FOUNDATIONS OF INTRODUCTORY CHEMISTRY-1



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Foundations of Introductory Chemistry-1

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This textmap is an introductory chemistry text aimed for a single semester or quarter beginning experience to the field. The textmaps survey some of the basic topics of chemistry. This survey should give student enough knowledge to appreciate the impact of chemistry in everyday life and, if necessary, prepare student for additional instruction in chemistry.

- 1: What Is Chemistry?

  What is chemistry? Simply put, chemistry is the study of the interactions of matter with other matter and with energy. This seems straightforward enough. However, the definition of chemistry includes a wide range of topics that must be understood to gain a mastery of the topic or even take additional courses in chemistry. In this book, we will lay the foundations of chemistry in a topic-by-topic fashion to provide you with the background you need to successfully understand chemistry.

  - 1.1: Basic Definitions
  - 1.2: Chemistry as a Science

- 2: Measurements

  Chemistry, like all sciences, is quantitative. It deals with quantities, things that have amounts and units. Dealing with quantities is very important in chemistry, as is relating quantities to each other. In this chapter, we will discuss how we deal with numbers and units, including how they are combined and manipulated.

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  - 2.3: The International System of Units
  - 2.4: Converting Units
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- 3: Atoms, Molecules, and Ions

  The basic building block of all matter is the atom. Curiously, the idea of atoms was first proposed in the fifth century BCE, when the Greek philosophers Leucippus and Democritus proposed their existence in a surprisingly modern fashion. However, their ideas never took hold among their contemporaries, and it wasn't until the early 1800s that evidence amassed to make scientists reconsider the idea. Today, the concept of the atom is central to the study of matter.

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- 4: Chemical Reactions and Equations

  Chemistry is largely about chemical changes. Indeed, if there were no chemical changes, chemistry as such would not exist! Chemical changes are a fundamental part of chemistry. Because chemical changes are so central, it may be no surprise that chemistry has developed some special ways of presenting them.

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- 5: Stoichiometry and the Mole
  We have already established that quantities are important in science, especially in chemistry. It is important to make accurate measurements of a variety of quantities when performing experiments. However, it is also important to be able to relate one measured quantity to another, unmeasured quantity. In this chapter, we will consider how we manipulate quantities to relate them to each other.

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- 6: Gases
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- 7: Energy and Chemistry
  Energy is a very important quantity in science and the world around us. Although most of our energy ultimately comes from the sun, much of the energy we use on a daily basis is rooted in chemical reactions. The gasoline in your car, the electricity in your house, the food in your diet - all provide substances for chemical reactions to provide energy (gasoline, food) or are produced from chemical reactions (electricity, about 50% of which is generated by burning coal).

  - 7.1: Energy
  - 7.2: Work and Heat
  - 7.3: Enthalpy and Chemical Reactions
  - 7.4 Internal Energy

- 8: Electronic Structure
  Atoms act the way they do because of their structure. We already know that atoms are composed of protons, neutrons, and electrons. Protons and neutrons are located in the nucleus, and electrons orbit around the nucleus. But we need to know the structural details to understand why atoms react the way they do. Virtually everything we know about atoms ultimately comes from light. Before we can understand the composition of atoms (especially electrons), we need to understand the properties of light.

  - 8.1: Light
  - 8.2: Quantum Numbers for Electrons
  - 8.3: Organization of Electrons in Atoms
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- 9: Chemical Bonds
  How do atoms make compounds? Typically they join together in such a way that they lose their identities as elements and adopt a new identity as a compound. These joins are called chemical bonds. But how do atoms join together? Ultimately, it all comes down to electrons. Before we discuss how electrons interact, we need to introduce a tool to simply illustrate electrons in an atom.
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- 10: Solutions
  A solution is a homogeneous mixture—a mixture of two or more substances that are so intimately mixed that the mixture behaves in many ways like a single substance. Many chemical reactions occur when the reactants are dissolved in solution. In this chapter, we will introduce concepts that are applicable to solutions and the chemical reactions that occur in them.
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- 11: 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.
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  - 13.1: Radioactivity
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- 14: Chemistry of Life: Organic and Biological Chemistry
  Organic chemistry involves the scientific study of the structure, properties, and reactions of organic compounds and organic materials, i.e., matter in its various forms that contain carbon atoms. Organic compounds form the basis of all earthly life and constitute a significant part of human endeavors in chemistry.
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CHAPTER OVERVIEW

1: What Is Chemistry?

What is chemistry? Simply put, chemistry is the study of the interactions of matter with other matter and with energy. This seems straightforward enough. However, the definition of chemistry includes a wide range of topics that must be understood to gain a mastery of the topic or even take additional courses in chemistry. In this book, we will lay the foundations of chemistry in a topic-by-topic fashion to provide you with the background you need to successfully understand chemistry.

1.1 Chemistry as a Science

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1.1 Chemistry as a Science

Learning Objective

- Learn what science is and how it works

Chemistry is a branch of science. Although science itself is difficult to define exactly, the following definition can serve as starting point. Science is the process of knowing about the natural universe through observation and experiment. Science is not the only process of knowing (e.g., the ancient Greeks simply sat and *thought*), but it has evolved over more than 350 years into the best process that humanity has devised to date to learn about the universe around us.

The process of science is usually stated as the *scientific method*, which is rather naïvely described as follows:

1. state a hypothesis,
2. test the hypothesis, and
3. refine the hypothesis.

Actually, however, the process is not that simple. (For example, I don't go into my lab every day and exclaim, "I am going to state a hypothesis today and spend the day testing it!") The process is not that simple because science and scientists have a body of knowledge that has already been identified as coming from the highest level of understanding, and most scientists build from that body of knowledge.

An educated guess about how the natural universe works is called a **hypothesis**. A scientist who is familiar with how part of the natural universe works—say, a chemist—is interested in furthering that knowledge. That person makes a reasonable guess—a hypothesis—that is designed to see if the universe works in a new way as well. Here's an example of a hypothesis: "if I mix one part of hydrogen with one part of oxygen, I can make a substance that contains both elements."

> *For a hypothesis to be termed a scientific hypothesis, it has to be something that can be supported or refuted through carefully crafted experimentation or observation.*

Most good hypotheses are grounded in previously understood knowledge and represent a testable extension of that knowledge. The scientist then devises ways to test if that guess is, or is not, correct. That is, the scientist plans experiments. **Experiments are tests of the natural universe to see if a guess (hypothesis) is correct**. An experiment to test our previous hypothesis would be to actually mix hydrogen and oxygen and see what happens. Most experiments include observations of small, well-defined parts of the natural universe designed to see results of the experiments.

A Scientific Hypothesis

A hypothesis is often written in the form of an if/then statement that gives a possibility (if) and explains what may happen because of the possibility (then). For example, if eating elemental sulfur repels ticks, then someone that is eating sulfur every day will not get ticks.



Why do we have to do experiments? Why do we have to test? Because the natural universe is not always so obvious, experiments are necessary. For example, it is fairly obvious that if you drop an object from a height, it will fall. Several hundred years ago (coincidentally, near the inception of modern science), the concept of gravity explained that test. However, is it obvious that the entire natural universe is composed of only about 115 fundamental chemical building blocks called elements? This wouldn't seem true if you looked at the world around you and saw all the different forms matter can take. In fact, the concept of *the element* is

only about 200 years old, and the last naturally occurring element was identified about 80 years ago. It took decades of tests and millions of experiments to establish what the elements actually are. These are just two examples; a myriad of such examples exists in chemistry and science in general.

When enough evidence has been collected to establish a general principle of how the natural universe works, the evidence is summarized in a **theory**. A theory is a general statement that explains a large number of observations. "All matter is composed of atoms" is a general statement, a theory, that explains many observations in chemistry. A theory is a very powerful statement in science. There are many statements referred to as "the theory of _____" or the "_____ theory" in science (where the blanks represent a word or concept). When written in this way, theories indicate that science has an overwhelming amount of evidence of its correctness. We will see several theories in the course of this text.

A specific statement that is thought to be never violated by the entire natural universe is called a **law**. A scientific law is the highest understanding of the natural universe that science has and is thought to be inviolate. For example, the fact that all matter attracts all other matter—the law of gravitation—is one such law. Note that the terms *theory* and *law* used in science have slightly different meanings from those in common usage; theory is often used to mean hypothesis ("I have a theory…"), whereas a law is an arbitrary limitation that can be broken but with potential consequences (such as speed limits). Here again, science uses these terms differently, and it is important to apply their proper definitions when you use these words in science. (Figure **1**)

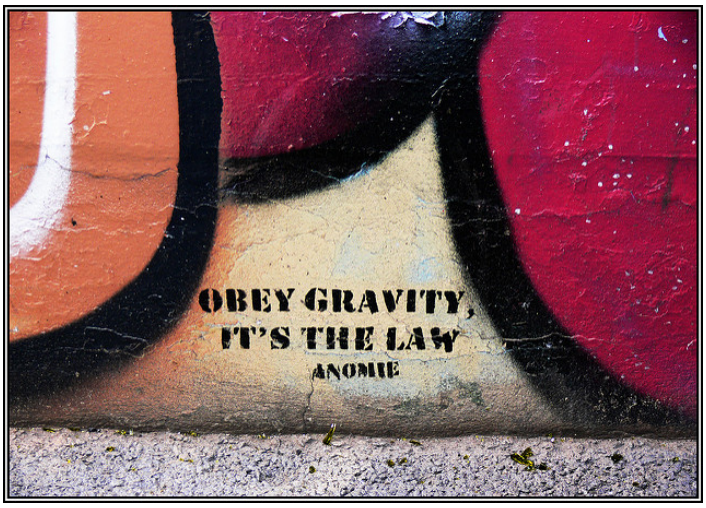


***Figure* 1:** *Defining a law. Does this graffiti mean "law" the way science defines "law"? Image used with permission (CC BY-SA-NC-ND; Koppenbadger).*

There is an additional phrase in our definition of science: "the natural universe." Science is concerned *only* with the natural universe. What is the natural universe? It's anything that occurs around us, well, naturally. Stars, planets, the appearance of life on earth, and how animals, plants, and other matter function are all part of the natural universe. Science is concerned with that—and *only* that.

Of course, there are other things that concern us. For example, is the English language part of science? Most of us can easily answer no; English is not science. English is certainly worth knowing (at least for people in predominantly English-speaking countries), but why isn't it science? English, or any human language, isn't science because ultimately it is *contrived*; it is made up. Think of it: the word spelled b-l-u-e represents a certain color, and we all agree what color that is. But what if we used the word h-a-r-d-n-r-f to describe that color? (Figure **2**) That would be fine—as long as everyone agreed. Anyone who has learned a second language must initially wonder why a certain word is used to describe a certain concept; ultimately, the speakers of that language agreed that a particular word would represent a particular concept. It was contrived.

That doesn't mean language isn't worth knowing. It is very important in society. But it's not *science*. Science deals only with what occurs naturally.

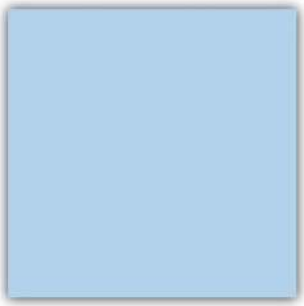


Figure 2: *English Is Not Science. How would you describe this color? Blue or hard? Either way, you're not doing science.*

Example 1: Identifying science

Which of the following fields would be considered science?

a. geology, the study of the earth
b. ethics, the study of morality
c. political science, the study of governance
d. biology, the study of living organisms

Solution

a. Because the earth is a natural object, the study of it is indeed considered part of science.
b. Ethics is a branch of philosophy that deals with right and wrong. Although these are useful concepts, they are not science.
c. There are many forms of government, but all are created by humans. Despite the fact that the word *science* appears in its name, political science is not true science.
d. Living organisms are part of the natural universe, so the study of them is part of science.

Exercise 1

Which is part of science, and which is not?

a. dynamics, the study of systems that change over time
b. aesthetics, the concept of beauty

Answer A

science

Answer B

not science

The field of science has gotten so big that it is common to separate it into more specific fields. First, there is mathematics, the language of science. All scientific fields use mathematics to express themselves—some more than others. Physics and astronomy are scientific fields concerned with the fundamental interactions between matter and energy. Chemistry, as defined previously, is the study of the interactions of matter with other matter and with energy. Biology is the study of living organisms, while geology is the study of the earth. Other sciences can be named as well. Understand that these fields are not always completely separate; the boundaries between scientific fields are not always readily apparent. Therefore, a scientist may be labeled a biochemist if he or she studies the chemistry of biological organisms.

Finally, understand that science can be either qualitative or quantitative. **Qualitative** implies a description of the quality of an object. For example, physical properties are generally qualitative descriptions: sulfur is yellow, your math book is heavy, or that statue is pretty. A **quantitative** description represents the specific amount of something; it means knowing how much of something is present, usually by counting or measuring it. As such, some quantitative descriptions would include 25 students in a class, 650 pages in a book, or a velocity of 66 miles per hour. Quantitative expressions are very important in science; they are also very important in chemistry.

Example 2: qualitative vs. quantitative Descriptions

Identify each statement as either a qualitative description or a quantitative description.

a. Gold metal is yellow.
b. A ream of paper has 500 sheets in it.
c. The weather outside is snowy.
d. The temperature outside is 24 degrees Fahrenheit.

Solution

a. Because we are describing a physical property of gold, this statement is qualitative.
b. This statement mentions a specific amount, so it is quantitative.
c. The word *snowy* is a description of how the day is; therefore, it is a qualitative statement.
d. In this case, the weather is described with a specific quantity—the temperature. Therefore, it is quantitative.

Exercise 2

Are these qualitative or quantitative statements?

a. Roses are red, and violets are blue.
b. Four score and seven years ago….

Answer A

qualitative

Answer B

quantitative

Food and Drink App: Carbonated Beverages

Some of the simple chemical principles discussed in this chapter can be illustrated with carbonated beverages: sodas, beer, and sparkling wines. Each product is produced in a different way, but they all have one thing in common. They are solutions of carbon dioxide dissolved in water.

Carbon dioxide is a compound composed of carbon and oxygen. Under normal conditions, it is a gas. If you cool it down enough, it becomes a solid known as dry ice. Carbon dioxide is an important compound in the cycle of life on earth.

Even though it is a gas, carbon dioxide can dissolve in water, just like sugar or salt can dissolve in water. When that occurs, we have a homogeneous mixture, or a solution, of carbon dioxide in water. However, very little carbon dioxide can dissolve in water. If the atmosphere were pure carbon dioxide, the solution would be only about 0.07% carbon dioxide. In reality, the air is only about 0.03% carbon dioxide, so the amount of carbon dioxide in water is reduced proportionally.

However, when soda and beer are made, manufacturers do two important things: they use pure carbon dioxide gas, and they use it at very high pressures. With higher pressures, more carbon dioxide can dissolve in the water. When the soda or beer container is sealed, the high pressure of carbon dioxide gas remains inside the package. (Of course, there are more ingredients in soda and beer besides carbon dioxide and water.)

When you open a container of soda or beer, you hear a distinctive *hiss* as the excess carbon dioxide gas escapes. But something else happens as well. The carbon dioxide in the solution comes out of solution as a bunch of tiny bubbles. These bubbles impart a pleasing sensation in the mouth, so much so that the soda industry sold over *225 billion* servings of soda in the United States alone in 2009.

Some sparkling wines are made in the same way—by forcing carbon dioxide into regular wine. Some sparkling wines (including champagne) are made by sealing a bottle of wine with some yeast in it. The yeast *ferments*, a process by which the yeast converts sugars into energy and excess carbon dioxide. The carbon dioxide produced by the yeast dissolves in the wine. Then, when the champagne bottle is opened, the increased pressure of carbon dioxide is released, and the drink bubbles just like an expensive glass of soda.



Figure 3: *Carbonated Beverages © Thinkstock Soda, beer, and sparkling wine take advantage of the properties of a solution of carbon dioxide in water.*

Key Takeaways

- Science is a process of knowing about the natural universe through observation and experiment.
- Scientists go through a rigorous process to determine new knowledge about the universe; this process is generally referred to as the scientific method.
- Science is broken down into various fields, of which chemistry is one.
- Science, including chemistry, is both qualitative and quantitative.

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CHAPTER OVERVIEW

2: Measurements

In 1983, an Air Canada airplane had to make an emergency landing because it unexpectedly ran out of fuel; ground personnel had filled the fuel tanks with a certain number of pounds of fuel, not kilograms of fuel. In 1999, the Mars Climate Orbiter spacecraft was lost attempting to orbit Mars because the thrusters were programmed in terms of English units, even though the engineers built the spacecraft using metric units. In 1993, a nurse mistakenly administered 23 units of morphine to a patient rather than the "2–3" units prescribed (the patient ultimately survived). These incidents occurred because people weren't paying attention to quantities.

Chemistry, like all sciences, is quantitative. It deals with *quantities*, things that have amounts and units. Dealing with quantities is very important in chemistry, as is relating quantities to each other. In this chapter, we will discuss how we deal with numbers and units, including how they are combined and manipulated.

2.1 Expressing Numbers - Scientific Notation

2.2 Expressing Numbers - Significant Figures

2.3 The International System of Units

2.4 Converting Units

2.5 Other Units - Temperature and Density

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2.1 Expressing Numbers - Scientific Notation

Learning Objectives

- Express a large number or a small number in scientific notation.
- Convert a number in scientific notation to standard conventional form.

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:

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

That is, 1,500,000 is the same as 1.5 times 1 million, and 1 million is 10 × 10 × 10 × 10 × 10 × 10, or 10^6 (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:

- $10^0 = 1$
- $10^1 = 10$
- $10^2 = 100$
- $10^3 = 1{,}000$
- $10^4 = 10{,}000$
- 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. × 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 first digit, so that the number being multiplied is *between 1 and 10*:

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

Example 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

Express each number in scientific notation.

a. 1,492
b. 102,000,000
c. 101,325

Answer a

Moving the decimal point 3 places to the left gives 1.492×10^3.

Answer b

The decimal point is assumed to be at the end of the number, so moving it 8 places to the left gives 1.02×10^8.

Answer c

Moving the decimal point 5 places to the left yields 1.01325×10^5.

To change a number in **scientific notation** to **standard form**, 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. Lastly, we drop the number 10 and its power.

$$1.5 \times 10^6 = 1.500000 = 1{,}500{,}000$$

✓ Example 2

Express each number in standard, or conventional notation.

a. 5.27×10^4
b. 1.0008×10^6

Answer a

Moving the decimal four places to the right and adding zeros give 52,700.

Answer b

Moving the decimal six places to the right and adding zeros give 1,000,800.

✓ Exercise 2

Express each number in standard, or conventional notation.

a. 6.98×10^8
b. 1.005×10^2

Answer a

Moving the decimal point eight places to the right and adding zeros give 698,000,000.

Answer b

Moving the decimal point two places to the right gives 100.5

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:

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

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:

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

Note:

In writing scientific notations, the convention is to have only one digit before the decimal point.

- Numbers that are greater than one have a positive power in scientific notation. If the decimal point is moved to the left n places, the power (n) of 10 is positive. $1{,}500{,}000 = 1.5 \times 10^{6}$
- Numbers that are less than one have a negative power in scientific notation. If the decimal point is moved to the right n places, the power (n) of 10 is negative. $0.006 = 6 \times 10^{-3}$

Example 3

Express each number in scientific notation.

a. 0.000006567
b. −0.0004004
c. 0.000000000000123

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}.

Exercise 3

Express each number in scientific notation.

a. 0.000355
b. 0.314159
c. −0.051204

Answer a

Moving the decimal point four places to the right gives 3.55×10^{-4}.

Answer b

Moving the decimal point one place to the right gives 3.14159×10^{-1}.

Answer c

Moving the decimal point one place to the right gives -5.1204×10^{-2}.

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

$$6 \times 10^{-3} = .006 = 0.006$$

Note

Changing a number in scientific notation to standard form:

- If the scientific notation has a positive power, the standard number is greater than one. Example: $8 \times 10^{4} = 80{,}000$
- If the scientific notation has a negative power, then the standard number is less than one. Example: $8 \times 10^{-2} = 0.08$

Example 4

Change the number in scientific notation to standard form.

a. 6.22×10^{-2}
b. 9.9×10^{-9}

Answer a

0.0622

Answer b

0.0000000099

Exercise 4

Change the number in scientific notation to standard form.

a. 9.98×10^{-5}
b. 5.109×10^{-8}

Answer a

0.0000998

Answer b

0.00000005109

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.

? Exercise 1

Why it is easier to use scientific notation to express very large or very small numbers?

Answer

Scientific notation is more convenient than listing a large number of zeros.

? Exercise 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?

Answer

The number of places the decimal point moves equals the power of 10. The power of 10 is 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.

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2.2 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**).

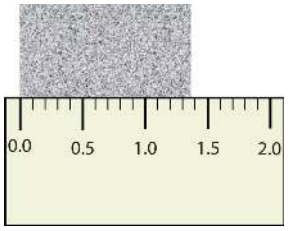


Figure **1**: Measuring an Object to the Correct Number of Digits. How many digits should be reported for the length of this object?

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 *three* 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

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

How many significant figures does each number have?

a. 2.1828
b. 0.005505
c. 55,050
d. 5
e. 500

Answer a

five

Answer b

four

Answer c

four

Answer d

one

Answer e

one

Rounding off numbers

Before dealing with the specifics of the rules for determining the significant figures in a calculated result, we need to be able to round numbers correctly. To **round** a number, first decide how many significant figures the number should have. Once you know that, round to that many digits, starting from the left. **If the number immediately to the right of the last significant digit is less than 5, it is dropped and the value of the last significant digit remains the same. If the number immediately to the right of the last significant digit is greater than or equal to 5, the last significant digit is increased by 1.**

Consider the measurement 207.518m. Right now, the measurement contains six significant figures. How would we successively round it to fewer and fewer significant figures? Follow the process as outlined in Table 1.5.1.

Table 1.5.1: Rounding examples

Number of Significant Figures	Rounded Value	Reasoning
6	207.518	All digits are significant
5	207.52	8 rounds the 1 up to 2
4	207.5	2 is dropped
3	208	5 rounds the 7 up to 8
2	210	8 is replaced by a 0 and rounds the 0 up to 1
1	200	1 is replaced by a 0

Notice that the more rounding that is done, the less reliable the figure is. An approximate value may be sufficient for some purposes, but scientific work requires a much higher level of detail.

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? 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.

> *In operations involving significant figures, the answer is reported in such a way that it reflects the reliability of the **least precise** operation. An answer is no more precise than the least precise number used to get the answer.*

Combining Numbers

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:

$$\underbrace{38.65}_{\text{4 sig figs}} \times \underbrace{105.93}_{\text{5 sig figs}} = \underbrace{4{,}094.1945}_{\text{reduce to 4 sig figs}}$$

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 4,000 has one significant figure and should be written as the number 4×10^4. 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 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 + 610.0 + 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 1,027 has its farthest-right significant figure in the ones column, our answer must be limited to the ones position: 2,000 which in scientific notation is 2.000×10^3.

Exercise 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

Answer a

$0.240 = 2.40 \times 10^{-1}$

Answer b

$1437 = 1.437 \times 10^3$

Answer c

$156 = 1.56 \times 10^2$

Answer d

$2.14 = 2.14 \times 10^0$

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.

Exercise 1

Explain why the concept of significant figures is important in scientific measurements.

Answer

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.

? Exercise 2

State the rules for determining the significant figures in a measurement.

Answer

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.

? Exercise 3

When do you round a number up, and when do you not round a number up?

Answer

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.
- The rule in multiplication and division is that the final answer should have the same number of significant figures as there are in the value with the fewest significant figures.
- The rule in addition and subtraction is that the final answer should have the same number of decimal places as the term with the fewest decimal places.

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2.3 The International System of Units

Learning Objectives

- Recognize the SI base units and explain the system of prefixes used with them.
- Define and calculate density.

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, 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:

$$K = °C + 273 \quad (1)$$

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.

Table 1: The Seven Base SI Units

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

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). 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.

Common prefixes and their multiplicative factors are listed in Table 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 **2**: Prefixes Used with SI Units

Prefix	Abbreviation	Multiplicative Factor	Multiplicative Factor in Scientific Notation
giga-	G	1,000,000,000 ×	10^{9} ×
mega-	M	1,000,000 ×	10^{6} ×
kilo-	k	1,000 ×	10^{3} ×
deca-	D	10 ×	10^{1} ×
deci-	d	1/10 ×	10^{-1} ×
centi-	c	1/100 ×	10^{-2} ×
milli-	m	1/1,000 ×	10^{-3} ×
micro-	μ*	1/1,000,000 ×	10^{-6} ×
nano-	n	1/1,000,000,000 ×	10^{-9} ×

*The letter μ 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.



Figure **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.

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/s^2. 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 × 2 cm, or 4 cm^2 (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.

