402 L. We calculate the number of moles of titrant:

moles HNO₃ = (0.04402 L)(0.0885 M) = 0.00390 mol HNO₃

Using the balanced chemical equation, we can determine the number of moles of Ca(OH)2 present in the analyte:

$$0.00390 \text{ fmol } HNO_3 \times \frac{1 \text{ mol } Ca(OH)_2}{2 \text{ fmol } HNO_3} = 0.00195 \text{ mol } Ca(OH)_2$$
(12.6.3)



Then we convert this to a mass using the molar mass of Ca(OH)2:

$$0.00195 \ \text{mol} \ Ca(OH)_2 \times \frac{74.1 \ g \ Ca(OH)_2}{\text{mol} \ Ca(OH)_2} = 0.144 \ g \ Ca(OH)_2 \tag{12.6.4}$$

Exercise 12.6.1

What mass of $H_2C_2O_4$ is present in a sample if it is titrated to its equivalence point with 18.09 mL of 0.2235 M NaOH? The balanced chemical reaction is as follows:

$$H_2C_2O_4 + 2 NaOH \rightarrow Na_2C_2O_4 + 2 H_2O$$

Answer

0.182 g

How does one know if a reaction is at its equivalence point? Usually, the person performing the titration adds a small amount of an **indicator**, a substance that changes color depending on the acidity or basicity of the solution. Because different indicators change colors at different levels of acidity, choosing the correct one is important in performing an accurate titration.

SUMMARY

A titration is the quantitative reaction of an acid and a base. Indicators are used to show that all the analyte has reacted with the titrant.



12.7: STRONG AND WEAK ACIDS AND BASES AND THEIR SALTS

LEARNING OBJECTIVES

- Define a strong and a weak acid and base.
- Recognize an acid or a base as strong or weak.
- Determine if a salt produces an acidic or a basic solution.

Except for their names and formulas, so far we have treated all acids as equals, especially in a chemical reaction. However, acids can be very different in a very important way. Consider HCl(aq). When HCl is dissolved in H₂O, it completely dissociates into $H^+(aq)$ and $Cl^-(aq)$ ions; all the HCl molecules become ions:

$$HCl \stackrel{100\%}{
ightarrow} H^+(aq) + Cl^-(aq)$$

Any acid that dissociates 100% into ions is called a **strong acid**. If it does not dissociate 100%, it is a **weak acid**. HC₂H₃O₂ is an example of a weak acid:

$$HC_2H_3O_2\stackrel{\sim 5\%}{\longrightarrow} H^+(aq)+C_2H_3O_2^-(aq)$$

Because this reaction does not go 100% to completion, it is more appropriate to write it as a reversible reaction:

$$HC_2H_3O_2 \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq) \; ,$$

As it turns out, there are very few strong acids, which are given in Table 12.7.1. If an acid is not listed here, it is a weak acid. It may be 1% ionized or 99% ionized, but it is still classified as a weak acid.

Acids	Bases
HCl	LiOH
HBr	NaOH
HI	КОН
HNO3	RbOH
H2SO4	CsOH
HClO3	Mg(OH)2
HClO4	Ca(OH)2
	Sr(OH)2
	Ba(OH)2

Table 12.7.1: Strong Acids and Bases

The issue is similar with bases: a **strong base** is a base that is 100% ionized in solution. If it is less than 100% ionized in solution, it is a **weak base**. There are very few strong bases (Table 12.7.1); any base not listed is a weak base. All strong bases are OH^- compounds. So a base based on some other mechanism, such as NH_3 (which does not contain OH^- ions as part of its formula), will be a weak base.

Example 12.7.1

Identify each acid or base as strong or weak.

- a. HCl
- b. Mg(OH)₂
- c. C5H5N

Solution

- a. Because HCl is listed in Table 12.7.1, it is a strong acid.
- b. Because Mg(OH)₂ is listed in Table 12.7.1, it is a strong base.
- c. The nitrogen in C5H5N would act as a proton acceptor and therefore can be considered a base, but because it does not contain an OH compound, it cannot be considered a strong base; it is a weak base.