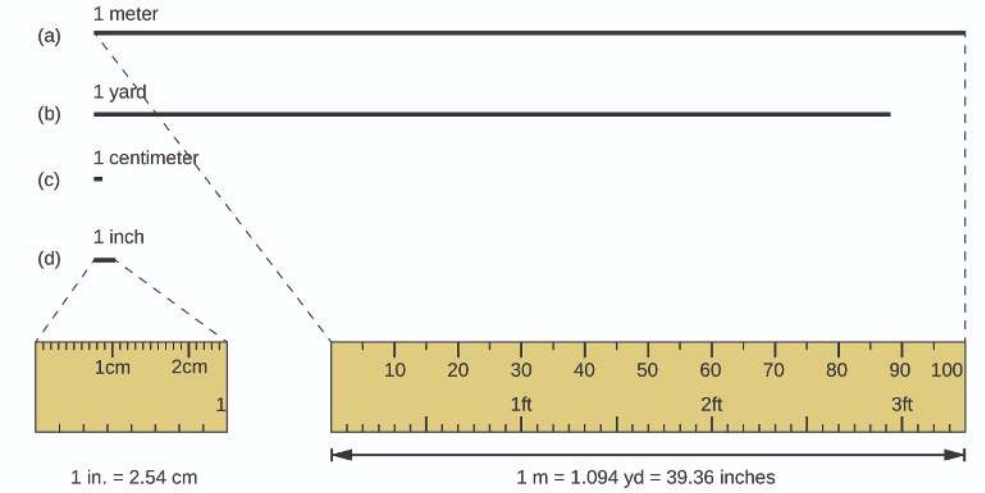


Figure **2**: The relative lengths of 1 m, 1 yd, 1 cm, and 1 in. are shown (not actual size), as well as comparisons of 2.54 cm and 1 in., and of 1 m and 1.094 yd. (CC BY 4.0; OpenStax)

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 m^3 (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. Below are approximate equivalents for some of the units used in chemistry.

Approximate Equivalents to Some SI Units

- 1 m ≈ 39.36 in. ≈ 3.28 ft ≈ 1.09 yd
- 1 in. ≈ 2.54 cm
- 1 km ≈ 0.62 mi
- 1 kg ≈ 2.20 lb
- 1 lb ≈ 454 g
- 1 L ≈ 1.06 qt
- 1 qt ≈ 0.946 L

As shown in Figure **3**, a liter is also 1,000 cm^3. By definition, there are 1,000 mL in 1 L, so 1 milliliter and 1 cubic centimeter represent the same volume.

$$1\ mL = 1\ cm^3 \tag{2}$$

Example 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 0.000000001 g.

Exercise 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

Answer a

km (1,000 m)

Answer b

mg (0.001 g)

Answer c

ns (0.000000001 s)

Answer d

cL (0.01L)

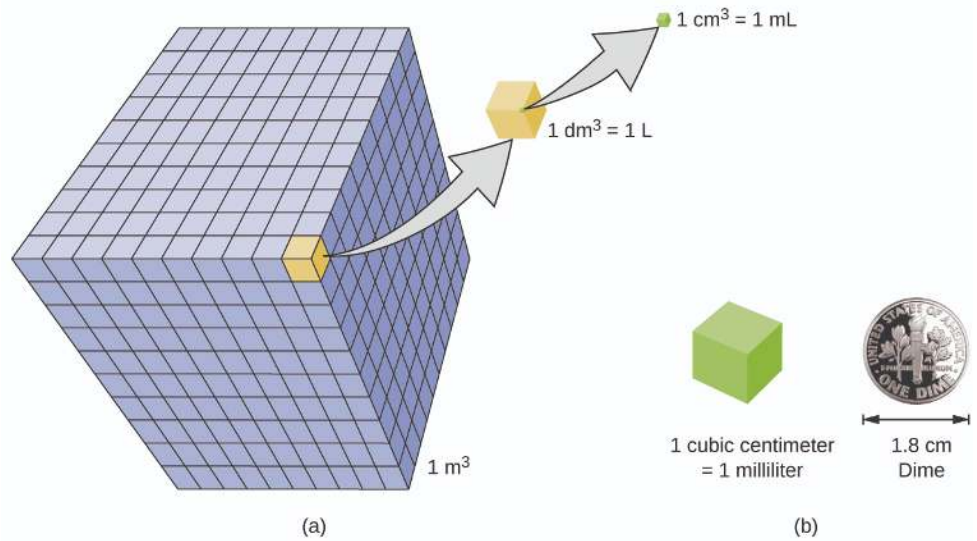


Figure **3**: Units of Volume. (a) The relative volumes are shown for cubes of 1 m^3, 1 dm^3 (1 L), and 1 cm^3 (1 mL) (not to scale). A liter (L) is defined as a cube 1 dm (1/10th of a meter) on a side. A milliliter (mL), 1/1,000th of a liter, is equal to 1 cubic centimeter. (b) The diameter of a dime is compared relative to the edge length of a 1-cm^3 (1-mL) cube. (CC BY 4.0; OpenStax)

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•m^2/s^2. (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.

$$\text{density} = \frac{\text{mass}}{\text{volume}} \tag{3}$$

Thus, the units of density are the units of mass divided by the units of volume: g/cm^3 or g/mL (for solids and liquids), g/L (for gases), kg/m^3, and so forth. For example, the density of water is about 1.00 g/cm^3, while the density of mercury is 13.6 g/mL. (Remember that 1 mL equals 1 cm^3.) 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. Table 1.6.3 shows the densities of some common substances.

Table **2**: Densities of Common Substances

Solids	Liquids	Gases (at 25 °C and 1 atm)
ice (at 0 °C) 0.92 g/cm^3	water 1.0 g/cm^3	dry air 1.20 g/L
oak (wood) 0.60–0.90 g/cm^3	ethanol 0.79 g/cm^3	oxygen 1.31 g/L
iron 7.9 g/cm^3	acetone 0.79 g/cm^3	nitrogen 1.14 g/L
copper 9.0 g/cm^3	glycerin 1.26 g/cm^3	carbon dioxide 1.80 g/L
lead 11.3 g/cm^3	olive oil 0.92 g/cm^3	helium 0.16 g/L
silver 10.5 g/cm^3	gasoline 0.70–0.77 g/cm^3	neon 0.83 g/L
gold 19.3 g/cm^3	mercury 13.6 g/cm^3	radon 9.1 g/L

Example 2: Density of Bone

What is the density of a section of bone if a 25.3 cm^3 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:

$$\begin{aligned} \text{density} &= \frac{mass}{volume} \\ &= \frac{27.8\ g}{25.3\ cm^3} \\ &= 1.10\ g/cm^3 \end{aligned}$$

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

? Exercise 2: Density of Oxygen

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

Answer

1.45 g/L

Density can be used to convert between the mass and the volume of a substance. This will be discussed in the next section.

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.
3. What is density?

Answers

1. Base units are the seven fundamental units of SI; derived units are constructed by making combinations of the base units; Two examples of base units: kilograms and meters (answers will vary); Two examples of derived units: grams per milliliter and joules (answers will vary).
2. yes; $\mathbf{mL} \times \frac{\mathbf{g}}{\mathbf{mL}} = \mathbf{g}$ (answers will vary)
3. Density is defined as the mass of an object divided by its volume

Key Takeaways

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

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2.4 Converting Units

Learning Objectives

- 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.

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

or

$$100\ \text{cm} = 1\ \text{m}$$

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

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

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 and the denominator has a value of 1:

$$\text{same quantity} \left\langle \frac{100\ \text{cm}}{1\ \text{m}} = 1 \right.$$

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:

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

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:

$$\frac{3.55\ \cancel{\text{m}}}{1} \times \frac{100\ \text{cm}}{1\ \cancel{\text{m}}}$$

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

$$\frac{3.55}{1} \times \frac{100\ \text{cm}}{1} = 355\ \text{cm} \tag{1}$$

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:

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

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), 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:

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

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 shows a **concept map** for constructing a proper conversion.

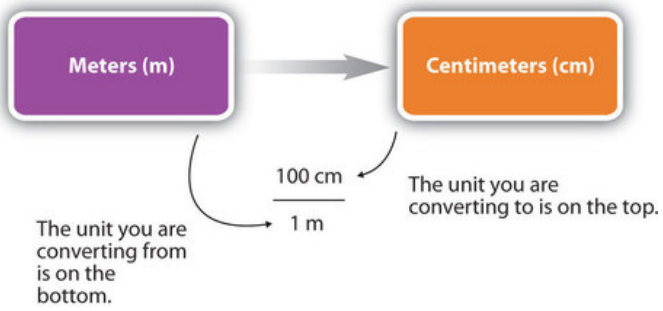


Figure 1: A Concept Map for Conversions. This is how you construct a conversion factor to convert from one unit to another.

Meters converted to centimeters. A fraction showing 100 cm over 1 m. The unit you convert to is on top, and the unit you convert from is on bottom.

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

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:

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

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.



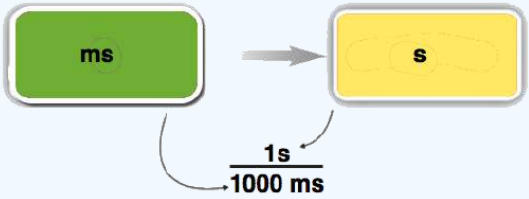
$$4.7 \cancel{L} \times \frac{1,000 \text{ mL}}{1 \cancel{L}} = 4,700 \text{ mL}$$

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:

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

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:



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

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

? Exercise 1

Perform each conversion.

a. 101,000 ns to seconds
b. 32.08 kg to grams

Answer a

$$101,000 \cancel{\text{ns}} \times \frac{1 \text{ s}}{1,000,000,000 \cancel{\text{ns}}} = 0.000101 \text{ s}$$

Answer b

$$32.08 \cancel{\text{kg}} \times \frac{1,000 \text{ g}}{1 \cancel{\text{kg}}} = 32,080 \text{ g}$$

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:

$$\frac{13.6\ \text{g}}{1\ \text{mL}} \text{ and } \frac{1\ \text{mL}}{13.6\ \text{g}}$$

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:

$$16\ \cancel{\text{mL}} \times \frac{13.6\ \text{g}}{1\ \cancel{\text{mL}}} = 217.6\ \text{g}$$

$$\approx 220\ \text{g}$$

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 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.

$$0.750\ \cancel{\text{g}} \times \frac{1\ \text{mL}}{13.6\ \cancel{\text{g}}} = 0.055147\ldots\ \text{mL}$$

$$\approx 0.0551\ \text{mL}$$

We have limited the final answer to three significant figures.

Exercise 2

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

Answer

$$100.0\ \cancel{\text{g}} \times \frac{1\ \text{L}}{1.3\ \cancel{\text{g}}} = 76.92307692\ \text{L} \approx 77\text{L}$$

Because the density (1.3 g/L) has only 2 significant figures, we are rounding off the final answer to 2 significant figures.

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/cm^3. Osteoporosis is diagnosed if the bone density is below 0.6–0.7 g/cm^3.

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:

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

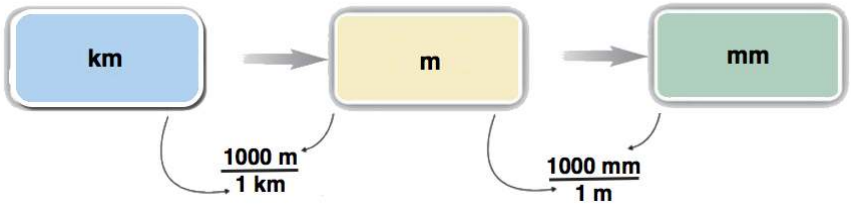
Then we take the result (54,700 m) and convert it to millimeters, remembering that there are $1,000 \text{ mm}$ for every 1 m:

$$\begin{aligned} 54,700 \cancel{\text{m}} \times \frac{1,000 \text{ mm}}{1 \cancel{\text{m}}} &= 54,700,000 \text{ mm} \\ &= 5.47 \times 10^7 \text{ mm} \end{aligned}$$

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:

Concept Map



Calculation

$$\begin{aligned} 54.7 \cancel{\text{km}} \times \frac{1,000 \cancel{\text{m}}}{1 \cancel{\text{km}}} \times \frac{1,000 \text{ mm}}{1 \cancel{\text{m}}} &= 54,700,000 \text{ mm} \\ &= 5.47 \times 10^7 \text{ mm} \end{aligned}$$

In each step, the previous unit is canceled and the next unit in the sequence is produced, each successive unit canceling out until only the unit needed in the answer is left.

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.

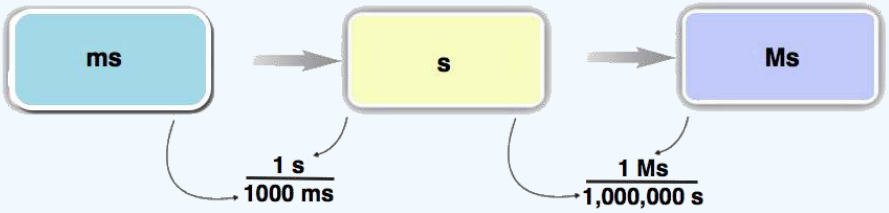
Example 3

Convert 58.2 ms to megaseconds in one multistep calculation.

Solution

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

Concept Map



Calculation

$$58.2 \cancel{\text{ms}} \times \frac{1 \cancel{\text{s}}}{1{,}000 \cancel{\text{ms}}} \times \frac{1 \text{ Ms}}{1{,}000{,}000 \cancel{\text{s}}} = 0.0000000582 \text{ Ms}$$

$$= 5.82 \times 10^{-8} \text{ Ms}$$

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

Exercise 3

Convert 43.007 mg to kilograms in one multistep calculation.

Answer

$$43.007 \cancel{\text{mg}} \times \frac{1 \cancel{\text{g}}}{1{,}000 \cancel{\text{mg}}} \times \frac{1 \text{ kg}}{1{,}000 \cancel{\text{g}}} = 0.000043007 \text{ kg}$$

$$= 4.3007 \times 10^{-5} \text{ kg}$$

.

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

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 $\mathbf{1.0 \times 10^{12}}$ *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.
3. Concept Map: Convert the given (nanoliters, nL) to liters; then convert liters to kiloliters.



1.0 times 10 to the 12th nL converts to 1000 Liters converts to 1 kiloLiter. One Liter is 1.0 times 10 to the 9th nL. One kiloLiter is 1000 Liters.

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2.5 Other Units - Temperature and Density

Learning Objective

- Learn about the various temperature scales that are commonly used in chemistry.
- Define density and use it as a conversion factor.

There are other units in chemistry that are important, and we will cover others over the course of the entire book. One of the fundamental quantities in science is temperature. Temperature is a measure of the average amount of energy of motion, or *kinetic energy*, a system contains. Temperatures are expressed using scales that use units called degrees, and there are several temperature scales in use. In the United States, the commonly used temperature scale is the *Fahrenheit scale* (symbolized by °F and spoken as "degrees Fahrenheit"). On this scale, the freezing point of liquid water (the temperature at which liquid water turns to solid ice) is 32°F, and the boiling point of water (the temperature at which liquid water turns to steam) is 212°F.

Science also uses other scales to express temperature. The Celsius scale (symbolized by °C and spoken as "degrees Celsius") is a temperature scale where 0°C is the freezing point of water and 100°C is the boiling point of water; the scale is divided into 100 divisions between these two landmarks and extended higher and lower. By comparing the Fahrenheit and Celsius scales, a conversion between the two scales can be determined:

$$^{\circ}\text{C} = (^{\circ}\text{F-32}) \times \tfrac{5}{9} \quad (1)$$

$$^{\circ}\text{F} = (^{\circ}\text{C} \times \tfrac{9}{5}) + 32 \quad (2)$$

Example 1: Conversions

a. What is 98.6 °F in degrees Celsius?
b. What is 25.0 °C in degrees Fahrenheit?

Solution

a. Using Equation 1, we have

$$\begin{aligned} ^{\circ}C &= (98.6 - 32) \times \frac{5}{9} \\ &= 66.6 \times \frac{5}{9} \\ &= 37.0^{\circ}C \end{aligned}$$

b. Using Equation 2, we have

$$\begin{aligned} ^{\circ}F &= \left(25.0 \times \frac{9}{5}\right) + 32 \\ &= 45.0 + 32 \\ &= 77.0^{\circ}F \end{aligned}$$

Exercise 1

a. Convert 0 °F to degrees Celsius.
b. Convert 212 °C to degrees Fahrenheit.

Answer a

−17.8 °C

Answer b

414 °F

The fundamental unit of temperature (another fundamental unit of science, bringing us to four) in SI is the kelvin (K). The Kelvin temperature scale (note that the name of the scale capitalizes the word *Kelvin*, but the unit itself is lowercase) uses degrees that are the same size as the Celsius degree, but the numerical scale is shifted up by 273.15 units. That is, the conversion between the Kelvin and Celsius scales is as follows:

$$K = {}^\circ C + 273.15$$

For most purposes, it is acceptable to use 273 instead of 273.15. Note that the Kelvin scale does not use the word *degrees*; a temperature of 295 K is spoken of as "two hundred ninety-five kelvins" and not "two hundred ninety-five degrees Kelvin."

The reason that the Kelvin scale is defined this way is because there exists a minimum possible temperature called absolute zero (zero kelvins). The Kelvin temperature scale is set so that 0 K is absolute zero, and temperature is counted upward from there. Normal room temperature is about 295 K, as seen in the following example.

Example 2: Room Temperature

If normal room temperature is 72.0°F, what is room temperature in degrees Celsius and kelvin?

Solution

First, we use the formula to determine the temperature in degrees Celsius:

$$\begin{aligned} {}^\circ C &= (72.0 - 32) \times \frac{5}{9} \\ &= 40.0 \times \frac{5}{9} \\ &= 22.2^\circ C \end{aligned}$$

Then we use the appropriate formula above to determine the temperature in the Kelvin scale:

$$\begin{aligned} K &= 22.2^\circ C + 273.15 \\ &= 295.4 K \end{aligned}$$

So, room temperature is about 295 K.

Exercise 2

What is 98.6°F on the Kelvin scale?

Answer

310.2 K

Figure 1 compares the three temperature scales. Note that science uses the Celsius and Kelvin scales almost exclusively; virtually no practicing chemist expresses laboratory-measured temperatures with the Fahrenheit scale. In fact, the United States is one of the few countries in the world that still uses the Fahrenheit scale on a daily basis. The other two countries are Liberia and Myanmar (formerly Burma). People driving near the borders of Canada or Mexico may pick up local radio stations on the other side of the border that express the daily weather in degrees Celsius, so do not get confused by their weather reports.

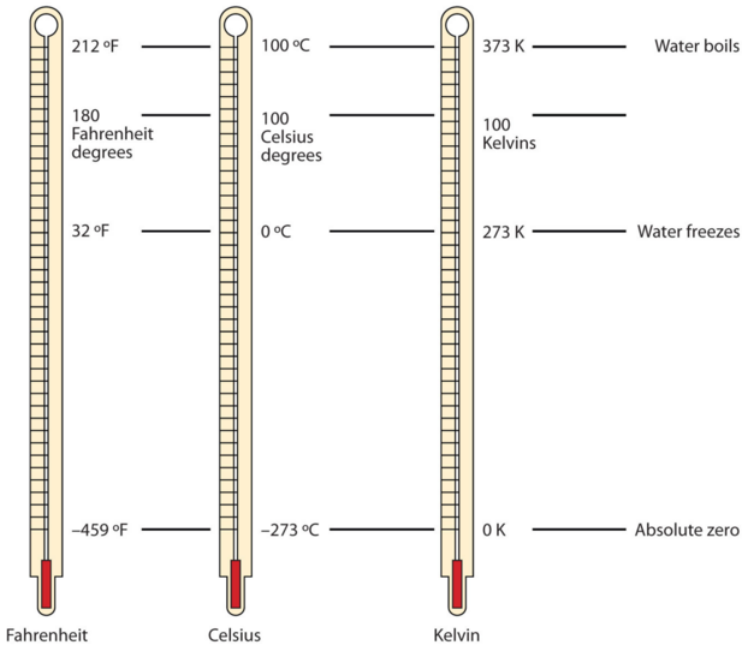


Figure 1: Fahrenheit, Celsius, and Kelvin Temperatures. A comparison of the three temperature scales.

Density

Density is a physical property that is defined as a substance's mass divided by its volume:

$$density = \frac{mass}{volume} \Rightarrow d = \frac{m}{v}$$

Density is usually a measured property of a substance, so its numerical value affects the significant figures in a calculation. Notice that density is defined in terms of two dissimilar units, mass and volume. That means that density overall has derived units, just like velocity. Common units for density include g/mL, g/cm^3, g/L, kg/L, and even kg/m^3. Densities for some common substances are listed in Table 1.

Table 1: Densities of Some Common Substances

Substance	Density (g/mL or g/cm^3)
water	1.0
gold	19.3
mercury	13.6
air	0.0012
cork	0.22–0.26
aluminum	2.7
iron	7.87

Because of how it is defined, density can act as a conversion factor for switching between units of mass and volume. For example, suppose you have a sample of aluminum that has a volume of 7.88 cm^3. How can you determine what mass of aluminum you have without measuring it? You can use the volume to calculate it. If you multiply the given volume by the known density (from Table 1), the volume units will cancel and leave you with mass units, telling you the mass of the sample:

$$7.88\ \cancel{cm^3} \times \frac{2.7\ g}{\cancel{cm^3}} = 21\ g\ \text{of aluminium}$$

where we have limited our answer to two significant figures.

Example 3: Mercury

What is the mass of 44.6 mL of mercury?

Solution

Use the density from Table 1 "Densities of Some Common Substances" as a conversion factor to go from volume to mass:

$$44.6 \cancel{mL} \times \frac{13.6\,g}{\cancel{mL}} = 607\,g$$

The mass of the mercury is 607 g.

Exercise 3

What is the mass of 25.0 cm^3 of iron?

Answer

197 g

Density can also be used as a conversion factor to convert mass to volume—but care must be taken. We have already demonstrated that the number that goes with density normally goes in the numerator when density is written as a fraction. Take the density of gold, for example:

$$d = 19.3\,g/mL = \frac{19.3\,g}{mL}$$

Although this was not previously pointed out, it can be assumed that there is a 1 in the denominator:

$$d = 19.3\,g/mL = \frac{19.3\,g}{mL}$$

That is, the density value tells us that we have 19.3 grams for every 1 milliliter of volume, and the 1 is an exact number. When we want to use density to convert from mass to volume, the numerator and denominator of density need to be switched—that is, we must take the *reciprocal* of the density. In so doing, we move not only the units, but also the numbers:

$$\frac{1}{d} = \frac{1\,mL}{19.3\,g}$$

This reciprocal density is still a useful conversion factor, but now the mass unit will cancel and the volume unit will be introduced. Thus, if we want to know the volume of 45.9 g of gold, we would set up the conversion as follows:

$$45.9 \cancel{g} \times \frac{1\,mL}{19.3\,\cancel{g}} = 2.38\,mL$$

Note how the mass units cancel, leaving the volume unit, which is what we are looking for.

Example 4: Calculating Volume from Density

A cork stopper from a bottle of wine has a mass of 3.78 g. If the density of cork is 0.22 g/cm^3, what is the volume of the cork?

Solution

To use density as a conversion factor, we need to take the reciprocal so that the mass unit of density is in the denominator. Taking the reciprocal, we find:

$$\frac{1}{d} = \frac{1\,cm^3}{0.22\,g}$$

We can use this expression as the conversion factor. So

$$3.78\ \cancel{g} \times \frac{1\ cm^3}{0.22\ \cancel{g}} = 17.2\ cm^3$$

? Exercise 4

What is the volume of 3.78 g of gold?

Answer

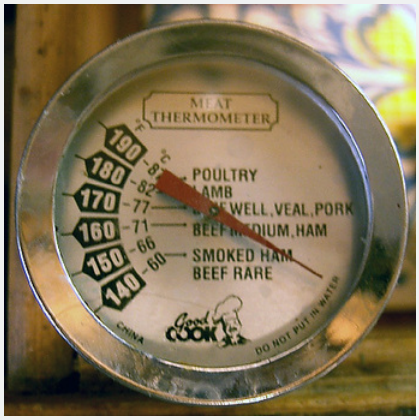
0.196 cm^3

Care must be used with density as a conversion factor. Make sure the mass units are the same, or the volume units are the same, before using density to convert to a different unit. Often, the unit of the given quantity must be first converted to the appropriate unit before applying density as a conversion factor.

Food and Drink Application: Cooking Temperatures

Because degrees Fahrenheit is the common temperature scale in the United States, kitchen appliances, such as ovens, are calibrated in that scale. A cool oven may be only 150°F, while a cake may be baked at 350°F and a chicken roasted at 400°F. The broil setting on many ovens is 500°F, which is typically the highest temperature setting on a household oven.

People who live at high altitudes, typically 2,000 ft above sea level or higher, are sometimes urged to use slightly different cooking instructions on some products, such as cakes and bread, because water boils at a lower temperature the higher in altitude you go, meaning that foods cook slower. For example, in Cleveland water typically boils at 212°F (100°C), but in Denver, the Mile-High City, water boils at about 200°F (93.3°C), which can significantly lengthen cooking times. Good cooks need to be aware of this.



A meat thermometer with a dial. Notice the markings for Fahrenheit (outer scale) and Celsius (inner scale) temperatures. Recipes for cooking food in an oven can use very different numbers, depending on the country you're in. (CC BY2.0 Bev Sykes)

At the other end is pressure cooking. A pressure cooker is a closed vessel that allows steam to build up additional pressure, which increases the temperature at which water boils. A good pressure cooker can get to temperatures as high as 252°F (122°C); at these temperatures, food cooks much faster than it normally would. Great care must be used with pressure cookers because of the high pressure and high temperature. (When a pressure cooker is used to sterilize medical instruments, it is called an *autoclave*.)

Other countries use the Celsius scale for everyday purposes. Therefore, oven dials in their kitchens are marked in degrees Celsius. It can be confusing for US cooks to use ovens abroad—a 425°F oven in the United States is equivalent to a 220°C oven in other countries. These days, many oven thermometers are marked with both temperature scales.

Key Takeaways

- Chemistry uses the Celsius and Kelvin scales to express temperatures.
- A temperature on the Kelvin scale is the Celsius temperature plus 273.15.
- The minimum possible temperature is absolute zero and is assigned 0 K on the Kelvin scale.
- Density relates the mass and volume of a substance.
- Density can be used to calculate volume from a given mass or mass from a given volume.

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CHAPTER OVERVIEW

4: Atoms, Molecules, and Ions

The basic building block of all matter is the atom. Curiously, the idea of atoms was first proposed in the fifth century BCE, when the Greek philosophers Leucippus and Democritus proposed their existence in a surprisingly modern fashion. However, their ideas never took hold among their contemporaries, and it wasn't until the early 1800s that evidence amassed to make scientists reconsider the idea. Today, the concept of the atom is central to the study of matter.

3.4 Acids
3.5 Masses of Atoms and Molecules
3.6 Monotomic Ions of Various Charges
4.01 The Elements and Symbols
4.1: Molecules and Chemical Nomenclature
4.2 Atomic Theory
4.3 Isotopes
4.4: The Periodic Table
4.5 Ions
4.6 Ionic Compounds

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3.4 Acids

Learning Objectives

- Define *acid*.
- Name a simple acid.

There is one other group of compounds that is important to us—acids—and these compounds have interesting chemical properties. Initially, we will define an acid as an ionic compound of the H^+ cation dissolved in water. To indicate that something is dissolved in water, we will use the phase label (aq) next to a chemical formula (where aq stands for "aqueous," a word that describes something dissolved in water). If the formula does not have this label, then the compound is treated as a molecular compound rather than an acid.

Acids have their own nomenclature system. If an acid is composed of only hydrogen and one other element, the name is *hydro-* + the stem of the other element + *-ic acid*. For example, the compound HCl(aq) is hydrochloric acid, while H_2S(aq) is hydrosulfuric acid. If these acids were not dissolved in water, the compounds would be called hydrogen chloride and hydrogen sulfide, respectively. Both of these substances are well known as molecular compounds; when dissolved in water, however, they are treated as acids.

If a compound is composed of hydrogen ions and a polyatomic anion, then the name of the acid is derived from the stem of the polyatomic ion's name. Typically, if the anion name ends in -ate, the name of the acid is the stem of the anion name plus *-ic acid*; if the related anion's name ends in -ite, the name of the corresponding acid is the stem of the anion name plus *-ous acid*. Table **1** lists the formulas and names of a variety of acids that you should be familiar with. You should recognize most of the anions in the formulas of the acids.

Table **1** Names and Formulas of Acids

Formula	Name
$HC_2H_3O_2$	acetic acid
$HClO_3$	chloric acid
HCl	hydrochloric acid
HBr	hydrobromic acid
HI	hydriodic acid
HF	hydrofluoric acid
HNO_3	nitric acid
$H_2C_2O_4$	oxalic acid
$HClO_4$	perchloric acid
H_3PO_4	phosphoric acid
H_2SO_4	sulfuric acid
H_2SO_3	sulfurous acid

Note: The "aq" label is omitted for clarity.

Example 1

Name each acid without consulting Table 3.9.

1. HBr

2. H_2SO_4

Solution

1. As a binary acid, the acid's name is *hydro-* + stem name + *-ic acid*. Because this acid contains a bromine atom, the name is hydrobromic acid.
2. Because this acid is derived from the sulfate ion, the name of the acid is the stem of the anion name + *-ic acid*. The name of this acid is sulfuric acid.

? Exercise 1

Name each acid.

a. HF
b. HNO_2

Answer a

hydrofluoric acid

Answer b

nitrous acid

All acids have some similar properties. For example, acids have a sour taste; in fact, the sour taste of some of our foods, such as citrus fruits and vinegar, is caused by the presence of acids in food. Many acids react with some metallic elements to form metal ions and elemental hydrogen. Acids make certain plant pigments change colors; indeed, the ripening of some fruits and vegetables is caused by the formation or destruction of excess acid in the plant. In Chapter 12, we will explore the chemical behavior of acids.

Acids are very prevalent in the world around us. We have already mentioned that citrus fruits contain acid; among other compounds, they contain citric acid, $H_3C_6H_5O_7(aq)$. Oxalic acid, $H_2C_2O_4(aq)$, is found in spinach and other green leafy vegetables. Hydrochloric acid not only is found in the stomach (stomach acid), but also can be bought in hardware stores as a cleaner for concrete and masonry. Phosphoric acid is an ingredient in some soft drinks.

Key Takeaways

- An acid is a compound of the H^+ ion dissolved in water.
- Acids have their own naming system.
- Acids have certain chemical properties that distinguish them from other compounds.

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3.5 Masses of Atoms and Molecules

Learning Objective

- Express the masses of atoms and molecules.

Because matter is defined as anything that has mass and takes up space, it should not be surprising to learn that atoms and molecules have mass.

Individual atoms and molecules, however, are very small, and the masses of individual atoms and molecules are also very small. For macroscopic objects, we use units such as grams and kilograms to state their masses, but these units are much too big to comfortably describe the masses of individual atoms and molecules. Another scale is needed.

Atomic Mass Unit

The atomic mass unit (u; some texts use amu, but this older style is no longer accepted) is defined as one-twelfth of the mass of a carbon-12 atom, an isotope of carbon that has six protons and six neutrons in its nucleus. By this scale, the mass of a proton is 1.00728 u, the mass of a neutron is 1.00866 u, and the mass of an electron is 0.000549 u. There will not be much error if you estimate the mass of an atom by simply counting the total number of protons and neutrons in the nucleus (i.e., identify its mass number) and ignore the electrons. Thus, the mass of carbon-12 is about 12 u, the mass of oxygen-16 is about 16 u, and the mass of uranium-238 is about 238 u. More exact masses are found in scientific references—for example, the exact mass of uranium-238 is 238.050788 u, so you can see that we are not far off by using the whole-number value as the mass of the atom.

What is the mass of an element? This is somewhat more complicated because most elements exist as a mixture of isotopes, each of which has its own mass. Thus, although it is easy to speak of the mass of an atom, when talking about the mass of an element, we must take the isotopic mixture into account.

Atomic Mass

The atomic mass of an element is a weighted average of the masses of the isotopes that compose an element. What do we mean by a weighted average? Well, consider an element that consists of two isotopes, 50% with mass 10 u and 50% with mass 11 u. A weighted average is found by multiplying each mass by its fractional occurrence (in decimal form) and then adding all the products. The sum is the weighted average and serves as the formal atomic mass of the element. In this example, we have the following:

$(^{50}/_{100}) \times 10$ u	$= 0.50 \times 10$ u	$= 5.0$ u
$(^{50}/_{100}) \times 11$ u	$= 0.50 \times 11$ u	$= 5.5$ u
	Sum	$= 10.5$ u = the atomic mass of our element

Note that no atom in our hypothetical element has a mass of 10.5 u; rather, that is the average mass of the atoms, weighted by their percent occurrence.

This example is similar to a real element. Boron exists as about 20% boron-10 (five protons and five neutrons in the nuclei) and about 80% boron-11 (five protons and six neutrons in the nuclei). The atomic mass of boron is calculated similarly to what we did for our hypothetical example, but the percentages are different:

$(^{20}/_{100}) \times 10$ u	$= 0.20 \times 10$ u	$= 2.0$ u
$(^{80}/_{100}) \times 11$ u	$= 0.80 \times 11$ u	$= 8.8$ u
	Sum	$= 10.8$ u = the atomic mass of boron

Thus, we use 10.8 u for the atomic mass of boron.

Virtually all elements exist as mixtures of isotopes, so atomic masses may vary significantly from whole numbers. Table 3.4.1 lists the atomic masses of some elements. The atomic masses in Table **1** are listed to three decimal places where possible, but in most

cases, only one or two decimal places are needed. Note that many of the atomic masses, especially the larger ones, are not very close to whole numbers. This is, in part, the effect of an increasing number of isotopes as the atoms increase in size. (The record number is 10 isotopes for tin.)

Table 1: Selected Atomic Masses of Some Elements (part 1)

Element Name	Atomic Mass (u)
Aluminum	26.981
Argon	39.948
Arsenic	74.922
Barium	137.327
Beryllium	9.012
Bismuth	208.980
Boron	10.811
Bromine	79.904
Calcium	40.078
Carbon	12.011
Chlorine	35.453
Cobalt	58.933
Copper	63.546
Fluorine	18.998
Gallium	69.723
Germanium	72.64
Gold	196.967
Helium	4.003
Hydrogen	1.008
Iodine	126.904
Iridium	192.217
Iron	55.845
Krypton	83.798
Lead	207.2
Lithium	6.941
Magnesium	24.305
Manganese	54.938
Mercury	200.59

Note: Atomic mass is given to three decimal places, if known.

Table 1: Selected Atomic Masses of Some Elements (part 2)

Element Name	Atomic Mass (u)
Molybdenum	95.94
Neon	20.180
Nickel	58.693
Nitrogen	14.007
Oxygen	15.999
Palladium	106.42
Phosphorus	30.974
Platinum	195.084
Potassium	39.098
Radium	n/a
Radon	n/a
Rubidium	85.468
Scandium	44.956
Selenium	78.96
Silicon	28.086
Silver	107.868
Sodium	22.990
Strontium	87.62
Sulfur	32.065
Tantalum	180.948
Tin	118.710
Titanium	47.867
Tungsten	183.84
Uranium	238.029
Xenon	131.293
Zinc	65.409
Zirconium	91.224
Molybdenum	95.94

Note: Atomic mass is given to three decimal places, if known.

Molecular Mass

Now that we understand that atoms have mass, it is easy to extend the concept to the mass of molecules. The molecular mass is the sum of the masses of the atoms in a molecule. This may seem like a trivial extension of the concept, but it is important to count the number of each type of atom in the molecular formula. Also, although each atom in a molecule is a particular isotope, we use the weighted average, or atomic mass, for each atom in the molecule.

For example, if we were to determine the molecular mass of dinitrogen trioxide, N_2O_3, we would need to add the atomic mass of nitrogen two times with the atomic mass of oxygen three times (the masses for each element are found on the periodic table):

2 N masses = 2 × 14.007 u	= 28.014 u
3 O masses = 3 × 15.999 u	= 47.997 u
Total	= 76.011 u = the molecular mass of N_2O_3

We would not be far off if we limited our numbers to one or even two decimal places.

Example 1:

What is the molecular mass of each substance?

1. NBr_3
2. C_2H_6

Solution

1. Add one atomic mass of nitrogen and three atomic masses of bromine:

1 N mass	= 14.007 u
3 Br masses = 3 × 79.904 u	= 239.712 u
Total	= 253.719 u = the molecular mass of NBr_3

2. Add two atomic masses of carbon and six atomic masses of hydrogen:

2 C masses = 2 × 12.011 u	= 24.022 u
6 H masses = 6 × 1.008 u	= 6.048 u
Total	= 30.070 u = the molecular mass of C_2H_6

The compound C_2H_6 also has a common name—ethane.

Exercise 1

What is the molecular mass of each substance?

a. SO_2
b. PF_3

Answer a

64.063 u

Answer b

87.968 u

Chemistry Is Everywhere: Sulfur Hexafluoride

On March 20, 1995, the Japanese terrorist group Aum Shinrikyo (Sanskrit for “Supreme Truth”) released some sarin gas in the Tokyo subway system; twelve people were killed, and thousands were injured (part (a) in the accompanying figure). Sarin (molecular formula $C_4H_{10}FPO_2$) is a nerve toxin that was first synthesized in 1938. It is regarded as one of the most deadly toxins known, estimated to be about 500 times more potent than cyanide. Scientists and engineers who study the spread of chemical weapons such as sarin (yes, there are such scientists) would like to have a less dangerous chemical, indeed one that is nontoxic, so they are not at risk themselves.

Sulfur hexafluoride is used as a model compound for sarin. SF_6 (a molecular model of which is shown in part (b) in the accompanying figure) has a similar molecular mass (about 146 u) as sarin (about 140 u), so it has similar physical properties in the vapor phase. Sulfur hexafluoride is also very easy to accurately detect, even at low levels, and it is not a normal part of the atmosphere, so there is little potential for contamination from natural sources. Consequently, SF_6 is also used as an aerial tracer for ventilation systems in buildings. It is nontoxic and very chemically inert, so workers do not have to take special precautions other than watching for asphyxiation.

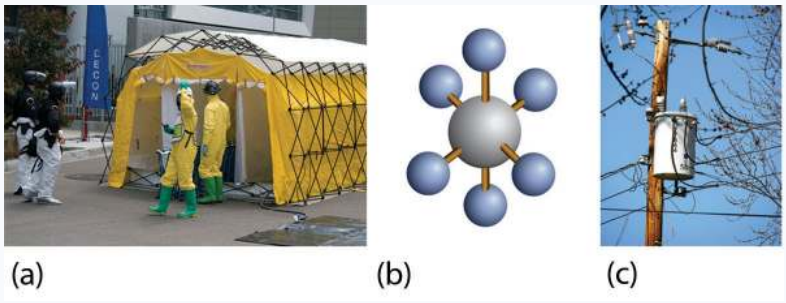


Figure 2: *Sarin and Sulfur Hexafluoride © Thinkstock (a) Properly protected workers clear out the Tokyo subway after the nerve toxin sarin was released. (b) A molecular model of SF_6. (c) A high-voltage electrical switchgear assembly that would be filled with SF_6 as a spark suppressant.*

Sulfur hexafluoride also has another interesting use: a spark suppressant in high-voltage electrical equipment. High-pressure SF_6 gas is used in place of older oils that may have contaminants that are environmentally unfriendly (part (c) in the accompanying figure).

Key Takeaways

- The atomic mass unit (u) is a unit that describes the masses of individual atoms and molecules.
- The atomic mass is the weighted average of the masses of all isotopes of an element.
- The molecular mass is the sum of the masses of the atoms in a molecule.

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3.6 Monotomic Ions of Various Charges

Table 1: *Additional Monatomic Ions of Various Charges*

Ions formed by losing a single electron	Rb^{+}
	Ag^{+}
	Au^{+}
Ions formed by losing two electrons	Fe^{2+}
	Co^{2+}
	Ni^{2+}
	Cu^{2+}
	Zn^{2+}
	Sn^{2+}
	Hg^{2+}
	Pb^{2+}
Ions formed by losing three electrons	Sc^{3+}
	Fe^{3+}
	Co^{3+}
	Ni^{3+}
	Au^{3+}
	Al^{3+}
	Cr^{3+}
Ions formed by losing four electrons	Ti^{4+}
	Sn^{4+}
	Pb^{4+}
Ions formed by gaining three electrons	N^{3-}
	P^{3-}

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4.01 The Elements and Symbols

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 1 shows some of the chemical elements.



Figure 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.

Table 1: Elemental Composition of Earth

Earth'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		

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 **1** lists the relative abundances of elements on Earth as a whole and in Earth's crust. Table **2** lists the relative abundances of elements in the human body. If you compare Table **1** and Table **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 **1**; carbon is part of the 0.174% representing "other" elements. How does the human body concentrate so many apparently rare elements?

Table **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** lists the names and symbols of some of the most familiar elements.

Table **3**: Element Names and Symbols

aluminum	Al	magnesium	Mg
argon	Ar	manganese	Mn
arsenic	As	mercury	Hg*
barium	Ba	neon	Ne
bismuth	Bi	nickel	Ni
boron	B	nitrogen	N
bromine	Br	oxygen	O
calcium	Ca	phosphorus	P
carbon	C	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	H	tin	Sn*
iron	Fe	tungsten	W†
iodine	I	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—*wolfram*.

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 1

Write the chemical symbol for each element without consulting Table **3** "Element Names and Symbols".

a. bromine
b. boron
c. carbon
d. calcium

e. gold

Answer a

Br

Answer b

B

Answer c

C

Answer d

Ca

Answer e

Au

Exercise 1

Write the chemical symbol for each element without consulting Table **3**.

a. manganese
b. magnesium
c. neon
d. nitrogen
e. silver

Example 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 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?

Answers

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

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4.1: Molecules and Chemical Nomenclature

Learning Objectives

- Define *molecule*.
- Name simple molecules based on their formulas.
- Determine a formula of a molecule based on its name.

There are many substances that exist as two or more atoms connected together so strongly that they behave as a single particle. These multiatom combinations are called molecules. A molecule is the smallest part of a substance that has the physical and chemical properties of that substance. In some respects, a molecule is similar to an atom. A molecule, however, is composed of more than one atom.

Table* 4.1.1*: *Elements That Exist as Diatomic Molecules*

Hydrogen (H_2)	Oxygen (O_2)	Nitrogen (N_2)	Fluorine (F_2)
Chlorine (Cl_2)	Bromine (Br_2)	Iodine (I_2)	

Some elements exist naturally as molecules. For example, hydrogen and oxygen exist as two-atom molecules. Other elements also exist naturally as **diatomic** molecules (Table 4.1.1). As with any molecule, these elements are labeled with a molecular formula, a formal listing of what and how many atoms are in a molecule. (Sometimes only the word *formula* is used, and its meaning is inferred from the context.) For example, the molecular formula for elemental hydrogen is H_2, with H being the symbol for hydrogen and the subscript 2 implying that there are two atoms of this element in the molecule. Other diatomic elements have similar formulas: O_2, N_2, and so forth.

Memorizing the diatomic molecules is worthwhile for our future endeavors and a variety mnemonics exist to help with memorization. **Br**I**N**C**l**H**O**F (pronounced "Brinklehoff") lists all of the diatomic elements in the name.



Fig.* 4.1.1*: *The element symbols for Bromine, Iodine, Nitrogen, Chlorine, Hydrogen, Oxygen and Fluorine spelling out "BrINClHOF" a handy mneumonic for memorizing the diatomic elements.*

Other elements exist as molecules—for example, sulfur normally exists as an eight-atom molecule, S_8, while phosphorus exists as a four-atom molecule, P_4 (Figure 4.1.1). Otherwise, we will assume that elements exist as individual atoms, rather than molecules. It is assumed that there is only one atom in a formula if there is no numerical subscript on the right side of an element's symbol.

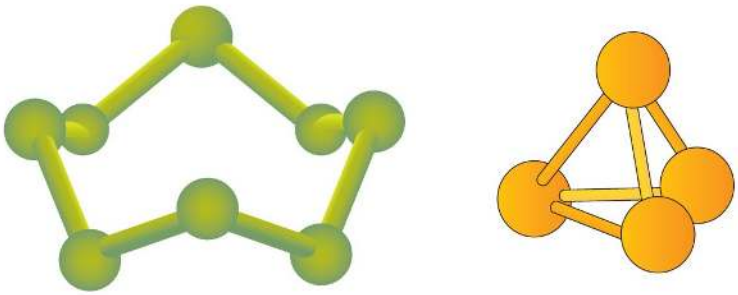


***Fig.* 4.1.2:** *Molecular Art of S_8 and P_4 Molecules. If each green ball represents a sulfur atom, then the diagram on the left represents an S_8 molecule. The molecule on the right shows that one form of elemental phosphorus exists, as a four-atom molecule.*

Figure **4.1.2** shows two examples of how we will be representing molecules in this text. An atom is represented by a small ball or sphere, which generally indicates where the nucleus is in the molecule. A cylindrical line connecting the balls represents the connection between the atoms that make this collection of atoms a molecule. This connection is called a **chemical bond**, the connection between two atoms in a molecule. In Chapter 9, we will explore the origin of chemical bonds. You will see other examples of this "ball and cylinder" representation of molecules throughout this book.

Many compounds exist as molecules. In particular, when nonmetals connect with other nonmetals, the compound typically exists as molecules. (Compounds between a metal and a nonmetal are different and will be considered in Section 3.4.) Furthermore, in some cases there are many different kinds of molecules that can be formed between any given elements, with all the different molecules having different chemical and physical properties. How do we tell them apart?

The answer is a very specific system of naming compounds, called *chemical nomenclature*. By following the rules of nomenclature, each and every compound has its own unique name, and each name refers to one and only one compound. Here, we will start with relatively simple molecules that have only two elements in them, the so-called ***binary compounds***:

1. Identify the elements in the molecule from its formula.
2. Begin the name with the element name of the first element. If there is more than one atom of this element in the molecular formula, use a numerical prefix to indicate the number of atoms, as listed in Table **4.1.2**. *Do not use the prefix* mono- *if there is only one atom of the first element.*
   - a numerical prefix indicating the number of atoms of the second element, plus
   - the stem of the element name (e.g., *ox* for oxygen, *chlor* for chlorine, etc.), plus
   - the suffix *-ide*.
3. Name the second element by using three pieces:
4. Combine the two words, leaving a space between them.

***Table* 4.1.2:** *Numerical Prefixes Used in Naming Molecular Compounds*

The Number of Atoms of an Element	Prefix
1	mono-
2	di-
3	tri-
4	tetra-
5	penta-
6	hexa-
7	hepta-
8	octa-
9	nona-
10	deca-

Let us see how these steps work for a molecule whose molecular formula is SO_2, which has one sulfur atom and two oxygen atoms—this completes step 1. According to step 2, we start with the name of the first element—sulfur. Remember, we don't use the *mono-* prefix for the first element. Now for step 3, we combine the numerical prefix *di-* (see Table **4.1.2**) with the stem *ox-* and the suffix *-ide*, to make *dioxide*. Bringing these two words together, we have the unique name for this compound—sulfur dioxide.

Why all this trouble? There is another common compound consisting of sulfur and oxygen whose molecular formula is SO_3, so the compounds need to be distinguished. SO_3 has three oxygen atoms in it, so it is a different compound with different chemical and

physical properties. The system of chemical nomenclature is designed to *give this compound its own unique name*. Its name, if you go through all the steps, is sulfur trioxide. Different compounds have different names.

In some cases, when a prefix ends in *a* or *o* and the element name begins with *o* we drop the *a* or *o* on the prefix. So we see *monoxide* or *pentoxide* rather than *monooxide* or *pentaoxide* in molecule names.

Example 4.1.1

Name each molecule.

a. PF_3
b. CO
c. Se_2Br_2

Solution

a. A molecule with a single phosphorus atom and three fluorine atoms is called phosphorus trifluoride.
b. A compound with one carbon atom and one oxygen atom is properly called carbon monoxide, not carbon monooxide.
c. There are two atoms of each element, selenium and bromine. According to the rules, the proper name here is *diselenium dibromide*.

Exercise 4.1.1

Name each molecule.

a. SF_4
b. P_2S_5

Answer a

sulfur tetrafluoride

Answer b

diphosphorus pentasulfide

One great thing about this system is that it works both ways. From the name of a compound, you should be able to determine its molecular formula. Simply list the element symbols, with a numerical subscript if there is more than one atom of that element, in the order of the name (we do not use a subscript 1 if there is only one atom of the element present; 1 is implied). From the name *nitrogen trichloride*, you should be able to get NCl_3 as the formula for this molecule. From the name *diphosphorus pentoxide*, you should be able to get the formula P_2O_5 (note the numerical prefix on the first element, indicating there is more than one atom of phosphorus in the formula).

Example 4.1.2

Give the formula for each molecule.

a. carbon tetrachloride
b. silicon dioxide
c. trisilicon tetranitride

Solution

a. The name *carbon tetrachloride* implies one carbon atom and four chlorine atoms, so the formula is CCl_4.
b. The name *silicon dioxide* implies one silicon atom and two oxygen atoms, so the formula is SiO_2.
c. We have a name that has numerical prefixes on both elements. *Tri-* means three, and *tetra-* means four, so the formula of this compound is Si_3N_4.