Exercise 12.7.1

Identify each acid or base as strong or weak.

a. RbOH

b. HNO₂



Answer a

strong base

Answer b

weak acid

Example 12.7.2

Write the balanced chemical equation for the dissociation of Ca(OH)2 and indicate whether it proceeds 100% to products or not. Solution

This is an ionic compound of Ca^{2+} ions and OH^{-} ions. When an ionic compound dissolves, it separates into its constituent ions: $(ce{Ca(OH)2 \rightarrow Ca^{2+}(aq) + 2OH^{-}(aq)} \land ca^{2+}(aq) + 2OH^{-}(aq))$

Because Ca(OH)₂ is listed in Table 12.7.1, this reaction proceeds 100% to products.

Exercise 12.7.2

Write the balanced chemical equation for the dissociation of hydrazoic acid (HN3) and indicate whether it proceeds 100% to products or not.

Answer

The reaction is as follows:

$$\mathrm{HN}_3
ightarrow \mathrm{H}^+(\mathrm{aq}) + \mathrm{N}^-_3(\mathrm{aq})$$

It does not proceed 100% to products because hydrazoic acid is not a strong acid.

Certain salts will also affect the acidity or basicity of aqueous solutions because some of the ions will undergo hydrolysis, just like NH3 does to make a basic solution. The general rule is that salts with ions that are part of strong acids or bases will not hydrolyze, while salts with ions that are part of weak acids or bases will hydrolyze.

Consider NaCl. When it dissolves in an aqueous solution, it separates into Na⁺ ions and Cl⁻ ions:

$$\mathrm{NaCl}
ightarrow \mathrm{Na}^+(\mathrm{aq}) + \mathrm{Cl}^-(\mathrm{aq})$$

Will the Na⁺(aq) ion hydrolyze? If it does, it will interact with the OH⁻ ion to make NaOH:

$$Na^+(aq) + H_2O \rightarrow NaOH + H^+(aq)$$

However, NaOH is a strong base, which means that it is 100% ionized in solution:

$${
m NaOH}
ightarrow {
m Na}^+({
m aq}) + {
m OH}^-({
m aq})$$

The free $OH^{-}(aq)$ ion reacts with the $H^{+}(aq)$ ion to remake a water molecule:

$$\mathrm{H^{+}(aq)} + \mathrm{OH^{-}(aq)} \rightarrow \mathrm{H_{2}O}$$

The net result? There is no change, so there is no effect on the acidity or basicity of the solution from the Na⁺(aq) ion. What about the Cl⁻ ion? Will it hydrolyze? If it does, it will take an H⁺ ion from a water molecule:

$$\mathrm{Cl^{-}(aq)} + \mathrm{H_{2}O} \rightarrow \mathrm{HCl} + \mathrm{OH^{-}}$$

However, HCl is a strong acid, which means that it is 100% ionized in solution:

$$\mathrm{HCl} \rightarrow \mathrm{H^{+}(aq)} + \mathrm{Cl^{-}(aq)}$$

The free $H^+(aq)$ ion reacts with the $OH^-(aq)$ ion to remake a water molecule:

$$\mathrm{H^{+}(aq)} + \mathrm{OH^{-}(aq)} \rightarrow \mathrm{H_{2}O}$$

The net result? There is no change, so there is no effect on the acidity or basicity of the solution from the Cl⁻(aq) ion. Because neither ion in NaCl affects the acidity or basicity of the solution, NaCl is an example of a neutral saltAn ionic compound that does not affect the acidity of its aqueous solution ..

Things change, however, when we consider a salt like NaC2H3O2. We already know that the Na⁺ ion won't affect the acidity of the solution. What about the acetate ion? If it hydrolyzes, it will take an H⁺ from a water molecule:



$\mathbf{C_2H_3O_2^-(aq)+H_2O} \rightleftharpoons \mathbf{HC_2H_3O_2+OH-(aq)}$

Does this happen? Yes, it does. Why? *Because* $HC_2H_3O_2$ is a weak acid. Any chance a weak acid has to form, it will (the same with a weak base). As some $C_2H_3O_2^-$ ions hydrolyze with H_2O to make the molecular weak acid, OH^- ions are produced. OH^- ions make solutions basic. Thus NaC₂H₃O₂ solutions are slightly basic, so such a salt is called a **basic salt**.