Exercise 4.1.2

Give the formula for each molecule.

a. disulfur difluoride
b. iodine pentabromide

Answer a

S_2F_2

Answer b

IBr_5

Some simple molecules have common names that we use as part of the formal system of chemical nomenclature. For example, H_2O is given the name *water*, not *dihydrogen monoxide*. NH_3 is called *ammonia*, while CH_4 is called *methane*. We will occasionally see other molecules that have common names; we will point them out as they occur.

Key Takeaways

- Molecules are groups of atoms that behave as a single unit.
- Some elements exist as molecules: hydrogen, oxygen, sulfur, and so forth.
- There are rules that can express a unique name for any given molecule, and a unique formula for any given name.

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4.2 Atomic Theory

Learning Objectives

- State the modern atomic theory.
- Learn how atoms are constructed.

The smallest piece of an element that maintains the identity of that element is called an **atom**. Individual atoms are extremely small. It would take about fifty million atoms in a row to make a line that is 1 cm long. The period at the end of a printed sentence has several million atoms in it. Atoms are so small that it is difficult to believe that all matter is made from atoms—but it is.

The concept that atoms play a fundamental role in chemistry is formalized by the **modern atomic theory**, first stated by John Dalton, an English scientist, in 1808. It consists of three parts:

1. All matter is composed of atoms.
2. Atoms of the same element are the same; atoms of different elements are different.
3. Atoms combine in whole-number ratios to form compounds.

These concepts form the basis of chemistry. Although the word *atom* comes from a Greek word that means "indivisible," we understand now that atoms themselves are composed of smaller parts called *subatomic particles*. The first part to be discovered was the **electron**, a tiny subatomic particle with a negative charge. It is often represented as e^-, with the right superscript showing the negative charge. Later, two larger particles were discovered. The **proton**, a subatomic particle with a positive charge, is a more massive (but still tiny) subatomic particle with a positive charge, represented as p^+. The neutron is a subatomic particle with about the same mass as a proton but no charge. It is represented as either n or n^0. We now know that all atoms of all elements are composed of electrons, protons, and (with one exception) neutrons. Table **1** summarizes the properties of these three subatomic particles.

Table 1: *Properties of the Three Subatomic Particles*

Name	Symbol	Mass (approx.; kg)	Charge
Proton	p^+	1.6×10^{-27}	1+
Neutron	n, n^0	1.6×10^{-27}	none
Electron	e^-	9.1×10^{-31}	1−

How are these particles arranged in atoms? They are not arranged at random. Experiments by Ernest Rutherford in England in the 1910s pointed to a nuclear model with atoms that has the protons and neutrons in a central nucleus with the electrons in orbit about the nucleus. The relatively massive protons and neutrons are collected in the center of an atom, in a region called the nucleus of the atom (plural *nuclei*). The electrons are outside the nucleus and spend their time orbiting in space about the nucleus. (Figure **1**).

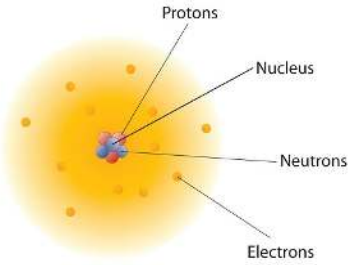


Figure 1: *The Structure of the Atom.Atoms have protons and neutrons in the center, making the nucleus, while the electrons orbit the nucleus.*

The modern atomic theory states that atoms of one element are the same, while atoms of different elements are different. What makes atoms of different elements different? **The fundamental characteristic that all atoms of the same element share is the *number of protons***. All atoms of hydrogen have one and only one proton in the nucleus; all atoms of iron have 26 protons in the nucleus. This number of protons is so important to the identity of an atom that it is called the **atomic number**, the number of protons in an atom of the element. Thus, hydrogen has an atomic number of 1, while iron has an atomic number of 26. Each element has its own characteristic atomic number.

Atoms of the same element can have different numbers of neutrons, however. Atoms of the same element (i.e., atoms with the same number of protons) with different numbers of neutrons are called **isotopes**. Most naturally occurring elements exist as isotopes. For example, most hydrogen atoms have a single proton in their nucleus. However, a small number (about one in a million) of hydrogen atoms have a proton and a neutron in their nuclei. This particular isotope of hydrogen is called deuterium. A very rare form of hydrogen has one proton and two neutrons in the nucleus; this isotope of hydrogen is called tritium. The sum of the number of protons and neutrons in the nucleus is called the **mass number** of the isotope.

Neutral atoms have the same number of electrons as they have protons, so their overall charge is zero. However, as we shall see later, this will not always be the case.

Example 1:

a. The most common carbon atoms have six protons and six neutrons in their nuclei. What are the atomic number and the mass number of these carbon atoms?
b. An isotope of uranium has an atomic number of 92 and a mass number of 235. What are the number of protons and neutrons in the nucleus of this atom?

Solution

a. If a carbon atom has six protons in its nucleus, its atomic number is 6. If it also has six neutrons in the nucleus, then the mass number is 6 + 6, or 12.
b. If the atomic number of uranium is 92, then that is the number of protons in the nucleus. Because the mass number is 235, then the number of neutrons in the nucleus is 235 − 92, or 143.

Exercise 1

The number of protons in the nucleus of a tin atom is 50, while the number of neutrons in the nucleus is 68. What are the atomic number and the mass number of this isotope?

Answer

Atomic number = 50, mass number = 118

When referring to an atom, we simply use the element's name: the term *sodium* refers to the element as well as an atom of sodium. But it can be unwieldy to use the name of elements all the time. Instead, chemistry defines a symbol for each element. The **atomic symbol** is a one- or two-letter abbreviation of the name of the element. By convention, the first letter of an element's symbol is always capitalized, while the second letter (if present) is lowercase. Thus, the symbol for hydrogen is H, the symbol for sodium is Na, and the symbol for nickel is Ni. Most symbols come from the English name of the element, although some symbols come from an element's Latin name. (The symbol for sodium, Na, comes from its Latin name, *natrium*.) Table **2** lists some common elements and their symbols. You should memorize the symbols in Table **2**, as this is how we will be representing elements throughout chemistry.

Table 2: Names and Symbols of Common Elements

Element Name	Symbol	Element Name	Symbol
Aluminum	Al	Mercury	Hg
Argon	Ar	Molybdenum	Mo
Arsenic	As	Neon	Ne
Barium	Ba	Nickel	Ni
Beryllium	Be	Nitrogen	N
Bismuth	Bi	Oxygen	O
Boron	B	Palladium	Pd
Bromine	Br	Phosphorus	P
Calcium	Ca	Platinum	Pt
Carbon	C	Potassium	K
Chlorine	Cl	Radium	Ra
Chromium	Cr	Radon	Rn
Cobalt	Co	Rubidium	Rb
Copper	Cu	Scandium	Sc
Fluorine	F	Selenium	Se
Gallium	Ga	Silicon	Si
Germanium	Ge	Silver	Ag
Gold	Au	Sodium	Na
Helium	He	Strontium	Sr
Hydrogen	H	Sulfur	S
Iodine	I	Tantalum	Ta
Iridium	Ir	Tin	Sn
Iron	Fe	Titanium	Ti
Krypton	Kr	Tungsten	W
Lead	Pb	Uranium	U
Lithium	Li	Xenon	Xe
Magnesium	Mg	Zinc	Zn
Manganese	Mn	Zirconium	Zr

The elements are grouped together in a special chart called the periodic table of all the elements. A simple periodic table is shown in Figure **2**, while one may view a more extensive periodic table. The elements on the periodic table are listed in order of increasing atomic number. The periodic table has a special shape that will become important to us when we consider the organization of electrons in atoms (Chapter 8). One immediate use of the periodic table helps us identify metals and nonmetals. Nonmetals are in the upper right corner of the periodic table, on one side of the heavy red line splitting the right-hand part of the chart. Light blue elements along the red line are metalloids and all other elements to the left of the red line are metals.

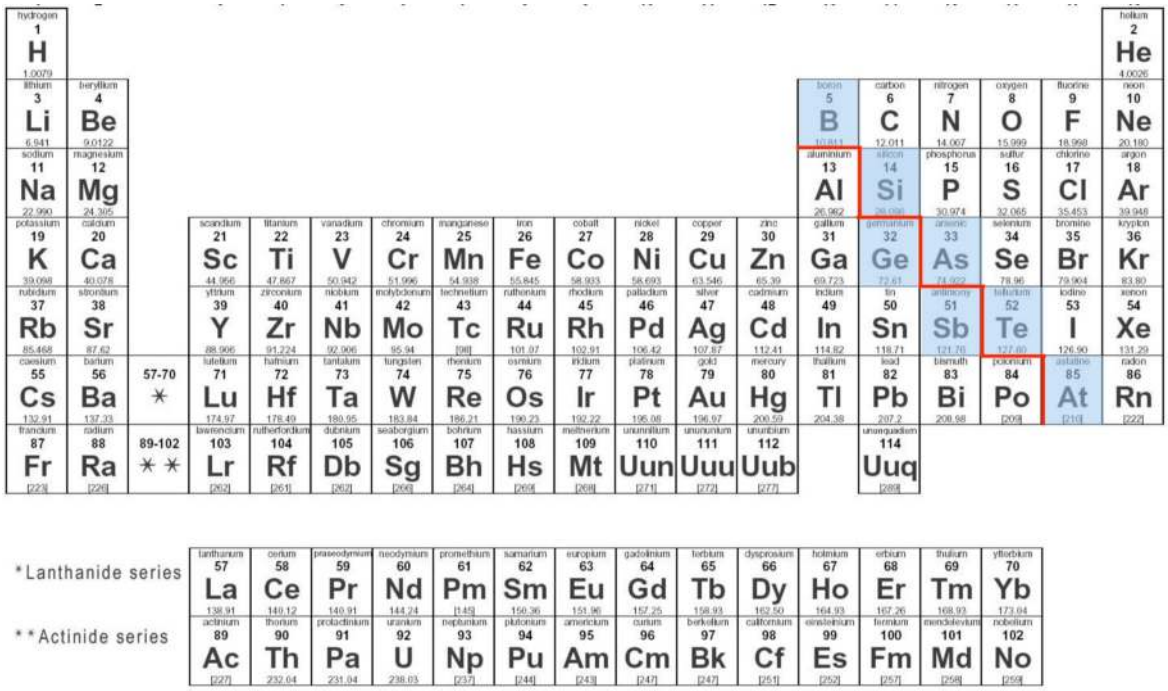


Figure 1: *A Simple Periodic Table*

There is an easy way to represent isotopes using the atomic symbols. We use the construction

$$ {}^{A}_{Z}X \tag{1}$$

where X is the symbol of the element, A is the mass number, and Z is the atomic number. Thus, for the isotope of carbon that has 6 protons and 6 neutrons, the symbol is

$$ {}^{12}_{6}C \tag{2}$$

where C is the symbol for the element, 6 represents the atomic number, and 12 represents the mass number.

Example 2:

a. What is the symbol for an isotope of uranium that has an atomic number of 92 and a mass number of 235?

b. How many protons and neutrons are in ${}^{56}_{26}Fe$

Solution

a. The symbol for this isotope is ${}^{235}_{92}U$

b. This iron atom has 26 protons and 56 − 26 = 30 neutrons.

Exercise 2

How many protons are in ${}^{23}_{11}Na$.

Answer

11 protons

It is also common to state the mass number after the name of an element to indicate a particular isotope. *Carbon-12* represents an isotope of carbon with 6 protons and 6 neutrons, while *uranium-238* is a

Key Takeaways

- Chemistry is based on the modern atomic theory, which states that all matter is composed of atoms.
- Atoms themselves are composed of protons, neutrons, and electrons.
- Each element has its own atomic number, which is equal to the number of protons in its nucleus.
- Isotopes of an element contain different numbers of neutrons.
- Elements are represented by an atomic symbol.
- The periodic table is a chart that organizes all the elements.

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4.3 Isotopes

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4.4: The Periodic Table

2.05: The Periodic Table

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4.5 Ions

Learning Objectives

- Know how ions form.
- Learn the characteristic charges that ions have.
- Construct a proper formula for an ionic compound.
- Generate a proper name for an ionic compound.

So far, we have discussed elements and compounds that are electrically neutral. They have the same number of electrons as protons, so the negative charges of the electrons is balanced by the positive charges of the protons. However, this is not always the case. Electrons can move from one atom to another; when they do, species with overall electric charges are formed. Such species are called ions. Species with overall positive charges are termed **cations**, while species with overall negative charges are called **anions**. Remember that ions are formed only when *electrons* move from one atom to another; a proton never moves from one atom to another. Compounds formed from positive and negative ions are **ionic compounds**.

Individual atoms can gain or lose electrons. When they do, they become *monatomic* ions. When atoms gain or lose electrons, they usually gain or lose a characteristic number of electrons and so take on a characteristic overall charge. Figure **1** shows some common ions in terms of how many electrons they lose (making cations) or gain (making anions), as well as their positions on the periodic table. There are several things to notice about the ions in Figure **1**. First, each element that forms cations is a metal, except for one (hydrogen), while each element that forms anions is a nonmetal. This is actually one of the chemical properties of metals and nonmetals: metals tend to form cations, while nonmetals tend to form anions. Second, elements that live in the first two columns and the last three columns of the period table show a defininte trend in charges. Every element in the first column forms a cation with charge 1+. Every element in the second column forms a cation with charge 2+. Elements in the third to last column almost all form an anion with a 2- charge and elements living in the second to last column almost all form anions with a 1- charge. The elements at the end of the periodic table do not form ions. We'll learn more about why this is the case in future chapters but for the time being if you can learn this trend it's fairly easy to determine the charge on most of the elements we see. Finally, most atoms form ions of a single characteristic charge. When sodium atoms form ions, they always form a 1+ charge, never a 2+ or 3+ or even 1− charge. Thus, if you commit the information in Figure **1** to memory, you will always know what charges most atoms form.

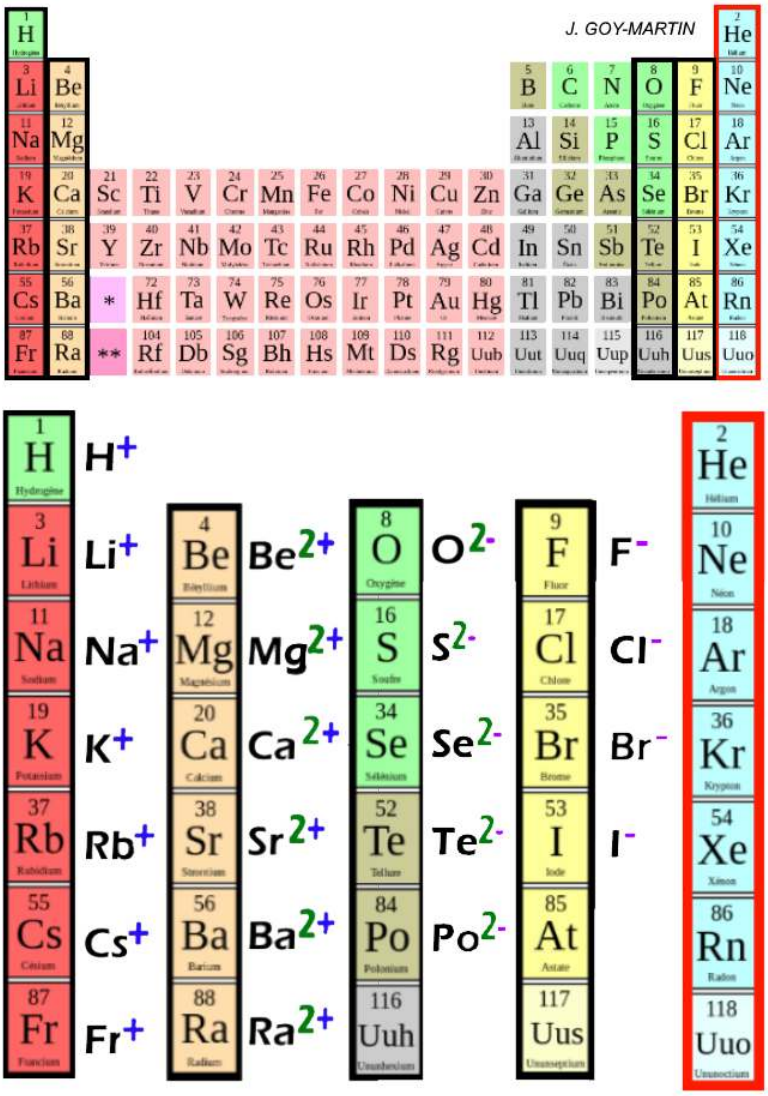


***Figure* 1:** *Groups on the periodic table and the charges on their ions*, By Homme en Noir - Own work, CC BY-SA 4.0, https://commons.wikimedia.org/w/inde...curid=66743988

While Figure 1 is helpful in determining the charge on a large number of our cations and anions it's hardly complete. A more complete table of ions and their charges can be found at Monotomic Ions of Various Charges. Examination of the table in the link given shows that there are some exceptions to the previous point. A few elements, all metals, can form more than one possible charge. For example, iron (Fe) atoms can form 2+ cations or 3+ cations. Cobalt (Co) is another element that can form more than one possible charged ion (2+ and 3+), while lead (Pb) can form 2+ or 4+ cations. Unfortunately, there is little understanding which two charges a metal atom may take, so it is best to just memorize the possible charges a particular element can have.

Note the convention for indicating an ion. The magnitude of the charge is listed as a right superscript next to the symbol of the element. If the charge is a single positive or negative one, the number 1 is not written; if the magnitude of the charge is greater than 1, then the number is written *before* the + or − sign. An element symbol without a charge written next to it is assumed to be the uncharged atom.

Naming ions

Naming an ion is straightforward. For a cation, simply use the name of the element and add the word *ion* (or if you want to be more specific, add *cation*) after the element's name. So Na^+ is the sodium ion; Ca^{2+} is the calcium ion. If the element has more than one possible charge, the value of the charge comes after the element name and before the word *ion*. Thus, Fe^{2+} is the iron two ion, while Fe^{3+} is the iron three ion. In print, we use roman numerals in parentheses to represent the charge on the ion, so these two iron ions would be represented as the iron(II) cation and the iron(III) cation, respectively.

For a monatomic anion, use the stem of the element name and append the suffix *-ide* to it, and then add *ion*. This is similar to how we named molecular compounds. Thus, Cl^- is the chloride ion, and N^{3-} is the nitride ion.

Example 1:

Name each species.

a. O^{2-}
b. Co
c. Co^{2+}

Solution

a. This species has a 2− charge on it, so it is an anion. Anions are named using the stem of the element name with the suffix *-ide* added. This is the oxide anion.
b. Because this species has no charge, it is an atom in its elemental form. This is cobalt.
c. In this case, there is a 2+ charge on the atom, so it is a cation. We note from Table 3.4.1 that cobalt cations can have two possible charges, so the name of the ion must specify which charge the ion has. This is the cobalt(II) cation.

Exercise 1

Name each species.

a. P^{3-}
b. Sr^{2+}

Answers

a. the phosphide anion
b. the strontium cation

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4.6 Ionic Compounds

Ionic Formulas

Chemical formulas for ionic compounds are called ionic formulas. A proper ionic formula has a cation and an anion in it; an ionic compound is never formed between two cations only or two anions only. If you've ever tried to force two refrigerator magnets together you'll remember that there was one side of each magnet that clicked together and there was one side of each magnet that pushed against the other. One side of each of our magnets is positive and one side of each of our magnets is negative. When the magnets push away from each other we're trying to force two like charges together. Ions behave the same way on the atomic scale. Two ions with the same charge will push away from each other. Two ions with opposite charges will be attracted to each other as being close to one another allows them to cancel out the additional charge they are carrying. A Ca^{2+} cation has twice as much charge as a Cl^- anion, so it will be able to attract and cancel out the charge on two Cl^- anions.

The key to writing proper ionic formulas is simple: the total positive charge must balance the total negative charge. Because the charges on the ions are characteristic, sometimes we have to have more than one of a cation or an anion to balance the overall positive and negative charges. It is conventional to use the lowest ratio of ions that are needed to balance the charges.

For example, consider the ionic compound between Na^+ and Cl^-. Each ion has a single charge, one positive and one negative, so we need only one ion of each to balance the overall charge. When writing the ionic formula, we follow two additional conventions: (1) write the formula for the cation first and the formula for the anion next, but (2) do not write the charges on the ions. Thus, for the compound between Na^+ and Cl^-, we have the ionic formula NaCl (Figure 1). The formula Na_2Cl_2 also has balanced charges, but the convention is to use the lowest ratio of ions, which would be one of each. (Remember from our conventions for writing formulas that we don't write a 1 subscript if there is only one atom of a particular element present.) For the ionic compound between magnesium cations (Mg^{2+}) and oxide anions (O^{2-}), again we need only one of each ion to balance the charges. By convention, the formula is MgO.



Figure 1: *NaCl = Table Salt © Thinkstock The ionic compound NaCl is very common.*

For the ionic compound between Mg^{2+} ions and Cl^- ions, we now consider the fact that the charges have different magnitudes, 2+ on the magnesium ion and 1− on the chloride ion. To balance the charges with the lowest number of ions possible, we need to have two chloride ions to balance the charge on the one magnesium ion. Rather than write the formula MgClCl, we combine the two chloride ions and write it with a 2 subscript: $MgCl_2$.

What is the formula $MgCl_2$ telling us? There are two chloride ions in the formula. Although chlorine as an element is a diatomic molecule, Cl_2, elemental chlorine is not part of this ionic compound. The chlorine is in the form of a negatively charged *ion*, not the neutral *element*. The 2 subscript is in the ionic formula because we need two Cl^- ions to balance the charge on one Mg^{2+} ion.

Example 2:

Write the proper ionic formula for each of the two given ions.

a. Ca^{2+} and Cl^-
b. Al^{3+} and F^-
c. Al^{3+} and O^{2-}

Solution

a. We need two Cl^- ions to balance the charge on one Ca^{2+} ion, so the proper ionic formula is $CaCl_2$.
b. We need three F^- ions to balance the charge on the Al^{3+} ion, so the proper ionic formula is AlF_3.
c. With Al^{3+} and O^{2-}, note that neither charge is a perfect multiple of the other. This means we have to go to a least common multiple, which in this case will be six. To get a total of 6+, we need two Al^{3+} ions; to get 6−, we need three O^{2-} ions. Hence the proper ionic formula is Al_2O_3.

Exercise 2

Write the proper ionic formulas for each of the two given ions.

a. Fe^{2+} and S^{2-}
b. Fe^{3+} and S^{2-}

Answers

a. FeS
b. Fe_2S_3

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CHAPTER OVERVIEW

6: Chemical Reactions and Equations

Chemistry is largely about chemical changes. Indeed, if there were no chemical changes, chemistry as such would not exist! Chemical changes are a fundamental part of chemistry. Because chemical changes are so central, it may be no surprise that chemistry has developed some special ways of presenting them.

Topic hierarchy

6.1: Chemical Changes and Chemical Reactions

6.2: The Chemical Equation - Writing and Balancing

Thumbnail: Reaction of sodium and water breaks the glass vessel. Image used with permission (CC SA-BY-3.0; Tony Mach).

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6.1: Chemical Changes and Chemical Reactions

In Chapter 2, we classified changes in our environment utilizing the concepts of *physical* and *chemical changes*. We said that a **physical change** alters the *appearance* of a substance without changing its molecular structure. Ice melts, water evaporates and mountains are slowly weathered into dust. All of these change the *characteristics* of substances, but they do not alter its basic structure. A **chemical change**, however, results in the transformation of one molecular substance into another. Gasoline burns, reacting with oxygen in the atmosphere, generating light, heat, and converting the carbon-based molecules into carbon dioxide gas and water vapor. When substances combine like this and undergo chemical changes, we say that a **chemical reaction** has occurred. Some chemical reactions are quite evident, like the burning of gasoline, and involve the production of **heat** or **light**. In other types of chemical reactions, **gases** are evolved, **color changes** occur and clear solutions become cloudy, with the ultimate formation of an insoluble substance (a **precipitate**). Chemical changes can also be quite obscure and their occurrence can only be detected by sophisticated chemical analysis.

Sometimes chemical changes occur spontaneously, others require the input of energy (heat) in order to occur. Chemical reactions can occur rapidly, like the explosive reaction of sodium metal in the presence of water, and others occur very slowly, like the rusting of iron or the tarnish that slowly develops on some metal surfaces exposed to air. In this chapter we will learn to represent chemical reactions using **chemical equations**. We will learn to **balance** these equations, explore **types** of reactions and learn to **predict products** from simple reactions. Central to all of this is the concept of the *chemical equation*.

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6.2: The Chemical Equation - Writing and Balancing

Learning Objectives

- Define *chemical equation*.
- Identify the parts of a chemical equation.