There are also salts whose aqueous solutions are slightly acidic. NH4Cl is an example. When NH4Cl is dissolved in H2O, it separates into $NH4^+$ ions and Cl^- ions. We have already seen that the Cl^- ion does not hydrolyze. However, the $NH4^+$ ion will:

$$\mathrm{NH}_{4}^{+}(\mathrm{aq}) + \mathrm{H}_{2}\mathrm{O} \rightleftharpoons \mathrm{NH}_{3}(\mathrm{aq}) + \mathrm{H}_{3}\mathrm{O}^{+}(\mathrm{aq})$$

Recall from Section 12.2, that H_{30}^+ ion is the hydronium ion, the more chemically proper way to represent the H^+ ion. This is the classic acid species in solution, so a solution of NH_4^+ (aq) ions is slightly acidic. NH_4Cl is an example of an **acid salt**. The molecule NH₃ is a weak base, and it will form when it can, just like a weak acid will form when it can.

So there are two general rules:

- 1. If an ion derives from a strong acid or base, it will not affect the acidity of the solution.
- 2. If an ion derives from a weak acid, it will make the solution basic; if an ion derives from a weak base, it will make the solution acidic.

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	- Т	4.	1.	•)	

Identify each salt as acidic, basic, or neutral.

- a. KCl
- b. KNO₂

c. NH₄Br

Solution

- a. The ions from KCl derive from a strong acid (HCl) and a strong base (KOH). Therefore, neither ion will affect the acidity of the solution, so KCl is a neutral salt.
- b. Although the K^+ ion derives from a strong base (KOH), the NO2⁻ ion derives from a weak acid (HNO2). Therefore the solution will be basic, and KNO2 is a basic salt.
- c. Although the Br⁻ ions derive from a strong acid (HBr), the NH4⁺ ion derives from a weak base (NH3), so the solution will be acidic, and NH4Br is an acidic salt.

Exercise 12.7.3

Identify each salt as acidic, basic, or neutral.

A. (C5H5NH)Cl B. Na2SO3 Answer a acidic Answer b basic

Some salts are composed of ions that come from both weak acids and weak bases. The overall effect on an aqueous solution depends on which ion exerts more influence on the overall acidity. We will not consider such salts here.

SUMMARY

Strong acids and bases are 100% ionized in aqueous solution. Weak acids and bases are less than 100% ionized in aqueous solution. Salts of weak acids or bases can affect the acidity or basicity of their aqueous solutions.



12.8: BUFFERS

LEARNING OBJECTIVES

- Define *buffer*.
- Correctly identify the two components of a buffer.

As indicated in Section 12.5, weak acids are relatively common, even in the foods we eat. But we occasionally encounter a strong acid or base, such as stomach acid, which has a strongly acidic pH of 1.7. By definition, strong acids and bases can produce a relatively large amount of H^+ or OH^- ions and consequently have marked chemical activities. In addition, very small amounts of strong acids and bases can change the pH of a solution very quickly. If 1 mL of stomach acid [approximated as 0.1 M HCl(aq)] were added to the bloodstream and no correcting mechanism were present, the pH of the blood would decrease from about 7.4 to about 4.7-a pH that is not conducive to continued living. Fortunately, the body has a mechanism for minimizing such dramatic pH changes.

The mechanism involves a **buffer**, a solution that resists dramatic changes in pH. Buffers do so by being composed of certain pairs of solutes: either a weak acid plus a salt derived from that weak acid or a weak base plus a salt of that weak base. For example, a buffer can be composed of dissolved $HC_2H_3O_2$ (a weak acid) and $NaC_2H_3O_2$ (the salt derived from that weak acid). Another example of a buffer is a solution containing NH_3 (a weak base) and NH_4Cl (a salt derived from that weak base).