A chemical reaction expresses a chemical change. For example, one chemical property of hydrogen is that it will react with oxygen to make water. We can write that as follows:

$$\textbf{hydrogen reacts with oxygen to make water}$$

We can represent this chemical change more succinctly as:

$$\textbf{hydrogen} + \textbf{oxygen} \rightarrow \textbf{water}$$

where the + sign means that the two substances interact chemically with each other and the → symbol implies that a chemical reaction takes place. But substances can also be represented by chemical formulas. Remembering that hydrogen and oxygen both exist as diatomic molecules, we can rewrite our chemical change as:

$$\mathrm{H_2 + O_2 \longrightarrow H_2O}$$

This is an example of a chemical equation, which is a concise way of representing a **chemical reaction**. The initial substances are called **reactants** and the final substances are called **products**.

Unfortunately, it is also an *incomplete* chemical equation. The law of conservation of matter says that matter cannot be created or destroyed. In chemical equations, the number of atoms of each element in the reactants must be the same as the number of atoms of each element in the products. If we count the number of hydrogen atoms in the reactants and products, we find two hydrogen atoms. But if we count the number of oxygen atoms in the reactants and products, we find that there are two oxygen atoms in the reactants, but only one oxygen atom in the products.

What can we do? Can we change the subscripts in the formula for water so that it has two oxygen atoms in it? No—you *cannot* change the formulas of individual substances, because the chemical formula for a given substance is characteristic of that substance. What you *can* do, however, is to change the number of molecules that react or are produced. We do this one element at a time, going from one side of the reaction to the other, changing the number of molecules of a substance until all elements have the same number of atoms on each side.

To accommodate the two oxygen atoms as reactants, let us assume that we have two water molecules as products:

$$\mathrm{H_2 + O_2 \longrightarrow 2\,H_2O}$$

The 2 in front of the formula for water is called a **coefficient**. Now there are the same number of oxygen atoms in the reactants as there are in the product. But in satisfying the need for the same number of oxygen atoms on both sides of the reaction, we have also changed the number of hydrogen atoms on the product side, so the number of hydrogen atoms is no longer equal. No problem, simply go back to the reactant side of the equation, and add a coefficient in front of the H_2. The coefficient that works is 2:

$$\mathrm{2\,H_2 + O_2 \longrightarrow 2\,H_2O}$$

There are now four hydrogen atoms in the reactants and also four atoms of hydrogen in the product. There are two oxygen atoms in the reactants and two atoms of oxygen in the product. The law of conservation of matter has been satisfied. When the reactants and products of a chemical equation have the same number of atoms of all elements present, we say that an equation is **balanced**. All proper chemical equations are balanced. If a substance does not have a coefficient written in front of it, it is assumed to be 1. Also, the convention is to use all whole numbers when balancing chemical equations. This sometimes makes us do a bit more "back and forth" work when balancing a chemical equation.

Example 6.2.1

Write and balance the chemical equation for each given chemical reaction.

1. Hydrogen and chlorine react to make HCl
2. Ethane, $\mathrm{C_2H_6}$, reacts with oxygen to make carbon dioxide and water.

Solution

1. Let us start by simply writing a chemical equation in terms of the formulas of the substances, remembering that both elemental hydrogen and chlorine are diatomic:

$$\mathrm{H_2 + Cl_2 \longrightarrow HCl}$$

There are two hydrogen atoms and two chlorine atoms in the reactants and one of each atom in the product. We can fix this by including the coefficient 2 on the product side:

$$\mathrm{H_2 + Cl_2 \longrightarrow 2\,HCl}$$

Now there are two hydrogen atoms and two chlorine atoms on both sides of the chemical equation, so it is balanced.

2. Start by writing the chemical equation in terms of the substances involved:

$$\mathrm{C_2H_6 + O_2 \longrightarrow CO_2 + H_2O}$$

We have two carbon atoms on the left, so we need two carbon dioxide molecules on the product side, so that each side has two carbon atoms; that element is balanced. We have six hydrogen atoms in the reactants, so we need six hydrogen atoms in the products. We can get this by having three water molecules:

$$\mathrm{C_2H_6 + O_2 \longrightarrow 2\,CO_2 + 3\,H_2O}$$

Now we have seven oxygen atoms in the products (four from the CO_2 and three from the H_2O). This means we need seven oxygen atoms in the reactants. However, because oxygen is a diatomic molecule, we can only get an even number of oxygen atoms at a time. We can achieve this by multiplying the other coefficients by 2:

$$\mathrm{2\,C_2H_6 + O_2 \longrightarrow 4\,CO_2 + 6\,H_2O}$$

By multiplying everything else by 2, we do not unbalance the other elements, and we now get an even number of oxygen atoms in the product—14. We can get 14 oxygen atoms on the reactant side by having 7 oxygen molecules:

$$\mathrm{2\,C_2H_6 + 7\,O_2 \longrightarrow 4\,CO_2 + 6\,H_2O}$$

As a check, recount everything to determine that each side has the same number of atoms of each element. This chemical equation is now balanced.

Exercise 6.2.1

Write and balance the chemical equation that represents nitrogen and hydrogen reacting to produce ammonia, NH_3.

Answer

\[\ce{N2 + 3H2 → 2NH3 \nonumber \nonumber \]

Many chemical equations also include phase labels for the substances: (s) for solid, (ℓ) for liquid, (g) for gas, and (aq) for aqueous (i.e., dissolved in water). Special conditions, such as temperature, may also be listed above the arrow. For example,

$$\mathrm{2\,NaHCO_3\,(s) \xrightarrow{200^\circ C} Na_2CO_3\,(s) + CO_2\,(g) + H_2O\,(l)}$$

Key Takeaways

- A chemical equation is a concise description of a chemical reaction.
- Proper chemical equations are balanced.

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CHAPTER OVERVIEW

8: Stoichiometry and the Mole

We have already established that quantities are important in science, especially in chemistry. It is important to make accurate measurements of a variety of quantities when performing experiments. However, it is also important to be able to relate one measured quantity to another, unmeasured quantity. In this chapter, we will consider how we manipulate quantities to relate them to each other.

8.1: Stoichiometry

8.2: The Mole

8.3: Percent Composition, Empirical and Molecular Formulas

8.4: Empirical Formulas

8.5: Molecular Formulas

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8.1: Stoichiometry

Learning Objectives

- Define *stoichiometry*.
- Relate quantities in a balanced chemical reaction on a molecular basis.

Consider a classic recipe for pound cake: 1 pound of eggs, 1 pound of butter, 1 pound of flour, and 1 pound of sugar. (That's why it's called "pound cake.") If you have 4 pounds of butter, how many pounds of sugar, flour, and eggs do you need? You would need 4 pounds each of sugar, flour, and eggs.

Now suppose you have 1.00 g H_2. If the chemical reaction follows the balanced chemical equation

$$2\,H_2\,(g) + O_2\,(g) \longrightarrow 2\,H_2O(\ell)$$

then what mass of oxygen do you need to make water?

Curiously, this chemical reaction question is very similar to the pound cake question. Both of them involve relating a quantity of one substance to a quantity of another substance or substances. The relating of one chemical substance to another using a balanced chemical reaction is called **stoichiometry**. Using stoichiometry is a fundamental skill in chemistry; it greatly broadens your ability to predict what will occur and, more importantly, how much is produced.

Let us consider a more complicated example. A recipe for pancakes calls for 2 cups (c) of pancake mix, 1 egg, and 1/2 c of milk. We can write this in the form of a chemical equation:

2 c mix + 1 egg + 1/2 c milk → 1 batch of pancakes

If you have 9 c of pancake mix, how many eggs and how much milk do you need? It might take a little bit of work, but eventually you will find you need 4½ eggs and 2¼ c milk.

How can we formalize this? We can make a conversion factor using our original recipe and use that conversion factor to convert from a quantity of one substance to a quantity of another substance. This is similar to the way we constructed a conversion factor between feet and yards in Chapter 2. Because one recipe's worth of pancakes requires 2 c of pancake mix, 1 egg, and 1/2 c of milk, we actually have the following mathematical relationships that relate these quantities:

2 c pancake mix ⇔ 1 egg ⇔ 1/2 c milk

where ⇔ is the mathematical symbol for "is equivalent to." This does not mean that 2 c of pancake mix equal 1 egg. However, *as far as this recipe is concerned*, these are the equivalent quantities needed for a single recipe of pancakes. So, any possible quantities of two or more ingredients must have the same numerical ratio as the ratios in the equivalence.

We can deal with these equivalences in the same way we deal with equalities in unit conversions: we can make conversion factors that essentially equal 1. For example, to determine how many eggs we need for 9 c of pancake mix, we construct the conversion factor:

$$\frac{1\,egg}{2\,c\,pancake\,mix}$$

This conversion factor is, in a strange way, equivalent to 1 because the recipe relates the two quantities. Starting with our initial quantity and multiplying by our conversion factor,

$$9\,\cancel{c\,pancake\,mix} \times \frac{1\,egg}{2\,\cancel{c\,pancake\,mix}} = 4.5\,eggs$$

Note how the units *cups pancake mix* canceled, leaving us with units of *eggs*. This is the formal, mathematical way of getting our amounts to mix with 9 c of pancake mix. We can use a similar conversion factor for the amount of milk:

$$9\,\cancel{c\,pancake\,mix} \times \frac{\frac{1}{2}\,c\,milk}{2\,\cancel{c\,pancake\,mix}} = 2.25\,c\,milk$$

Again, units cancel, and new units are introduced.

A balanced chemical equation is nothing more than *a recipe for a chemical reaction*. The difference is that a balanced chemical equation is written in terms of atoms and molecules, not cups, pounds, and eggs.

For example, consider the following chemical equation:

$$2\,H_2\,(g) + O_2\,(g) \longrightarrow 2\,H_2O(\ell)$$

We can interpret this as, literally, "two hydrogen molecules react with one oxygen molecule to make two water molecules." That interpretation leads us directly to some equivalencies, just as our pancake recipe did:

$$2H_2 \text{ molecules} \Leftrightarrow 1O_2 \text{ molecule} \Leftrightarrow 2H_2O \text{ molecules}$$

These equivalences allow us to construct conversion factors:

$$\frac{2\,molecules\,H_2}{1\,molecule\,O_2} \quad \frac{2\,molecules\,H_2}{2\,molecules\,H_2O} \quad \frac{1\,molecule\,H_2}{2\,molecules\,H_2O}$$

and so forth. These conversions can be used to relate quantities of one substance to quantities of another. For example, suppose we need to know how many molecules of oxygen are needed to react with 16 molecules of H_2. As we did with converting units, we start with our given quantity and use the appropriate conversion factor:

$$\cancel{16\,molecules\,H_2} \times \frac{1\,molecules\,O_2}{\cancel{2\,molecules\,H_2}} = 8\,molecules\,O_2$$

Note how the unit *molecules H2* cancels algebraically, just as any unit does in a conversion like this. The conversion factor came directly from the coefficients in the balanced chemical equation. This is another reason why a properly balanced chemical equation is important.

Example 8.1.1

How many molecules of SO_3 are needed to react with 144 molecules of Fe_2O_3 given this balanced chemical equation?

$$Fe_2O_3 + 3\,SO_3 \longrightarrow Fe_2(SO_4)_3$$

Solution

We use the balanced chemical equation to construct a conversion factor between Fe_2O_3 and SO_3. The number of molecules of Fe_2O_3 goes on the bottom of our conversion factor so it cancels with our given amount, and the molecules of SO_3 go on the top. Thus, the appropriate conversion factor is

$$\frac{3\,molecules\,SO_3}{1\,molecule\,Fe_2O_3}$$

Starting with our given amount and applying the conversion factor, the result is

$$144\ \cancel{molecules}\ Fe_2O_3 \times \frac{3\,molecules\,SO_3}{1\ \cancel{molecule}\ Fe_2O_3} = 432\,molecules\,SO_3$$

We need 432 molecules of SO_3 to react with 144 molecules of Fe_2O_3.

Exercise 8.1.1

How many molecules of H_2 are needed to react with 29 molecules of N_2 to make ammonia if the balanced chemical equation is:

$$N_2 + 3\,H_2 \longrightarrow 2\,NH_3?$$

Answer

87 molecules

Chemical equations also allow us to make conversions regarding the number of atoms in a chemical reaction, because a chemical formula lists the number of atoms of each element in a compound. The formula H_2O indicates that there are two hydrogen atoms and one oxygen atom in each molecule, and these relationships can be used to make conversion factors:

$$\frac{2\,atoms\,H}{1\,molecule\,H_2O} \quad \frac{1\,molecule\,H_2O}{1\,atom\,O}$$

Conversion factors like this can also be used in stoichiometry calculations.

Example 8.1.2

How many molecules of NH_3 can you make if you have 228 atoms of H_2?

Solution

From the formula, we know that one molecule of NH_3 has three H atoms. Use that fact as a conversion factor:

$$228\ \cancel{atoms\,H} \times \frac{1\,molecule\,NH_3}{3\ \cancel{atoms\,H}} = 76\,NH_3$$

Exercise 8.1.2

How many molecules of $Fe_2(SO_4)_3$ can you make from 777 atoms of S?

Answer

259 molecules

Summary

Quantities of substances can be related to each other using balanced chemical equations.

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8.2: The Mole

Learning Objectives

- Describe the unit *mole*.
- Relate the mole quantity of substance to its mass.

So far, we have been talking about chemical substances in terms of individual atoms and molecules. Yet we do not typically deal with substances an atom or a molecule at a time; we work with millions, billions, and trillions of atoms and molecules at a time. We need a way to deal with macroscopic, rather than microscopic, amounts of matter. We need a unit of amount that relates quantities of substances on a scale that we can interact with.

Chemistry uses a unit called mole. A **mole** (mol) is a number of things equal to the number of atoms in exactly 12 g of carbon-12. Experimental measurements have determined that this number is very large:

$$1 \text{ mol} = 6.02214179 \times 10^{23} \text{ things}$$

Understand that a mole means a specific number of things, just like a dozen means a certain number of things—twelve, in the case of a dozen. But a mole is a much larger number of things. These things can be atoms, or molecules, or eggs; however, in chemistry, we usually use the mole to refer to the amounts of atoms or molecules. Although the number of things in a mole is known to eight decimal places, it is usually fine to use only two or three decimal places in calculations. The numerical value of things in a mole is often called *Avogadro's number* (N_A). *Avogadro's number* is also known as the *Avogadro constant*, after Amadeo Avogadro, an Italian chemist who first proposed its importance.

Example 8.2.1

How many molecules are present in 2.76 mol of H_2O? How many atoms is this?

Solution

The definition of a mole is an equality that can be used to construct a conversion factor. Also, because we know that there are three atoms in each molecule of H_2O, we can also determine the number of atoms in the sample.

$$2.76 \ \cancel{mol\ H_2O} \times \frac{6.022 \times 10^{23} molecules\ H_2O}{\cancel{mol\ H_2O}} = 1.66 \times 10^{24} molecules\ H_2O$$

To determine the total number of atoms, we have

$$1.66 \times 10^{24} \ \cancel{molecules\ H_2O} \times \frac{3\ atoms}{1\ molecule} = 4.99 \times 10^{24}\ atoms$$

Exercise 8.2.1

How many molecules are present in 4.61×10^{-2} mol of O_2?

Answer

2.78×10^{22} molecules

How big is a mole? It is very large. Suppose you had a mole of dollar bills that need to be counted. If everyone on earth (about 6 billion people) counted one bill per second, it would take about 3.2 million years to count all the bills. A mole of sand would fill a cube about 32 km on a side. A mole of pennies stacked on top of each other would have about the same diameter as our galaxy, the Milky Way. A mole is a lot of things—but atoms and molecules are very tiny. One mole of carbon atoms would make a cube that is 1.74 cm on a side, small enough to carry in your pocket.

Why is the mole unit so important? It represents the link between the microscopic and the macroscopic, especially in terms of mass. *A mole of a substance has the same mass in grams as one unit (atom or molecules) has in atomic mass units*. The mole unit

allows us to express amounts of atoms and molecules in visible amounts that we can understand.

For example, we already know that, by definition, a mole of carbon has a mass of exactly 12 g. This means that exactly 12 g of C has 6.022×10^{23} atoms:

$$12 \text{ g C} = 6.022 \times 10^{23} \text{ atoms C}$$

We can use this equality as a conversion factor between the number of atoms of carbon and the number of grams of carbon. How many grams are there, say, in 1.50×10^{25} atoms of carbon? This is a one-step conversion:

$$1.50 \times 10^{25} \cancel{\text{atoms C}} \times \frac{12.0000\,g\,C}{6.022 \times 10^{23} \cancel{\text{atoms C}}} = 299\,g\,C$$

But it also goes beyond carbon. Previously we defined atomic and molecular masses as the number of atomic mass units per atom or molecule. Now we can do so in terms of grams. The atomic mass of an element is the number of grams in 1 mol of atoms of that element, while the molecular mass of a compound is the number of grams in 1 mol of molecules of that compound. Sometimes these masses are called **molar masses** to emphasize the fact that they are the mass for 1 mol of things. (The term *molar* is the adjective form of mole and has nothing to do with teeth.)

Here are some examples. The mass of a hydrogen atom is 1.0079 u; the mass of 1 mol of hydrogen atoms is 1.0079 g. Elemental hydrogen exists as a diatomic molecule, H_2. One molecule has a mass of 1.0079 + 1.0079 = 2.0158 u, while 1 mol H_2 has a mass of 2.0158 g. A molecule of H_2O has a mass of about 18.01 u; 1 mol H_2O has a mass of 18.01 g. A single unit of NaCl has a mass of 58.45 u; NaCl has a molar mass of 58.45 g. In each of these moles of substances, there are 6.022×10^{23} units: 6.022×10^{23} atoms of H, 6.022×10^{23} molecules of H_2 and H_2O, 6.022×10^{23} units of NaCl ions. These relationships give us plenty of opportunities to construct conversion factors for simple calculations.

Example 8.2.2: Sugar

What is the molar mass of sugar ($C_6H_{12}O_6$)?

Solution

To determine the molar mass, we simply add the atomic masses of the atoms in the molecular formula; but express the total in grams per mole, not atomic mass units. The masses of the atoms can be taken from the periodic table.

Solutions to Example 5.3.2

6 C = 6 × 12.011	= 72.066
12 H = 12 × 1.0079	= 12.0948
6 O = 6 × 15.999	= 95.994
TOTAL	= 180.155 g/mol

Per convention, the unit *grams per mole* is written as a fraction.

Exercise 8.2.2

What is the molar mass of $AgNO_3$?

Answer

169.87 g/mol

Knowing the molar mass of a substance, we can calculate the number of moles in a certain mass of a substance and vice versa, as these examples illustrate. The molar mass is used as the conversion factor.

Example 8.2.3

What is the mass of 3.56 mol of $HgCl_2$? The molar mass of $HgCl_2$ is 271.49 g/mol.

Solution

Use the molar mass as a conversion factor between moles and grams. Because we want to cancel the mole unit and introduce the gram unit, we can use the molar mass as given:

$$3.56 \cancel{mol\ HgCl_2} \times \frac{271.49\ g\ HgCl_2}{\cancel{mol\ HgCl_2}} = 967\ g\ HgCl_2$$

Exercise 8.2.3

What is the mass of 33.7 mol of $\mathbf{H_2O}$?

Answer

607 g

Example 8.2.4

How many moles of H_2O are present in 240.0 g of water (about the mass of a cup of water)?

Solution

Use the molar mass of H_2O as a conversion factor from mass to moles. The molar mass of water is

$$(1.0079 + 1.0079 + 15.999) = 18.015\ g/mol.$$

However, because we want to cancel the gram unit and introduce moles, we need to take the reciprocal of this quantity, or 1 mol/18.015 g:

$$240.0\ \cancel{g\ H_2O} \times \frac{1\ mol\ H_2O}{18.015\ \cancel{g\ H_2O}} = 13.32\ mol\ H_2O$$

Exercise 8.2.4

How many moles are present in 35.6 g of H_2SO_4 (molar mass = 98.08 g/mol)?

Answer

0.363 mol

Other conversion factors can be combined with the definition of mole—density, for example.

Example 8.2.5

The density of ethanol is 0.789 g/mL. How many moles are in 100.0 mL of ethanol? The molar mass of ethanol is 46.08 g/mol.

Solution

Here, we use density to convert from volume to mass and then use the molar mass to determine the number of moles.

$$100\ \cancel{ml}\ ethanol \times \frac{0.789\ g}{\cancel{ml}} \times \frac{1\ mol}{46.08\ \cancel{g}} = 1.71\ mol\ ethanol$$

Exercise 8.2.5

If the density of benzene, C_6H_6, is 0.879 g/mL, how many moles are present in 17.9 mL of benzene?

Answer

0.201 mol

Summary

The mole is a key unit in chemistry. The molar mass of a substance, in grams, is numerically equal to one atom's or molecule's mass in atomic mass units.

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8.3: Percent Composition, Empirical and Molecular Formulas

Skills to Develop

- Compute the percent composition of a compound
- Determine the empirical formula of a compound
- Determine the molecular formula of a compound

In the previous section, we discussed the relationship between the bulk mass of a substance and the number of atoms or molecules it contains (moles). Given the chemical formula of the substance, we were able to determine the amount of the substance (moles) from its mass, and vice versa. But what if the chemical formula of a substance is unknown? In this section, we will explore how to apply these very same principles in order to derive the chemical formulas of unknown substances from experimental mass measurements.

Percent Composition

The elemental makeup of a compound defines its chemical identity, and chemical formulas are the most succinct way of representing this elemental makeup. When a compound's formula is unknown, measuring the mass of each of its constituent elements is often the first step in the process of determining the formula experimentally. The results of these measurements permit the calculation of the compound's percent composition, defined as the percentage by mass of each element in the compound. For example, consider a gaseous compound composed solely of carbon and hydrogen. The percent composition of this compound could be represented as follows:

$$\%\mathrm{H} = \frac{\text{mass H}}{\text{mass compound}} \times 100\% \tag{8.3.1}$$

$$\%\mathrm{C} = \frac{\text{mass C}}{\text{mass compound}} \times 100\% \tag{8.3.2}$$

If analysis of a 10.0-g sample of this gas showed it to contain 2.5 g H and 7.5 g C, the percent composition would be calculated to be 25% H and 75% C:

$$\%\mathrm{H} = \frac{2.5\ \text{g H}}{10.0\ \text{g compound}} \times 100\% = 25\% \tag{8.3.3}$$

$$\%\mathrm{C} = \frac{7.5\ \text{g C}}{10.0\ \text{g compound}} \times 100\% = 75\% \tag{8.3.4}$$

Example 8.3.1: Calculation of Percent Composition

Analysis of a 12.04-g sample of a liquid compound composed of carbon, hydrogen, and nitrogen showed it to contain 7.34 g C, 1.85 g H, and 2.85 g N. What is the percent composition of this compound?

Solution

To calculate percent composition, we divide the experimentally derived mass of each element by the overall mass of the compound, and then convert to a percentage:

$$\%\mathrm{C} = \frac{7.34\ \text{g C}}{12.04\ \text{g compound}} \times 100\% = 61.0\%$$

$$\%\mathrm{H} = \frac{1.85\ \text{g H}}{12.04\ \text{g compound}} \times 100\% = 15.4\%$$

$$\%\mathrm{N} = \frac{2.85\ \text{g N}}{12.04\ \text{g compound}} \times 100\% = 23.7\%$$

The analysis results indicate that the compound is 61.0% C, 15.4% H, and 23.7% N by mass.

Exercise 8.3.1

A 24.81-g sample of a gaseous compound containing only carbon, oxygen, and chlorine is determined to contain 3.01 g C, 4.00 g O, and 17.81 g Cl. What is this compound's percent composition?

Answer

12.1% C, 16.1% O, 71.8% Cl

Determining Percent Composition from Formula Mass

Percent composition is also useful for evaluating the relative abundance of a given element in different compounds of known formulas. As one example, consider the common nitrogen-containing fertilizers ammonia (NH_3), ammonium nitrate (NH_4NO_3), and urea (CH_4N_2O). The element nitrogen is the active ingredient for agricultural purposes, so the mass percentage of nitrogen in the compound is a practical and economic concern for

consumers choosing among these fertilizers. For these sorts of applications, the percent composition of a compound is easily derived from its formula mass and the atomic masses of its constituent elements. A molecule of NH_3 contains one N atom weighing 14.01 amu and three H atoms weighing a total of (3 × 1.008 amu) = 3.024 amu. The formula mass of ammonia is therefore (14.01 amu + 3.024 amu) = 17.03 amu, and its percent composition is:

$$\%\text{N} = \frac{14.01\ \text{amu N}}{17.03\ \text{amu NH}_3} \times 100\% = 82.27\% \tag{8.3.5}$$

$$\%\text{H} = \frac{3.024\ \text{amu N}}{17.03\ \text{amu NH}_3} \times 100\% = 17.76\% \tag{8.3.6}$$

This same approach may be taken considering a pair of molecules, a dozen molecules, or a mole of molecules, etc. The latter amount is most convenient and would simply involve the use of molar masses instead of atomic and formula masses, as demonstrated Example **8.3.2**. As long as we know the chemical formula of the substance in question, we can easily derive percent composition from the formula mass or molar mass.

Example 8.3.2: Determining Percent Composition from a Molecular Formula

Aspirin is a compound with the molecular formula $C_9H_8O_4$. What is its percent composition?

Solution

To calculate the percent composition, we need to know the masses of C, H, and O in a known mass of $C_9H_8O_4$. It is convenient to consider 1 mol of $C_9H_8O_4$ and use its molar mass (180.159 g/mole, determined from the chemical formula) to calculate the percentages of each of its elements:

$$\%\text{C} = \frac{9\ \text{mol C} \times \text{molar mass C}}{\text{molar mass } C_9H_{18}O_4} \times 100 = \frac{9 \times 12.01\ \text{g/mol}}{180.159\ \text{g/mol}} \times 100 = \frac{108.09\ \text{g/mol}}{180.159\ \text{g/mol}} \times 100$$
$$\%\text{C} = 60.00\,\%\,\text{C}$$

$$\%\text{H} = \frac{8\ \text{mol H} \times \text{molar mass H}}{\text{molar mass } C_9H_{18}O_4} \times 100 = \frac{8 \times 1.008\ \text{g/mol}}{180.159\ \text{g/mol}} \times 100 = \frac{8.064\ \text{g/mol}}{180.159\ \text{g/mol}} \times 100$$
$$\%\text{H} = 4.476\,\%\,\text{H}$$

$$\%\text{O} = \frac{4\ \text{mol O} \times \text{molar mass O}}{\text{molar mass } C_9H_{18}O_4} \times 100 = \frac{4 \times 16.00\ \text{g/mol}}{180.159\ \text{g/mol}} \times 100 = \frac{64.00\ \text{g/mol}}{180.159\ \text{g/mol}} \times 100$$
$$\%\text{O} = 35.52\%$$

Note that these percentages sum to equal 100.00% when appropriately rounded.

Exercise 8.3.2

To three significant digits, what is the mass percentage of iron in the compound Fe_2O_3?

Answer

69.9% Fe

Determination of Empirical Formulas

As previously mentioned, the most common approach to determining a compound's chemical formula is to first measure the masses of its constituent elements. However, we must keep in mind that chemical formulas represent the relative *numbers*, not masses, of atoms in the substance. Therefore, any experimentally derived data involving mass must be used to derive the corresponding numbers of atoms in the compound. To accomplish this, we can use molar masses to convert the mass of each element to a number of moles. We then consider the moles of each element relative to each other, converting these numbers into a whole-number ratio that can be used to derive the empirical formula of the substance. Consider a sample of compound determined to contain 1.71 g C and 0.287 g H. The corresponding numbers of atoms (in moles) are:

$$1.17\ \text{g C} \times \frac{1\ \text{mol C}}{12.01\ \text{g C}} = 0.142\ \text{mol C} \tag{8.3.7}$$

$$0.287\ \text{g H} \times \frac{1\ \text{mol H}}{1.008\ \text{g H}} = 0.284\ \text{mol H} \tag{8.3.8}$$

Thus, we can accurately represent this compound with the formula $C_{0.142}H_{0.248}$. Of course, per accepted convention, formulas contain whole-number subscripts, which can be achieved by dividing each subscript by the smaller subscript:

$$\text{C}_{\frac{0.142}{0.142}}\ \text{H}_{\frac{0.248}{0.142}}\ \text{or}\ \text{CH}_2 \tag{8.3.9}$$

(Recall that subscripts of "1" are not written, but rather assumed if no other number is present.)

The empirical formula for this compound is thus CH_2. This may or not be the compound's *molecular formula* as well; however, we would need additional information to make that determination (as discussed later in this section).

Consider as another example a sample of compound determined to contain 5.31 g Cl and 8.40 g O. Following the same approach yields a tentative empirical formula of:

$$\mathrm{Cl_{0.150}O_{0.525}} = \mathrm{Cl}\,\frac{0.150}{0.150}\,\mathrm{O}\,\frac{0.525}{0.150} = \mathrm{ClO_{3.5}} \tag{8.3.10}$$

In this case, dividing by the smallest subscript still leaves us with a decimal subscript in the empirical formula. To convert this into a whole number, we must multiply each of the subscripts by two, retaining the same atom ratio and yielding Cl_2O_7 as the final empirical formula.

In summary, empirical formulas are derived from experimentally measured element masses by:

1. Deriving the number of moles of each element from its mass
2. Dividing each element's molar amount by the smallest molar amount to yield subscripts for a tentative empirical formula
3. Multiplying all coefficients by an integer, if necessary, to ensure that the smallest whole-number ratio of subscripts is obtained

Figure **8.3.1** outlines this procedure in flow chart fashion for a substance containing elements A and X.

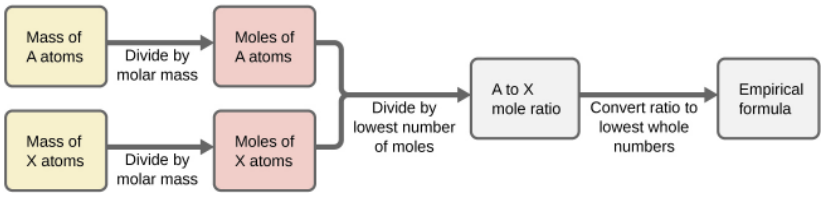


Figure* 8.3.1: The empirical formula of a compound can be derived from the masses of all elements in the sample.*

Example 8.3.3: Determining an Empirical Formula from Masses of Elements

A sample of the black mineral hematite (Figure **8.3.2**), an oxide of iron found in many iron ores, contains 34.97 g of iron and 15.03 g of oxygen. What is the empirical formula of hematite?



***Figure* 8.3.2*:** Hematite is an iron oxide that is used in jewelry. (credit: Mauro Cateb)*

Solution

For this problem, we are given the mass in grams of each element. Begin by finding the moles of each:

$$34.97\ \mathrm{g\ Fe}\left(\frac{\mathrm{mol\ Fe}}{55.85\ \mathrm{g}}\right) = 0.6261\ \mathrm{mol\ Fe}$$

$$15.03\ \mathrm{g\ O}\left(\frac{\mathrm{mol\ O}}{16.00\ \mathrm{g}}\right) = 0.9394\ \mathrm{mol\ O}$$

Next, derive the iron-to-oxygen molar ratio by dividing by the lesser number of moles:

$$\frac{0.6261}{0.6261} = 1.000\ \mathrm{mol\ Fe}$$

$$\frac{0.9394}{0.6261} = 1.500\ \mathrm{mol\ O}$$

The ratio is 1.000 mol of iron to 1.500 mol of oxygen ($Fe_1O_{1.5}$). Finally, multiply the ratio by two to get the smallest possible whole number subscripts while still maintaining the correct iron-to-oxygen ratio:

$$2(\mathrm{Fe_1O_{1.5}}) = \mathrm{Fe_2O_3}$$

The empirical formula is $\boldsymbol{Fe_2O_3}$.

Exercise 8.3.3

What is the empirical formula of a compound if a sample contains 0.130 g of nitrogen and 0.370 g of oxygen?

Answer:

$\boldsymbol{N_2O_5}$



***Video* 8.3.1**: *Additional worked examples illustrating the derivation of empirical formulas are presented in the brief video clip.*

Deriving Empirical Formulas from Percent Composition

Finally, with regard to deriving empirical formulas, consider instances in which a compound's percent composition is available rather than the absolute masses of the compound's constituent elements. In such cases, the percent composition can be used to calculate the masses of elements present in any convenient mass of compound; these masses can then be used to derive the empirical formula in the usual fashion.

Example 8.3.4: Determining an Empirical Formula from Percent Composition

The bacterial fermentation of grain to produce ethanol forms a gas with a percent composition of 27.29% C and 72.71% O (Figure **8.3.3**). What is the empirical formula for this gas?



***Figure* 8.3.3**: *An oxide of carbon is removed from these fermentation tanks through the large copper pipes at the top. (credit: "Dual Freq"/Wikimedia Commons)*

Solution Since the scale for percentages is 100, it is most convenient to calculate the mass of elements present in a sample weighing 100 g. The calculation is "most convenient" because, per the definition for percent composition, the mass of a given element in grams is numerically equivalent to the element's mass percentage. This numerical equivalence results from the definition of the "percentage" unit, whose name is derived from the Latin phrase *per centum* meaning "by the hundred." Considering this definition, the mass percentages provided may be more conveniently expressed as fractions:

$$27.29\,\%\,\mathrm{C} = \frac{27.29\ \mathrm{g\ C}}{100\ \mathrm{g\ compound}}$$

$$72.71\,\%\,\mathrm{O} = \frac{72.71\ \mathrm{g\ O}}{100\ \mathrm{g\ compound}}$$

The molar amounts of carbon and hydrogen in a 100-g sample are calculated by dividing each element's mass by its molar mass:

$$27.29\ \text{g C}\left(\frac{\text{mol C}}{12.01\ \text{g}}\right) = 2.272\ \text{mol C}$$

$$72.71\ \text{g O}\left(\frac{\text{mol O}}{16.00\ \text{g}}\right) = 4.544\ \text{mol O}$$

Coefficients for the tentative empirical formula are derived by dividing each molar amount by the lesser of the two:

$$\frac{2.272\ \text{mol C}}{2.272} = 1$$

$$\frac{4.544\ \text{mol O}}{2.272} = 2$$

Since the resulting ratio is one carbon to two oxygen atoms, the empirical formula is CO_2.

Exercise 8.3.4

What is the empirical formula of a compound containing 40.0% C, 6.71% H, and 53.28% O?

Answer:

CH_2O

Derivation of Molecular Formulas

Recall that empirical formulas are symbols representing the *relative* numbers of a compound's elements. Determining the *absolute* numbers of atoms that compose a single molecule of a covalent compound requires knowledge of both its empirical formula and its molecular mass or molar mass. These quantities may be determined experimentally by various measurement techniques. Molecular mass, for example, is often derived from the mass spectrum of the compound (see discussion of this technique in the previous chapter on atoms and molecules).

Molecular formulas are derived by comparing the compound's molecular or molar mass to its empirical formula mass. As the name suggests, an empirical formula mass is the sum of the average atomic masses of all the atoms represented in an empirical formula. If we know the molecular (or molar) mass of the substance, we can divide this by the empirical formula mass in order to identify the number of empirical formula units per molecule.

The table below lists families of compounds with the same empirical formula

Empirical Formula	Empirical Formula Molar Mass	Molecular Formula	Molecular Formula Molar Mass	Molecular Formula Mass/Empirical Formula Mass
CH_3	15.035 g/mole	CH_3	15.035 g/mole	$\frac{15.035\ \frac{g}{mole}}{15.035\ \frac{g}{mole}} = 1$ (8.3.11)
CH_3	15.035 g/mole	C_2H_6	30.07 g/mole	$\frac{30.07\ \frac{g}{mole}}{15.035\ \frac{g}{mole}} = 2$ (8.3.12)
CH_3	15.035 g/mole	C_3H_9	45.105 g/mole	$\frac{45.104\ \frac{g}{mole}}{15.035\ \frac{g}{mole}} = 3$ (8.3.13)
CH_4O	33.04 g/mole	CH_4O	32.04 g/mole	$\frac{32.04\ \frac{g}{mole}}{32.04\ \frac{g}{mole}} = 1$ (8.3.14)
CH_4O	33.04 g/mole	$C_2H_8O_2$	64.08 g/mole	$\frac{64.08\ \frac{g}{mole}}{32.04\ \frac{g}{mole}} = 2$ (8.3.15)
CH_4O	33.04 g/mole	$C_3H_{12}O_3$	96.13 g/mole	$\frac{96.13\ \frac{g}{mole}}{32.04\ \frac{g}{mole}} \approx 3$ (8.3.16)

$$\frac{\text{molecular or molar mass}\left(\text{amu or }\frac{\text{g}}{\text{mol}}\right)}{\text{empirical formula mass}\left(\text{amu or }\frac{\text{g}}{\text{mol}}\right)} = n\ \text{formula units/molecule} \tag{8.3.17}$$

The molecular formula is then obtained by multiplying each subscript in the empirical formula by n, as shown by the generic empirical formula A_xB_y:

Double subscripts: use braces to clarify

For example, consider a covalent compound whose empirical formula is determined to be CH_2O. The empirical formula mass for this compound is approximately 30 amu (the sum of 12 amu for one C atom, 2 amu for two H atoms, and 16 amu for one O atom). If the compound's molecular mass is determined to be 180 amu, this indicates that molecules of this compound contain six times the number of atoms represented in the empirical formula:

$$\frac{180\ \text{amu/molecule}}{30\ \frac{\text{amu}}{\text{formula unit}}} = 6\ \text{formula units/molecule} \tag{8.3.18}$$

Molecules of this compound are then represented by molecular formulas whose subscripts are six times greater than those in the empirical formula:

$$(CH_2O)_6 = C_6H_{12}O_6 \tag{8.3.19}$$

Note that this same approach may be used when the molar mass (g/mol) instead of the molecular mass (amu) is used. In this case, we are merely considering one mole of empirical formula units and molecules, as opposed to single units and molecules.

Example 8.3.5: Determination of the Molecular Formula for Nicotine

Nicotine, an alkaloid in the nightshade family of plants that is mainly responsible for the addictive nature of cigarettes, contains 74.02% C, 8.710% H, and 17.27% N. If 40.57 g of nicotine contains 0.2500 mol nicotine, what is the molecular formula?

Solution

Determining the molecular formula from the provided data will require comparison of the compound's empirical formula mass to its molar mass. As the first step, use the percent composition to derive the compound's empirical formula. Assuming a convenient, a 100-g sample of nicotine yields the following molar amounts of its elements:

$$(74.02\ \text{g C})\left(\frac{1\ \text{mol C}}{12.01\ \text{g C}}\right) = 6.163\ \text{mol C} \tag{8.3.20}$$

$$(8.710\ \text{g H})\left(\frac{1\ \text{mol H}}{1.01\ \text{g H}}\right) = 8.624\ \text{mol H} \tag{8.3.21}$$

$$(17.27\ \text{g N})\left(\frac{1\ \text{mol N}}{14.01\ \text{g N}}\right) = 1.233\ \text{mol N} \tag{8.3.22}$$

Next, we calculate the molar ratios of these elements relative to the least abundant element, **N**.

$$\left(\frac{6.163\ \text{mol C}}{1.233\ \text{mol N}}\right) = \left(\frac{4.998\ \text{mol C}}{1\ \text{mol N}}\right) = \left(\frac{5\ \text{mol C}}{1\ \text{mol N}}\right) \tag{8.3.23}$$

$$\left(\frac{8.624\ \text{mol H}}{1.233\ \text{mol N}}\right) = \left(\frac{6.994\ \text{mol H}}{1\ \text{mol N}}\right) = \left(\frac{7\ \text{mol H}}{1\ \text{mol N}}\right) \tag{8.3.24}$$

$$\left(\frac{1.233\ \text{mol N}}{1.233\ \text{mol N}}\right) = \left(\frac{1\ \text{mol N}}{1\ \text{mol N}}\right) \tag{8.3.25}$$

The C-to-N and H-to-N molar ratios are adequately close to whole numbers, and so the empirical formula is C_5H_7N. The empirical formula mass for this compound is therefore 81.13 amu/formula unit, or 81.13 g/mol formula unit.

We calculate the molar mass for nicotine from the given mass and molar amount of compound:

$$\frac{40.57\ \text{g nicotine}}{0.2500\ \text{mol nicotine}} = \frac{162.3\ \text{g}}{\text{mol}} \tag{8.3.26}$$

Comparing the molar mass and empirical formula mass indicates that each nicotine molecule contains two formula units:

$$\frac{162.3\ \text{g/mol}}{81.13\ \frac{\text{g}}{\text{formula unit}}} = 2\ \text{formula units/molecule} \tag{8.3.27}$$

Thus, we can derive the molecular formula for nicotine from the empirical formula by multiplying each subscript by two:

$$(C_5H_7N)_2 = C_{10}H_{14}N_2 \tag{8.3.28}$$

Exercise 8.3.5

What is the molecular formula of a compound with a percent composition of 49.47% C, 5.201% H, 28.84% N, and 16.48% O, and a molecular mass of 194.2 amu?

Answer:

$C_8H_{10}N_4O_2$

Summary

The chemical identity of a substance is defined by the types and relative numbers of atoms composing its fundamental entities (molecules in the case of covalent compounds, ions in the case of ionic compounds). A compound's percent composition provides the mass percentage of each element in the compound, and it is often experimentally determined and used to derive the compound's empirical formula. The empirical formula mass of a covalent compound may be compared to the compound's molecular or molar mass to derive a molecular formula.

Key Equations

- $\%X = \frac{\text{mass X}}{\text{mass compound}} \times 100\%$
- $\frac{\text{molecular or molar mass}\left(\text{amu or } \frac{\text{g}}{\text{mol}}\right)}{\text{empirical formula mass}\left(\text{amu or } \frac{\text{g}}{\text{mol}}\right)} = n\ \text{formula units/molecule}$
- $(A_xB_y)_n = A_{nx}B_{ny}$

Glossary

empirical formula mass
sum of average atomic masses for all atoms represented in an empirical formula

percent composition
percentage by mass of the various elements in a compound

Contributors

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8.4: Empirical Formulas

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CHAPTER OVERVIEW

13: Gases

Of the three basic phases of matter—solids, liquids, and gases—only one of them has predictable physical properties: gases. In fact, the study of the properties of gases was the beginning of the development of modern chemistry from its alchemical roots. The interesting thing about some of these properties is that they are independent of the identity of the gas. That is, it doesn't matter if the gas is helium gas, oxygen gas, or sulfur vapors; some of their behavior is predictable and, as we will find, very similar. In this chapter, we will review some of the common behaviors of gases.

Let us start by reviewing some properties of gases. Gases have no definite shape or volume; they tend to fill whatever container they are in. They can compress and expand, sometimes to a great extent. Gases have extremely low densities, one-thousandth or less the density of a liquid or solid. Combinations of gases tend to mix together spontaneously; that is, they form solutions. Air, for example, is a solution of mostly nitrogen and oxygen. Any understanding of the properties of gases must be able to explain these characteristics.

13.10: Gas Stoichometry
13.1: Kinetic Theory of Gases
13.2: Gas Pressure
13.4: Gas Laws - Charles Law - Volume and Temperature
13.5: Gas Laws - Gay-Lussac's Law - Pressure and Temperature
13.7: Gas Laws - Combined Gas Law - Pressure, Volume and Temperature
13.8: The Ideal Gas Law and Some Applications

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13.10: Gas Stoichometry

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13.1: Kinetic Theory of Gases

Learning Objectives

- State the major concepts behind the kinetic theory of gases.
- Relate the general properties of gases to the kinetic theory.

Gases were among the first substances studied in terms of the modern scientific method, which was developed in the 1600s. It did not take long to recognize that gases all shared certain physical behaviors, suggesting that all gases could be described by one all-encompassing theory. Today, that theory is the **kinetic theory of gases**. The kinetic theory of gases is based on the following statements:

1. Gases consist of tiny particles of matter that are in constant motion.
2. Gas particles are constantly colliding with each other and the walls of a container. These collisions are elastic—that is, there is no net loss of energy from the collisions.
3. Gas particles are separated by large distances, with the size of a gas particle tiny compared to the distances that separate them.
4. There are no interactive forces (i.e., attraction or repulsion) between the particles of a gas.
5. The average speed of gas particles is dependent on the temperature of the gas.

Figure 13.1.1 shows a representation of how we mentally picture the gas phase.

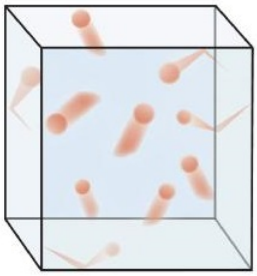


Figure 13.1.1: The Kinetic Theory of Gases. The kinetic theory of gases describes this state of matter as composed of tiny particles in constant motion, with a lot of distance between the particles.

This model of gases explains some of the physical properties of gases. Because most of a gas is empty space, a gas has a low density and can expand or contract under the appropriate influence. The fact that gas particles are in constant motion means that two or more gases will always mix, as the particles from the individual gases move and collide with each other.

An **ideal gas** is a gas that exactly follows the statements of the kinetic theory. Unfortunately, *real gases* are not ideal. Many gases deviate slightly from agreeing perfectly with the kinetic theory of gases. However, most gases adhere to the statements, and the kinetic theory of gases is well accepted by the scientific community.

- The physical behavior of gases is explained by the kinetic theory of gases.
- An ideal gas adheres exactly to the kinetic theory of gases.

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13.2: Gas Pressure

Skills to Develop

- Define the property of pressure
- Define and convert among the units of pressure measurements
- Describe the operation of common tools for measuring gas pressure

The earth's atmosphere exerts a pressure, as does any other gas. Although we do not normally notice atmospheric pressure, we are sensitive to pressure changes—for example, when your ears "pop" during take-off and landing while flying, or when you dive underwater. Gas pressure is caused by the force exerted by gas molecules colliding with the surfaces of objects (Figure **13.2.1**). Although the force of each collision is very small, any surface of appreciable area experiences a large number of collisions in a short time, which can result in a high pressure. In fact, normal air pressure is strong enough to crush a metal container when not balanced by equal pressure from inside the container.

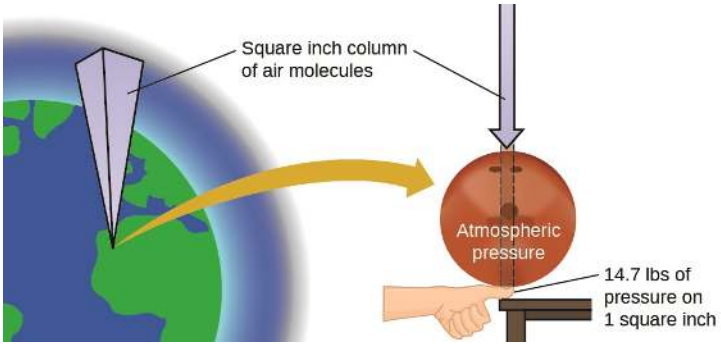


Figure* 13.2.1: The atmosphere above us exerts a large pressure on objects at the surface of the earth, roughly equal to the weight of a bowling ball pressing on an area the size of a human thumbnail.*

Atmospheric pressure is caused by the weight of the column of air molecules in the atmosphere above an object, such as the tanker car. At sea level, this pressure is roughly the same as that exerted by a full-grown African elephant standing on a doormat, or a typical bowling ball resting on your thumbnail. These may seem like huge amounts, and they are, but life on earth has evolved under such atmospheric pressure. If you actually perch a bowling ball on your thumbnail, the pressure experienced is twice the usual pressure, and the sensation is unpleasant.



A dramatic illustration of atmospheric pressure is provided in this brief video, which shows a railway tanker car imploding when its internal pressure is decreased.

Pressure is defined as the force exerted on a given area:

$$P = \frac{F}{A} \tag{13.2.1}$$

Since pressure is directly proportional to force and inversely proportional to area (Equation **13.2.1**), pressure can be increased either by either **increasing** the amount of force or by **decreasing** the area over which it is applied. Correspondingly, pressure

can be decreased by either **decreasing** the force or **increasing** the area.

Let's apply the definition of pressure (Equation 13.2.1) to determine which would be more likely to fall through thin ice in Figure 13.2.2.—the elephant or the figure skater?