Let us use an HC2H3O2/NaC2H3O2 buffer to demonstrate how buffers work. If a strong base-a source of OH⁻(aq) ions-is added to the buffer solution, those OH⁻ ions will react with the HC2H3O2 in an acid-base reaction:

$HC_2H_3O_2(aq) + OH^{-}(aq) \rightarrow H_2O(\ell) + C_2H_3O_2^{-}(aq)$

Rather than changing the pH dramatically by making the solution basic, the added OH⁻ ions react to make H₂O, so the pH does not change much.

If a strong acid-a source of H^+ ions-is added to the buffer solution, the H^+ ions will react with the anion from the salt. Because HC2H3O2 is a weak acid, it is not ionized much. This means that if lots of H^+ ions and C2H3O2⁻ ions are present in the same solution, they will come together to make HC2H3O2:

$$H^{+}(aq) + C_{2}H_{3}O_{2}^{-}(aq) \rightarrow HC_{2}H_{3}O_{2}(aq)$$

Rather than changing the pH dramatically and making the solution acidic, the added H⁺ ions react to make molecules of a weak acid. Fig. 12.8.1 illustrates both actions of a buffer.



Fig. 12.8.1 The Actions of Buffers. Buffers can react with both strong acids (top) and strong bases (side) to minimize large changes in pH.

Buffers made from weak bases and salts of weak bases act similarly. For example, in a buffer containing NH₃ and NH₄Cl, NH₃ molecules can react with any excess H^+ ions introduced by strong acids:



NH3(aq) + $H^+(aq) \rightarrow NH4^+(aq)$

while the $NH4^+(aq)$ ion can react with any OH^- ions introduced by strong bases:

$NH4^+(aq) + OH^-(aq) \rightarrow NH3(aq) + H2O(\ell)$

Example 12.8.1:

Which combinations of compounds can make a buffer solution?

- 1. HCHO₂ and NaCHO₂
- 2. HCl and NaCl
- 3. CH₃NH₂ and CH₃NH₃Cl
- 4. NH3 and NaOH

Solution

- 1. HCHO2 is formic acid, a weak acid, while NaCHO2 is the salt made from the anion of the weak acid (the formate ion [CHO2⁻]). The combination of these two solutes would make a buffer solution.
- 2. HCl is a strong acid, not a weak acid, so the combination of these two solutes would not make a buffer solution.
- 3. CH3NH2 is methylamine, which is like NH3 with one of its H atoms substituted with a CH3 group. Because it is not listed in Table 12.5.1, we can assume that it is a weak base. The compound CH3NH3Cl is a salt made from that weak base, so the combination of these two solutes would make a buffer solution.
- 4. NH3 is a weak base, but NaOH is a strong base. The combination of these two solutes would not make a buffer solution.

Exercise 12.8.1

Which combinations of compounds can make a buffer solution?

- 1. NaHCO3 and NaCl
- 2. H3PO4 and NaH2PO4
- 3. NH3 and (NH4)3PO4
- 4. NaOH and NaCl

Answers

- 1. no
- 2. yes
- 3. yes

4. no

Buffers work well only for limited amounts of added strong acid or base. Once either solute is completely reacted, the solution is no longer a buffer, and rapid changes in pH may occur. We say that a buffer has a certain **capacity**. Buffers that have more solute dissolved in them to start with have larger capacities, as might be expected.

Human blood has a buffering system to minimize extreme changes in pH. One buffer in blood is based on the presence of HCO_3^- and H_2CO_3 [the second compound is another way to write $CO_2(aq)$]. With this buffer present, even if some stomach acid were to find its way directly into the bloodstream, the change in the pH of blood would be minimal. Inside many of the body's cells, there is a buffering system based on phosphate ions.

FOOD AND DRINK APP: THE ACID THAT EASES PAIN

Although medicines are not exactly "food and drink," we do ingest them, so let's take a look at an acid that is probably the most common medicine: acetylsalicylic acid, also known as aspirin. Aspirin is well known as a pain reliever and antipyretic (fever reducer).