***Figure* 13.2.2**: *Although (a) an elephant's weight is large, creating a very large force on the ground, (b) the figure skater exerts a much higher pressure on the ice due to the small surface area of her skates. (credit a: modification of work by Guido da Rozze; credit b: modification of work by Ryosuke Yagi).*

A large African elephant can weigh 7 tons, supported on four feet, each with a diameter of about 1.5 ft (footprint area of 250 in^2), so the pressure exerted by each foot is about 14 lb/in^2:

$$\text{pressure per elephant foot} = 14,000\frac{\text{lb}}{\text{elephant}} \times \frac{1\text{ elephant}}{4\text{ feet}} \times \frac{1\text{ foot}}{250\text{ in}^2} = 14\text{ lb/in}^2 \tag{13.2.2}$$

The figure skater weighs about 120 lbs, supported on two skate blades, each with an area of about 2 in^2, so the pressure exerted by each blade is about 30 lb/in^2:

$$\text{pressure per skate blade} = 120\frac{\text{lb}}{\text{skater}} \times \frac{1\text{ skater}}{2\text{ blades}} \times \frac{1\text{ blade}}{2\text{ in}^2} = 30\text{ lb/in}^2 \tag{13.2.3}$$

Even though the elephant is more than one hundred-times heavier than the skater, it exerts less than one-half of the pressure and would therefore be less likely to fall though thin ice. On the other hand, if the skater removes her skates and stands with bare feet (or regular footwear) on the ice, the larger area over which her weight is applied greatly reduces the pressure exerted:

$$\text{pressure per human foot} = 120\frac{\text{lb}}{\text{skater}} \times \frac{1\text{ skater}}{2\text{ feet}} \times \frac{1\text{ foot}}{30\text{ in}^2} = 2\text{ lb/in}^2 \tag{13.2.4}$$

The SI unit of pressure is the pascal (Pa), with 1 Pa = 1 N/m^2, where N is the newton, a unit of force defined as 1 kg m/s^2. One pascal is a small pressure; in many cases, it is more convenient to use units of kilopascal (1 kPa = 1000 Pa) or bar (1 bar = 100,000 Pa). In the United States, pressure is often measured in pounds of force on an area of one square inch—pounds per square inch (psi)—for example, in car tires. Pressure can also be measured using the unit atmosphere (atm), which originally represented the average sea level air pressure at the approximate latitude of Paris (45°). Table 13.2.1 provides some information on these and a few other common units for pressure measurements

***Table* 13.2.1**: *Pressure Units*

Unit Name and Abbreviation	Definition or Relation to Other Unit	Comment
pascal (Pa)	1 Pa = 1 N/m^2	recommended IUPAC unit
kilopascal (kPa)	1 kPa = 1000 Pa	
pounds per square inch (psi)	air pressure at sea level is ~14.7 psi	
atmosphere (atm)	1 atm = 101,325 Pa	air pressure at sea level is ~1 atm
bar (bar, or b)	1 bar = 100,000 Pa (exactly)	commonly used in meteorology
millibar (mbar, or mb)	1000 mbar = 1 bar	
inches of mercury (in. Hg)	1 in. Hg = 3386 Pa	used by aviation industry, also some weather reports
torr	$1\ \text{torr} = \frac{1}{760}\ \text{atm}$	named after Evangelista Torricelli, inventor of the barometer
millimeters of mercury (mm Hg)	1 mm Hg ~1 torr	

Example 13.2.1: Conversion of Pressure Units

The United States National Weather Service reports pressure in both inches of Hg and millibars. Convert a pressure of 29.2 in. Hg into:

a. torr
b. atm
c. kPa
d. mbar

Solution

This is a unit conversion problem. The relationships between the various pressure units are given in Table 9.2.1.

a. $29.2\ \cancel{\text{in Hg}} \times \frac{25.4\ \cancel{\text{mm}}}{1\ \cancel{\text{in}}} \times \frac{1\ \text{torr}}{1\ \cancel{\text{mm Hg}}} = 742\ \text{torr}$

b. $742\ \cancel{\text{torr}} \times \frac{1\ \text{atm}}{760\ \cancel{\text{torr}}} = 0.976\ \text{atm}$

c. $742\ \cancel{\text{torr}} \times \frac{101.325\ \text{kPa}}{760\ \cancel{\text{torr}}} = 98.9\ \text{kPa}$

d. $98.9\ \cancel{\text{kPa}} \times \frac{1000\ \cancel{\text{Pa}}}{1\ \cancel{\text{kPa}}} \times \frac{1\ \cancel{\text{bar}}}{100,000\ \cancel{\text{Pa}}} \times \frac{1000\ \text{mbar}}{1\ \cancel{\text{bar}}} = 989\ \text{mbar}$

Exercise 13.2.1

A typical barometric pressure in Kansas City is 740 torr. What is this pressure in atmospheres, in millimeters of mercury, in kilopascals, and in bar?

Answer

0.974 atm; 740 mm Hg; 98.7 kPa; 0.987 bar

We can measure atmospheric pressure, the force exerted by the atmosphere on the earth's surface, with a barometer (Figure **13.2.3**). A barometer is a glass tube that is closed at one end, filled with a nonvolatile liquid such as mercury, and then inverted and immersed in a container of that liquid. The atmosphere exerts pressure on the liquid outside the tube, the column of liquid exerts

pressure inside the tube, and the pressure at the liquid surface is the same inside and outside the tube. The height of the liquid in the tube is therefore proportional to the pressure exerted by the atmosphere.

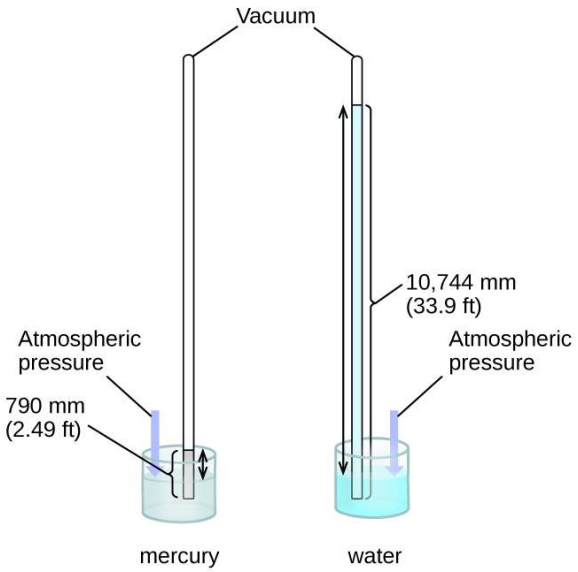


***Figure* 13.2.3**: *In a barometer, the height, h, of the column of liquid is used as a measurement of the air pressure. Using very dense liquid mercury (left) permits the construction of reasonably sized barometers, whereas using water (right) would require a barometer more than 30 feet tall.*

If the liquid is water, normal atmospheric pressure will support a column of water over 10 meters high, which is rather inconvenient for making (and reading) a barometer. Because mercury (Hg) is about 13.6-times denser than water, a mercury barometer only needs to be $\frac{1}{13.6}$ as tall as a water barometer—a more suitable size. Standard atmospheric pressure of 1 atm at sea level (101,325 Pa) corresponds to a column of mercury that is about 760 mm (29.92 in.) high. The torr was originally intended to be a unit equal to one millimeter of mercury, but it no longer corresponds exactly. The pressure exerted by a fluid due to gravity is known as hydrostatic pressure, p:

$$p = h\rho g \tag{13.2.5}$$

where

- h is the height of the fluid,
- ρ is the density of the fluid, and
- g is acceleration due to gravity.

Example 13.2.2: Calculation of Barometric Pressure

Show the calculation supporting the claim that atmospheric pressure near sea level corresponds to the pressure exerted by a column of mercury that is about 760 mm high. The density of mercury = $13.6\ g/cm^3$.

Solution

The hydrostatic pressure is given by Equation 13.2.5, with $h = 760\ mm$, $\rho = 13.6\ g/cm^3$, and $g = 9.81\ m/s^2$. Plugging these values into the Equation 13.2.5 and doing the necessary unit conversions will give us the value we seek. (Note: We are expecting to find a pressure of ~101,325 Pa:)

$$101,325\ N/\mathrm{m}^2 = 101,325\ \frac{\mathrm{kg}\cdot\mathrm{m/s}^2}{\mathrm{m}^2} = 101,325\ \frac{\mathrm{kg}}{\mathrm{m}\cdot\mathrm{s}^2} \tag{13.2.6}$$

$$\begin{aligned} p &= \left(760\ \mathrm{mm} \times \frac{1\ \mathrm{m}}{1000\ \mathrm{mm}}\right) \times \left(\frac{13.6\ \mathrm{g}}{1\ \mathrm{cm}^3} \times \frac{1\ \mathrm{kg}}{1000\ \mathrm{g}} \times \frac{(100\ \mathrm{cm})^3}{(1\ \mathrm{m})^3}\right) \times \left(\frac{9.81\ \mathrm{m}}{1\ \mathrm{s}^2}\right) \\ &= (0.760\ \mathrm{m})(13,600\ \mathrm{kg/m}^3)(9.81\ \mathrm{m/s}^2) = 1.01 \times 10^5\ \mathrm{kg/ms}^2 = 1.01 \times 10^5 N/\mathrm{m}^2 \\ &= 1.01 \times 10^5\ \mathrm{Pa} \end{aligned}$$

Exercise 13.2.2

Calculate the height of a column of water at 25 °C that corresponds to normal atmospheric pressure. The density of water at this temperature is 1.0 g/cm^3.

Answer

10.3 m

Application: Measuring Blood Pressure

Blood pressure is measured using a device called a sphygmomanometer (Greek *sphygmos* = "pulse"). It consists of an inflatable cuff to restrict blood flow, a manometer to measure the pressure, and a method of determining when blood flow begins and when it becomes impeded (Figure **13.2.5**). Since its invention in 1881, it has been an essential medical device. There are many types of sphygmomanometers: manual ones that require a stethoscope and are used by medical professionals; mercury ones, used when the most accuracy is required; less accurate mechanical ones; and digital ones that can be used with little training but that have limitations. When using a sphygmomanometer, the cuff is placed around the upper arm and inflated until blood flow is completely blocked, then slowly released. As the heart beats, blood forced through the arteries causes a rise in pressure. This rise in pressure at which blood flow begins is the *systolic pressure*—the peak pressure in the cardiac cycle. When the cuff's pressure equals the arterial systolic pressure, blood flows past the cuff, creating audible sounds that can be heard using a stethoscope. This is followed by a decrease in pressure as the heart's ventricles prepare for another beat. As cuff pressure continues to decrease, eventually sound is no longer heard; this is the *diastolic pressure*—the lowest pressure (resting phase) in the cardiac cycle. Blood pressure units from a sphygmomanometer are in terms of millimeters of mercury (mm Hg).



***Figure* 13.2.5:** *(a) A medical technician prepares to measure a patient's blood pressure with a sphygmomanometer. (b) A typical sphygmomanometer uses a valved rubber bulb to inflate the cuff and a diaphragm gauge to measure pressure. (credit a: modification of work by Master Sgt. Jeffrey Allen)*

Meteorology, Climatology, and Atmospheric Science

Throughout the ages, people have observed clouds, winds, and precipitation, trying to discern patterns and make predictions: when it is best to plant and harvest; whether it is safe to set out on a sea voyage; and much more. We now face complex weather and atmosphere-related challenges that will have a major impact on our civilization and the ecosystem. Several different scientific disciplines use chemical principles to help us better understand weather, the atmosphere, and climate. These are meteorology, climatology, and atmospheric science. Meteorology is the study of the atmosphere, atmospheric phenomena, and atmospheric effects on earth's weather. Meteorologists seek to understand and predict the weather in the short term, which can save lives and benefit the economy. Weather forecasts (Figure **13.2.5**) are the result of thousands of measurements of air pressure, temperature, and the like, which are compiled, modeled, and analyzed in weather centers worldwide.

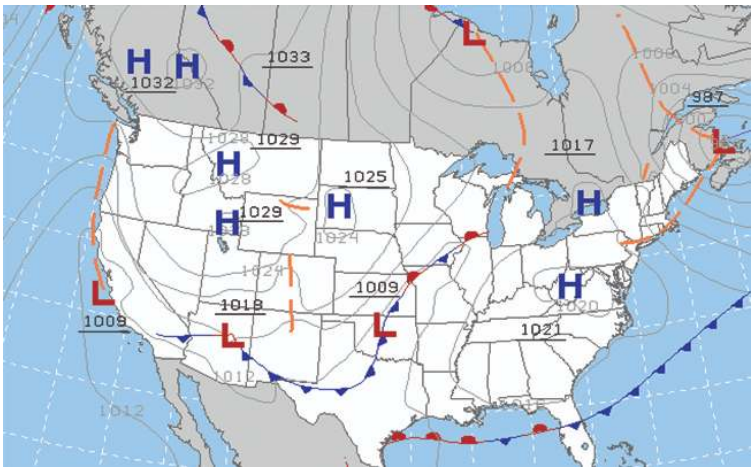


Figure* 13.2.6*: *Meteorologists use weather maps to describe and predict weather. Regions of high (H) and low (L) pressure have large effects on weather conditions. The gray lines represent locations of constant pressure known as isobars. (credit: modification of work by National Oceanic and Atmospheric Administration)*

In terms of weather, low-pressure systems occur when the earth's surface atmospheric pressure is lower than the surrounding environment: Moist air rises and condenses, producing clouds. Movement of moisture and air within various weather fronts instigates most weather events.

The atmosphere is the gaseous layer that surrounds a planet. Earth's atmosphere, which is roughly 100–125 km thick, consists of roughly 78.1% nitrogen and 21.0% oxygen, and can be subdivided further into the regions shown in Figure **13.2.7**: the exosphere (furthest from earth, > 700 km above sea level), the thermosphere (80–700 km), the mesosphere (50–80 km), the stratosphere (second lowest level of our atmosphere, 12–50 km above sea level), and the troposphere (up to 12 km above sea level, roughly 80% of the earth's atmosphere by mass and the layer where most weather events originate). As you go higher in the troposphere, air density and temperature both decrease.

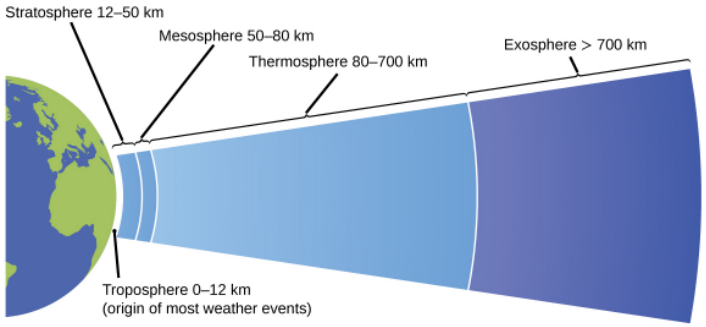


Figure* 13.2.7*: *Earth's atmosphere has five layers: the troposphere, the stratosphere, the mesosphere, the thermosphere, and the exosphere.*

Climatology is the study of the climate, averaged weather conditions over long time periods, using atmospheric data. However, climatologists study patterns and effects that occur over decades, centuries, and millennia, rather than shorter time frames of hours, days, and weeks like meteorologists. Atmospheric science is an even broader field, combining meteorology, climatology, and other scientific disciplines that study the atmosphere.

Summary

Gases exert pressure, which is force per unit area. The pressure of a gas may be expressed in the SI unit of pascal or kilopascal, as well as in many other units including torr, atmosphere, and bar. Atmospheric pressure is measured using a barometer; other gas pressures can be measured using one of several types of manometers.

Key Equations

- $P = \frac{F}{A}$

Glossary

atmosphere (atm)
unit of pressure; 1 atm = 101,325 Pa

bar
(bar or b) unit of pressure; 1 bar = 100,000 Pa

barometer
device used to measure atmospheric pressure

hydrostatic pressure
pressure exerted by a fluid due to gravity

pascal (Pa)
SI unit of pressure; 1 Pa = 1 N/m^2

pounds per square inch (psi)
unit of pressure common in the US

pressure
force exerted per unit area

torr
unit of pressure; $1 \text{ torr} = \frac{1}{760} \text{ atm}$

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13.8: The Ideal Gas Law and Some Applications

Learning Objectives

- Learn the ideal gas law.
- Apply the ideal gas law to any set of conditions of a gas.
- Apply the ideal gas law to molar volumes, density, and stoichiometry problems.

So far, the gas laws we have considered have all required that the gas change its conditions; then we predict a resulting change in one of its properties. Are there any gas laws that relate the physical properties of a gas at any given time? Consider a further extension of the combined gas law to include *n*. By analogy to Avogadro's law, *n* is positioned in the denominator of the fraction, opposite the volume. So

$$\frac{PV}{nT} = constant \tag{13.8.1}$$

Because pressure, volume, temperature, and amount are the only four independent physical properties of a gas, the constant in the above equation is truly a constant; indeed, because we do not need to specify the identity of a gas to apply the gas laws, this constant is the same for all gases. We define this constant with the symbol *R*, so the previous equation is written as

$$\frac{PV}{nT} = R \tag{13.8.2}$$

which is usually rearranged as

$$PV = nRT \tag{13.8.3}$$

This equation is called the **ideal gas law**. It relates the four independent properties of a gas at any time. The constant *R* is called the ideal gas law constant. Its value depends on the units used to express pressure and volume.

Table 6.6.1 - Values of the Ideal Gas Law Constant lists the numerical values of R.

Numerical Value	Units
0.08205	$\frac{L*atm}{mol*K}$
62.36	$\frac{L·torr}{mol·K} = \frac{L·mmHg}{mol·K}$
8.314	$\frac{J}{mol·K}$

The ideal gas law is used like any other gas law, with attention paid to the unit and making sure that temperature is expressed in Kelvin. However, *the ideal gas law does not require a change in the conditions of a gas sample*. The ideal gas law implies that if you know any three of the physical properties of a gas, you can calculate the fourth property.

Example 13.8.1:

A 4.22 mol sample of Ar has a pressure of 1.21 atm and a temperature of 34°C. What is its volume?

Solution

The first step is to convert temperature to kelvins:

34 + 273 = 307 K

Now we can substitute the conditions into the ideal gas law:

$$(1.21 atm)(V) = (4.22\, mol)(0.08205 \frac{L \cdot atm}{mol \cdot K})(307\, K) \tag{13.8.4}$$

The *atm* unit is in the numerator of both sides, so it cancels. On the right side of the equation, the *mol* and *K* units appear in the numerator and the denominator, so they cancel as well. The only unit remaining is *L*, which is the unit of volume that we are looking for. We isolate the volume variable by dividing both sides of the equation by 1.21:

$$V = \frac{(4.22)(0.08205)(307)}{1.21} L \tag{13.8.5}$$

Then solving for volume, we get V = 87.9 L

Exercise 13.8.1

A 0.0997 mol sample of O_2 has a pressure of 0.692 atm and a temperature of 333 K. What is its volume?

Answer

3.94 L

Example 13.8.2:

At a given temperature, 0.00332 g of Hg in the gas phase has a pressure of 0.00120 mmHg and a volume of 435 L. What is its temperature?

Solution

We are not given the number of moles of Hg directly, but we are given a mass. We can use the molar mass of Hg to convert to the number of moles.

$$0.00332\ \cancel{g\ Hg} \times \frac{1\ mol\ Hg}{200.59\ \cancel{g\ Hg}} = 0.0000165\ mol = 1.65 \times 10^{-5} mol \tag{13.8.6}$$

Pressure is given in units of millimeters of mercury. We can either convert this to atmospheres or use the value of the ideal gas constant that includes the mmHg unit. We will take the second option. Substituting into the ideal gas law,

$$(0.00332\ mm\ Hg)(435\ L) = (1.65 \times 10^{-5} mol)(62.36 \frac{L \cdot mmHg}{mol \cdot K})T \tag{13.8.7}$$

The mmHg, L, and mol units cancel, leaving the K unit, the unit of temperature. Isolating T all by itself on one side, we get

$$T = \frac{(0.00332)(435)}{(1.65 \times 10^{-5})(62.36)} K \tag{13.8.8}$$

Then solving for K, we get T = 1,404 K

Exercise 13.8.2

For a 0.00554 mol sample of H_2, P = 23.44 torr and T = 557 K. What is its volume?

Answer

8.21 L

The ideal gas law can also be used in stoichiometry problems.

Example 13.8.3:

What volume of H_2 is produced at 299 K and 1.07 atm when 55.8 g of Zn metal react with excess HCl?

$$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$

Solution

Here we have a stoichiometry problem where we need to find the number of moles of H_2 produced. Then we can use the ideal gas law, with the given temperature and pressure, to determine the volume of gas produced. First, the number of moles of H_2 is calculated:

$$55.8\ \cancel{g\ Zn} \times \frac{1\ \cancel{mol\ Zn}}{65.41\ \cancel{g\ Zn}} \times \frac{1\ mol\ H_2}{1\ \cancel{mol\ Zn}} = 0.853\ H_2 \tag{13.8.9}$$

Now that we know the number of moles of gas, we can use the ideal gas law to determine the volume, given the other conditions:

$$(1.07atm)V = (0.853\,mol)(0.08205\frac{L \cdot atm}{mol \cdot K})(299\,K) \tag{13.8.10}$$

All the units cancel except for L, for volume, which means V = 19.6 L

Exercise 13.8.3

What pressure of HCl is generated if 3.44 g of Cl_2 are reacted in 4.55 L at 455 K?

$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$

Answer

0.796 atm

It should be obvious by now that some physical properties of gases depend strongly on the conditions. What we need is a set of standard conditions so that properties of gases can be properly compared to each other. **Standard Temperature and Pressure (STP)** is defined as exactly 100 kPa of pressure (0.986 atm) and 273 K (0°C). For simplicity, we will use 1 atm as standard pressure. Defining STP allows us to compare more directly the properties of gases that differ from each other.

One property shared among gases is a molar volume. The **molar volume** is the volume of 1 mol of a gas. At STP, the molar volume of a gas can be easily determined by using the ideal gas law:

$$(1\,atm)V = (1\,mol)(0.08205\frac{L \cdot atm}{mol \cdot K})(273\,K) \tag{13.8.11}$$

All the units cancel except for L, the unit of volume. So V = 22.4 L

Note that we have not specified the identity of the gas; we have specified only that the pressure is 1 atm and the temperature is 273 K. This makes for a very useful approximation: *any gas at STP has a volume of 22.4 L per mole of gas*; that is, the molar volume at STP is 22.4 L/mol (Fig. 6.6.1 Molar Volume). This molar volume makes a useful conversion factor in stoichiometry problems if the conditions are at STP. If the conditions are not at STP, a molar volume of 22.4 L/mol is not applicable. However, if the conditions are not at STP, the combined gas law can be used to calculate what the volume of the gas would be if at STP; then the 22.4 L/mol molar volume can be used.

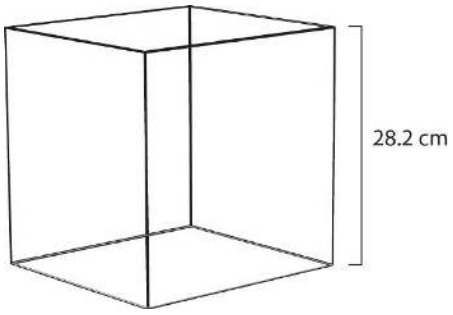


Fig. 6.6.1: Molar Volume. A mole of gas at STP occupies 22.4 L, the volume of a cube that is 28.2 cm on a side.

Example 13.8.4:

How many moles of Ar are present in 38.7 L at STP?

Solution

We can use the molar volume, 22.4 L/mol, as a conversion factor, but we need to reverse the fraction so that the L units cancel and mol units are introduced. It is a one-step conversion:

$$38.7\,\cancel{L} \times \frac{1\,mol}{22.4\,\cancel{L}} = 1.73\,mol \tag{13.8.12}$$

Exercise 13.8.4

What volume does 4.87 mol of Kr have at STP?

Answer

109 L

Example 13.8.5:

What volume of H_2 is produced at STP when 55.8 g of Zn metal react with excess HCl?

$$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$

Solution

This is a stoichiometry problem with a twist: we need to use the molar volume of a gas at STP to determine the final answer. The first part of the calculation is the same as in a previous example:

$$55.8\ g\ Zn \times \frac{1\ mol\ Zn}{65.41\ g\ Zn} \times \frac{1\ mol\ H_2}{1\ mol\ Zn} = 0.853\ H_2 \tag{13.8.13}$$

Now we can use the molar volume, 22.4 L/mol, because the gas is at STP:

$$0.853\ mol\ H_2 \times \frac{22.4\ L}{1\ mol\ H_2} = 19.1\ L\ H_2 \tag{13.8.14}$$

Alternatively, we could have applied the molar volume as a third conversion factor in the original stoichiometry calculation.

Exercise 13.8.5

What volume of HCl is generated if 3.44 g of Cl_2 are reacted at STP?

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$$

Answer

2.17 L

The ideal gas law can also be used to determine the densities of gases. Density, recall, is defined as the mass of a substance divided by its volume:

$$d = \frac{m}{V} \tag{13.8.15}$$

Assume that you have exactly 1 mol of a gas. If you know the identity of the gas, you can determine the molar mass of the substance. Using the ideal gas law, you can also determine the volume of that mole of gas, using whatever the temperature and pressure conditions are. Then you can calculate the density of the gas by using

$$density = \frac{molar\ mass}{molar\ volume} \tag{13.8.16}$$

Example 13.8.6:

What is the density of N_2 at 25°C and 0.955 atm?