The structure of aspirin is shown in the accompanying figure. The acid part is circled; it is the H atom in that part that can be donated as aspirin acts as a Brønsted-Lowry acid. Because it is not given in Table 12.5.1, acetylsalicylic acid is a weak acid. However, it is still an acid, and given that some people consume relatively large amounts of aspirin daily, its acidic nature can cause problems in the stomach lining, despite the stomach's defenses against its own stomach acid.





Fig. 12.8.2 The Molecular Structure of Aspirin. The circled atoms are the acid part of the molecule.

Because the acid properties of aspirin may be problematic, many aspirin brands offer a "buffered aspirin" form of the medicine. In these cases, the aspirin also contains a buffering agent-usually MgO-that regulates the acidity of the aspirin to minimize its acidic side effects.

As useful and common as aspirin is, it was formally marketed as a drug starting in 1899. The US Food and Drug Administration (FDA), the governmental agency charged with overseeing and approving drugs in the United States, wasn't formed until 1906. Some have argued that if the FDA had been formed before aspirin was introduced, aspirin may never have gotten approval due to its potential for side effects-gastrointestinal bleeding, ringing in the ears, Reye's syndrome (a liver problem), and some allergic reactions. However, recently aspirin has been touted for its effects in lessening heart attacks and strokes, so it is likely that aspirin is here to stay.

SUMMARY

A buffer is a solution that resists sudden changes in pH.



12.9: ACIDS AND BASES (EXERCISES)

Additional Exercises

- 1. Write the balanced chemical equation between Zn metal and HCl(aq). The other product is ZnCl₂.
- 2. Write the neutralization reaction in which ZnCl₂, also found in Exercise 1, is the salt product.
- 3. Why isn't an oxide compound like CaO considered a salt? (Hint: what acid-base combination would be needed to make it if it were a salt?)
- 4. Metal oxides are considered basic because they react with H₂O to form OH compounds. Write the chemical equation for a reaction that forms a base when CaO is combined with H₂O.
- 5. Write the balanced chemical equation between aluminum hydroxide and sulfuric acid.
- 6. Write the balanced chemical equation between phosphoric acid and barium hydroxide.
- 7. Write the equation for the chemical reaction that occurs when caffeine $(C_8H_{10}N_4O_2)$ acts as a Brønsted-Lowry base.
- 8. Citric acid (C6H8O7) is the acid found in citrus fruits. It can lose a maximum of three H⁺ ions in the presence of a base. Write the chemical equations for citric acid acting stepwise as a Brønsted-Lowry acid.
- 9. Can an amphiprotic substance be a strong acid and a strong base at the same time? Explain your answer.
- 10. Can an amphiprotic substance be a weak acid and a weak base at the same time? If so, explain why and give an example.
- 11. Under what conditions will the equivalence point of a titration be slightly acidic?
- 12. Under what conditions will the equivalence point of a titration be slightly basic?
- 13. Write the chemical equation for the autoionization of NH3.
- 14. Write the chemical equation for the autoionization of HF.
- 15. What is the pOH range for an acidic solution?
- 16. What is the pOH range for a basic solution?
- 17. The concentration of commercial HCl is about 12 M. What is its pH and pOH?
- 18. The concentration of concentrated H₂SO₄ is about 18 M. Assuming only one H⁺ comes off the H₂SO₄ molecule, what is its pH and pOH? What would the pH and pOH be if the second H⁺ were also ionized?

ANSWERS

1. $Zn + 2HCl \rightarrow ZnCl_2 + H_2$ 2. 3. The O^{2-} ion would come from H₂O, which is not considered a classic acid in the Arrhenius sense. 4. 5. $2Al(OH)_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 6H_2O$ 6. 7. $C_8H_{10}N_4O_2 + H_2O \rightarrow C_8H_{10}N_4O_2H^+ + OH^-$; the H⁺ ion attaches to one of the N atoms in the caffeine molecule. 8. 9. As a strong acid or base, an amphiprotic substance reacts 100% as an acid or a base, so it cannot be a base or an acid at the same time. 10. 11. if the salt produced is an acidic salt 12. 13. NH3 + NH3 \rightarrow NH4⁺ + NH2⁻ 14. 15. pOH > 7 16. 17. pH = -1.08; pOH = 15.08