Solution

First, we must convert the temperature into kelvins:

$$25 + 273 = 298\ K$$

If we assume exactly 1 mol of N_2, then we know its mass: 28.0 g. Using the ideal gas law, we can calculate the volume:

$$(0.955\ atm)V = (1\ mol)(0.08205\frac{L \cdot atm}{mol \cdot K})(298\ K) \tag{13.8.17}$$

All the units cancel except for L, the unit of volume. So V = 25.6 L

Knowing the molar mass and the molar volume, we can determine the density of N_2 under these conditions:

$$d = \frac{28.0\,g}{25.6\,L} = 1.09\,g/L \tag{13.8.18}$$

Exercise 13.8.6

What is the density of CO_2 at a pressure of 0.0079 atm and 227 K? (These are the approximate atmospheric conditions on Mars.)

Answer

0.019 g/L

Note
Chemistry Is Everywhere: Breathing

Breathing (more properly called *respiration*) is the process by which we draw air into our lungs so that our bodies can take up oxygen from the air. Let us apply the gas laws to breathing.

Start by considering pressure. We draw air into our lungs because the diaphragm, a muscle underneath the lungs, moves down to reduce pressure in the lungs, causing external air to rush in to fill the lower-pressure volume. We expel air by the diaphragm pushing against the lungs, increasing pressure inside the lungs and forcing the high-pressure air out. What are the pressure changes involved? A quarter of an atmosphere? A tenth of an atmosphere? Actually, under normal conditions, it's only 1 or 2 torr of pressure difference that makes us breathe in and out.

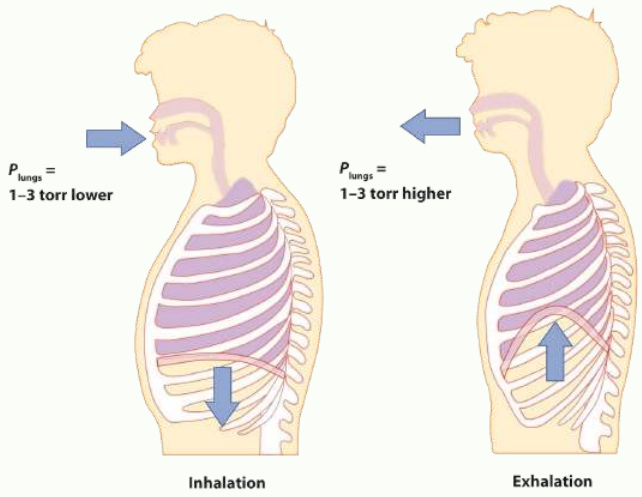


Fig. 6.6.2 Breathing Mechanics. Breathing involves pressure differences between the inside of the lungs and the air outside. The pressure differences are only a few torr.

A normal breath is about 0.50 L. If room temperature is about 22°C, then the air has a temperature of about 295 K. With normal pressure being 1.0 atm, how many moles of air do we take in for every breath? The ideal gas law gives us an answer:

$$(1.0\,atm)(0.50\,L) = n(0.08205\frac{L \cdot atm}{mol \cdot K})(295\,K) \tag{13.8.19}$$

Solving for the number of moles, we get

n = 0.021 mol air

This ends up being about 0.6 g of air per breath—not much but enough to keep us alive.

Summary

- The ideal gas law relates the four independent physical properties of a gas at any time.
- The ideal gas law can be used in stoichiometry problems whose chemical reactions involve gases.
- Standard temperature and pressure (STP) are a useful set of benchmark conditions to compare other properties of gases.

- At STP, gases have a volume of 22.4 L per mole.
- The ideal gas law can be used to determine densities of gases.

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CHAPTER OVERVIEW

11: Electronic Structure

Atoms act the way they do because of their structure. We already know that atoms are composed of protons, neutrons, and electrons. Protons and neutrons are located in the nucleus, and electrons orbit around the nucleus. But we need to know the structural details to understand why atoms react the way they do. Virtually everything we know about atoms ultimately comes from light. Before we can understand the composition of atoms (especially electrons), we need to understand the properties of light.

11.1: Light

11.2: Quantum Numbers for Electrons

11.3: Organization of Electrons in Atoms

11.4: Electronic Structure and the Periodic Table

11.5: Periodic Trends

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11.1: Light

Learning Objectives

- Describe light with its frequency and wavelength.
- Describe light as a particle of energy.

What is known as light is more properly called *electromagnetic radiation*. We know from experiments that light acts as a wave. As such, it can be described as having a frequency and a wavelength. The **wavelength** of light is the distance between corresponding points in two adjacent light cycles, and the **frequency** of light is the number of cycles of light that pass a given point in one second. Wavelength is typically represented by λ, the lowercase Greek letter *lambda*, while frequency is represented by ν, the lowercase Greek letter *nu* (although it looks like a Roman "vee," it is actually the Greek equivalent of the letter "en"). Wavelength has units of length (meters, centimeters, etc.), while frequency has units of *per second*, written as s^{-1} and sometimes called a *hertz* (Hz). Figure **11.1.1** - Characteristics of Light Waves, shows how these two characteristics are defined.

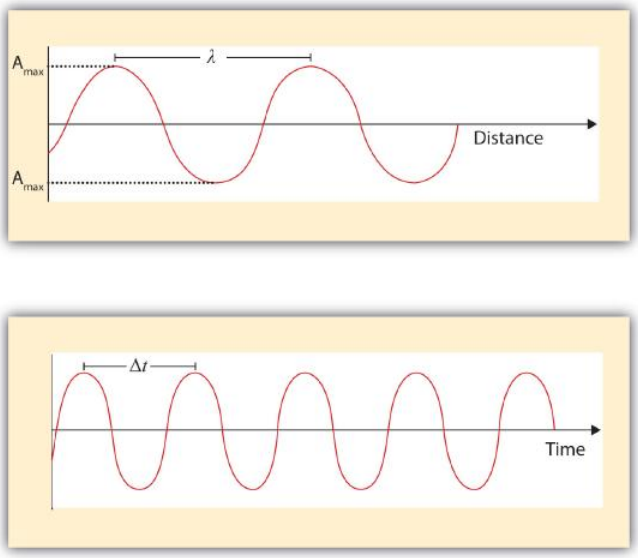


Figure **11.1.1**: Characteristics of Light Waves. Light acts as a wave and can be described by a wavelength λ and a frequency ν.

One property of waves is that their speed is equal to their wavelength times their frequency. That means we have

$$speed = \lambda\nu$$

For light, however, speed is actually a universal constant when light is traveling through a vacuum (or, to a very good approximation, air). The measured speed of light (c) in a vacuum is 2.9979×10^8 m/s, or about 3.00×10^8 m/s. Thus, we have

$$c = \lambda\nu$$

Because the speed of light is a constant, the wavelength and the frequency of light are related to each other: as one increases, the other decreases and vice versa. We can use this equation to calculate what one property of light has to be when given the other property.

Example 11.1.1

What is the frequency of light if its wavelength is 5.55×10^{-7} m?

Solution

We use the equation that relates the wavelength and frequency of light with its speed. We have

$$3.00 \times 10^8 m/s = \left(5.55 \times 10^{-7} m\right)\nu$$

We divide both sides of the equation by 5.55×10^{-7} m and get

$$\nu = 5.41 \times 10^{14} s^{-1}$$

Note how the m units cancel, leaving s in the denominator. A unit in a denominator is indicated by a −1 power, s^{-1}, and read as "per second."

? Exercise 11.1.1

What is the wavelength of light if its frequency is 1.55×10^{10} s^{-1}?

Answer

0.0194 m, or 19.4 mm

Light also behaves like a package of energy. It turns out that for light, the energy of the "package" of energy is proportional to its frequency. (For most waves, energy is proportional to wave amplitude, or the height of the wave.) The mathematical equation that relates the energy (E) of light to its frequency is

$$E = h\nu$$

where ν is the frequency of the light, and h is a constant called Planck's constant. Its value is 6.626×10^{-34} J·s—a very small number that is another fundamental constant of our universe, like the speed of light. The units on Planck's constant may look unusual, but these units are required so that the algebra works out.

✓ Example 11.1.2

What is the energy of light if its frequency is 1.55×10^{10} s^{-1}?

Solution

Using the formula for the energy of light, we have

$E = (6.626 \times 10^{-34}$ J·s$)(1.55 \times 10^{10}$ $s^{-1})$

Seconds are in the numerator and the denominator, so they cancel, leaving us with joules, the unit of energy. So

$E = 1.03 \times 10^{-23}$ J

This is an extremely small amount of energy—but this is for only one light wave.

? Exercise 11.1.2

What is the frequency of a light wave if its energy is 4.156×10^{-20} J?

Answer

6.27×10^{13} s^{-1}

Because a light wave behaves like a little particle of energy, light waves have a particle-type name: the photon. It is not uncommon to hear light described as photons.

Wavelengths, frequencies, and energies of light span a wide range; the entire range of possible values for light is called the **electromagnetic spectrum**. We are mostly familiar with visible light, which is light having a wavelength range between about 400 nm and 700 nm. Light can have much longer and much shorter wavelengths than this, with corresponding variations in frequency and energy. Figure **11.1.2** shows the entire electromagnetic spectrum and how certain regions of the spectrum are labeled. You may already be familiar with some of these regions; they are all light—with different frequencies, wavelengths, and energies.

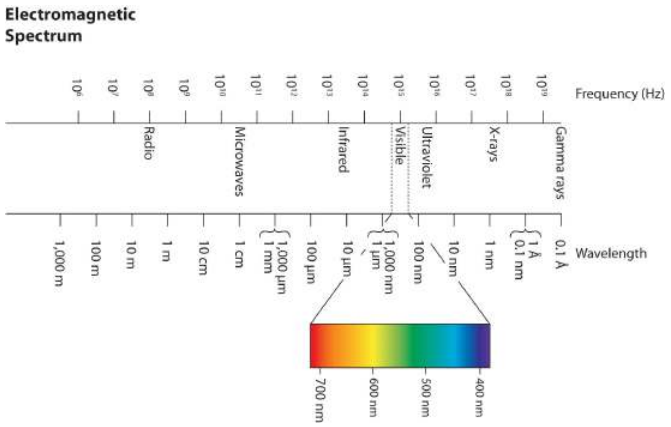


Figure **11.1.2**: The Electromagnetic Spectrum. The electromagnetic spectrum, with its various regions labeled. The borders of each region are approximate.

Summary

Light acts like a wave, with a frequency and a wavelength. The frequency and wavelength of light are related by the speed of light, a constant. Light acts like a particle of energy, whose value is related to the frequency of light.

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11.2: Quantum Numbers for Electrons

Learning Objectives

- Explain what spectra are.
- Learn the quantum numbers that are assigned to electrons.

There are two fundamental ways of generating light: either heat an object up so hot it glows or pass an electrical current through a sample of matter (usually a gas). Incandescent lights and fluorescent lights generate light via these two methods, respectively.

A hot object gives off a continuum of light. We notice this when the visible portion of the electromagnetic spectrum is passed through a prism: the prism separates light into its constituent colors, and all colors are present in a continuous rainbow (part (a) in Figure **11.2.1** - Prisms and Light). This image is known as a **continuous spectrum**. However, when electricity is passed through a gas and light is emitted and this light is passed though a prism, we see only certain lines of light in the image (part (b) in Figure **11.2.1** - Prisms and Light). This image is called a line spectrum. It turns out that every element has its own unique, characteristic line spectrum.

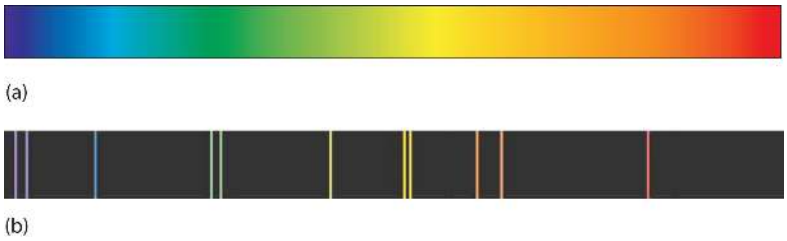


Figure* 11.2.1*: *Prisms and Light. (a) A glowing object gives off a full rainbow of colors, which are noticed only when light is passed through a prism to make a continuous spectrum. (b) However, when electricity is passed through a gas, only certain colors of light are emitted. Here are the colors of light in the line spectrum of Hg.*

Why does the light emitted from an electrically excited gas have only certain colors, while light given off by hot objects has a continuous spectrum? For a long time, it was not well explained. Particularly simple was the spectrum of hydrogen gas, which could be described easily by an equation; no other element has a spectrum that is so predictable (Figure **11.2.2** - Hydrogen Spectrum).



Figure* 11.2.2*: *Hydrogen Spectrum. The spectrum of hydrogen was particularly simple and could be predicted by a simple mathematical expression.*

In 1913, the Danish scientist Niels Bohr suggested a reason why the hydrogen atom spectrum looked this way. He suggested that the electron in a hydrogen atom could not have any random energy, having *only* certain fixed values of energy that were indexed by the number *n* (the **quantum number**). Quantities that have certain specific values are **quantized** values. Bohr suggested that the energy of the electron in hydrogen was quantized because it was in a specific orbit. Because the energies of the electron can have only certain values, the changes in energies can have only certain values (somewhat similar to a staircase: not only are the stair steps set at specific heights but the height between steps is fixed). Finally, Bohr suggested that the energy of light emitted from electrified hydrogen gas was equal to the energy difference of the electron's energy states:

$$E_{light} = h\nu = \frac{hc}{\lambda} = \Delta E_{electron} \tag{11.2.1}$$

This means that only certain frequencies - (and thus, certain wavelengths (\lambda)) of light are emitted. Figure **11.2.3** - Bohr's Model of the Hydrogen Atom, shows a model of the hydrogen atom based on Bohr's ideas.

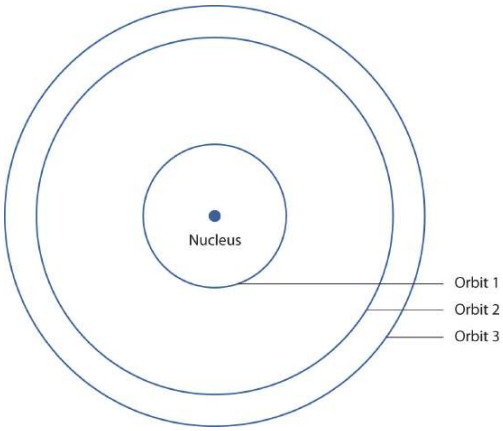


Figure* 11.2.3*: *Bohr's Model of the Hydrogen Atom. Bohr's description of the hydrogen atom had specific orbits for the electron, which had quantized energies.*

Bohr's ideas were useful but were applied only to the hydrogen atom. However, later researchers generalized Bohr's ideas into a new theory called **quantum mechanics**, which explains the behavior of electrons as if they were acting as a wave, not as particles. Quantum mechanics predicts two major things: quantized energies for electrons of all atoms (not just hydrogen) and an organization of electrons within atoms. Electrons are no longer thought of as being randomly distributed around a nucleus or restricted to certain orbits (in that regard, Bohr was wrong). Instead, electrons are collected into groups and subgroups that explain much about the chemical behavior of the atom.

In the quantum-mechanical model of an atom, the state of an electron is described by four quantum numbers, not just the one predicted by Bohr. The first quantum number is called the **principal quantum number(n).** The principal quantum number largely determines the energy of an electron. Electrons in the same atom that have the same principal quantum number are said to occupy an electron **shell** of the atom. The principal quantum number can be any nonzero positive integer: 1, 2, 3, 4,….

Within a shell, there may be multiple possible values of the next quantum number, the **angular momentum quantum number(ℓ)**. The ℓ quantum number has a minor effect on the energy of the electron but also affects the spatial distribution of the electron in three-dimensional space—that is, the shape of an electron's distribution in space. The value of the ℓ quantum number can be any integer between 0 and $n - 1$: ℓ = 0, 1, 2,…, $n - 1$

Thus, for a given value of n, there are different possible values of ℓ:

If n equals	ℓ can be
1	0
2	0 or 1
3	0, 1, or 2
4	0, 1, 2, or 3

and so forth. Electrons within a shell that have the same value of ℓ are said to occupy a **subshell** in the atom. Commonly, instead of referring to the numerical value of ℓ, a letter represents the value of ℓ (to help distinguish it from the principal quantum number):

If ℓ equals	The letter is
0	*s*
1	*p*
2	*d*
3	*f*

The next quantum number is called the **magnetic quantum number (m_ℓ)**. For any value of ℓ, there are $2\ell + 1$ possible values of m_ℓ, ranging from $-\ell$ to ℓ:

$$-\ell < m_\ell < \ell \tag{11.2.2}$$

or

$$|m_\ell| < \ell \tag{11.2.3}$$

The following explicitly lists the possible values of m_ℓ for the possible values of ℓ:

If ℓ equals	The m_ℓ values can be
0	0
1	−1, 0, or 1
2	−2, −1, 0, 1, or 2
3	−3, −2, −1, 0, 1, 2, or 3

The particular value of m_ℓ dictates the orientation of an electron's distribution in space. When ℓ is zero, m_ℓ can be only zero, so there is only one possible orientation. When ℓ is 1, there are three possible orientations for an electron's distribution. When ℓ is 2, there are five possible orientations of electron distribution. This goes on and on for other values of ℓ, but we need not consider any higher values of ℓ here. Each value of m_ℓ designates a certain orbital. Thus, there is only one orbital when ℓ is zero, three orbitals when ℓ is 1, five orbitals when ℓ is 2, and so forth. The m_ℓ quantum number has no effect on the energy of an electron unless the electrons are subjected to a magnetic field—hence its name.

The ℓ quantum number dictates the general shape of electron distribution in space (Figure **11.2.4** - Electron Orbitals). Any s orbital is spherically symmetric (Figure **11.2.4*a*** - Electron Orbitals, and there is only one orbital in any s subshell. Any p orbital has a two-lobed, dumbbell-like shape (Figure **11.2.4*b*** - Electron Orbitals); because there are three of them, we normally represent them as pointing along the x-, y-, and z-axes of Cartesian space. The d orbitals are four-lobed rosettes (Figure **11.2.4*c*** - Electron Orbitals they are oriented differently in space (the one labeled d_{z^2} has two lobes and a torus instead of four lobes, but it is equivalent to the other orbitals). When there is more than one possible value of m_ℓ, each orbital is labeled with one of the possible values. It should be noted that the diagrams in Figure **11.2.4** are estimates of the electron distribution in space, not surfaces electrons are fixed on.

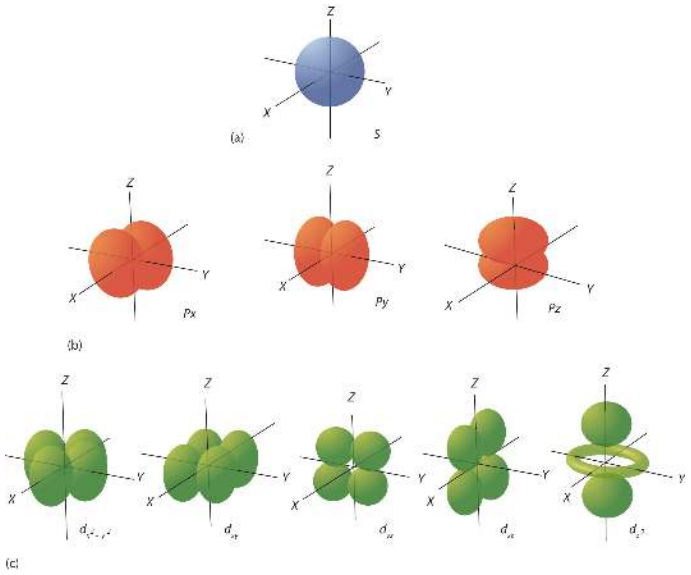


Figure* 11.2.4*: *Electron Orbitals. (a) The lone s orbital is spherical in distribution. (b) The three p orbitals are shaped like dumbbells, and each one points in a different direction. (c) The five d orbitals are rosette in shape, except for the* Math input error *orbital, which is a "dumbbell + torus" combination. They are all oriented in different directions.*

The final quantum number is the **spin quantum number** (m_S). Electrons and other subatomic particles behave as if they are spinning (we cannot tell if they really are, but they behave as if they are). Electrons themselves have two possible spin states, and because of mathematics, they are assigned the quantum numbers +1/2 and −1/2. These are the only two possible choices for the spin quantum number of an electron.

Example 11.2.1:

Of the set of quantum numbers $\{n, \ell, m_\ell, m_S\}$, which are possible and which are not allowed?

a. {3, 2, 1, +1/2}
b. {2, 2, 0, −1/2}
c. {3, −1, 0, +1/2}

Solution

a. The principal quantum number n must be an integer, which it is here. The quantum number ℓ must be less than n, which it is. The m_ℓ quantum number must be between $-\ell$ and ℓ, which it is. The spin quantum number is +1/2, which is allowed. Because this set of quantum numbers follows all restrictions, it is possible.
b. The quantum number n is an integer, but the quantum number ℓ must be less than n, which it is not. Thus, this is not an allowed set of quantum numbers.
c. The principal quantum number n is an integer, but ℓ is not allowed to be negative. Therefore this is not an allowed set of quantum numbers.

Exercise 11.2.1

Of the set of quantum numbers $\{n, \ell, m_\ell, m_S\}$, which are possible and which are not allowed?

a. {4, 2, −2, 1}
b. {3, 1, 0, −1/2}

Answers

a. Spin must be either +1/2 or −1/2, so this set of quantum number is not allowed.
b. allowed

Chemistry Is Everywhere: Neon Lights

A neon light is basically an electrified tube with a small amount of gas in it. Electricity excites electrons in the gas atoms, which then give off light as the electrons go back into a lower energy state. However, many so-called “neon” lights don’t contain neon!

Although we know now that a gas discharge gives off only certain colors of light, without a prism or other component to separate the individual light colors, we see a composite of all the colors emitted. It is not unusual for a certain color to predominate. True neon lights, with neon gas in them, have a reddish-orange light due to the large amount of red-, orange-, and yellow-colored light emitted. However, if you use krypton instead of neon, you get a whitish light, while using argon yields a blue-purple light. A light filled with nitrogen gas glows purple, as does a helium lamp. Other gases—and mixtures of gases—emit other colors of light. Ironically, despite its importance in the development of modern electronic theory, hydrogen lamps emit little visible light and are rarely used for illumination purposes.



Neon lights. The different colors of these "neon" lights are caused by gases other than neon in the discharge tubes. Human/Need/Desire. Neon sculpture by Bruce Nauman (1983), who has been characterized as a conceptual artist. Image used with permission (CC BY-SA 3.0; eschipul).

Key Takeaways

Electrons in atoms have quantized energies. The state of electrons in atoms is described by four quantum numbers.

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11.3: Organization of Electrons in Atoms

Learning Objectives

- Learn how electrons are organized within atoms.
- Represent the organization of electrons by an electron configuration.

Now that you know that electrons have quantum numbers, how are they arranged in atoms? The key to understanding electronic arrangement is summarized in the **Pauli exclusion principle:** no two electrons in an atom can have the same set of four quantum numbers. This dramatically limits the number of electrons that can exist in a shell or a subshell.

Electrons are typically organized around an atom by starting at the lowest possible quantum numbers first, which are the shells-subshells with lower energies. Consider H, an atom with a single electron only. Under normal conditions, the single electron would go into the n = 1 shell, which has only a single s subshell with one orbital (because m_ℓ can equal only 0). The convention is to label the shell-subshell combination with the number of the shell and the letter that represents the subshell. Thus, the electron goes in the 1s shell-subshell combination. It is usually not necessary to specify the m_ℓ or m_s quantum numbers, but for the H atom, the electron has $m_\ell = 0$ (the only possible value) and an m_s of either +1/2 or −1/2.

The He atom has two electrons. The second electron can also go into the 1s shell-subshell combination, but only if its spin quantum number is different from the first electron's spin quantum number. Thus, the sets of quantum numbers for the two electrons are {1, 0, 0, +1/2} and {1, 0, 0, −1/2}. Notice that the overall set is different for the two electrons, as required by the Pauli exclusion principle.

The next atom is Li, with three electrons. However, now the Pauli exclusion principle implies that we cannot put that electron in the 1s shell-subshell because no matter how we try, this third electron would have the same set of four quantum numbers as one of the first two electrons. So this third electron must be assigned to a different shell-subshell combination. However, the n = 1 shell doesn't have another subshell; it is restricted to having just $\ell = 0$, or an s subshell. Therefore, this third electron has to be assigned to the n = 2 shell, which has an s ($\ell = 0$) subshell and a p ($\ell = 1$) subshell. Again, we usually start with the lowest quantum number, so this third electron is assigned to the 2s shell-subshell combination of quantum numbers.

The Pauli exclusion principle has the net effect of limiting the number of electrons that can be assigned a shell-subshell combination of quantum numbers. For example, in any s subshell, no matter what the shell number, there can be a maximum of only two electrons. Once the s subshell is filled up, any additional electrons must go to another subshell in the shell (if it exists), or to a higher-numbered shell. A similar analysis shows that a p subshell can hold a maximum of six electrons. A d subshell can hold a maximum of 10 electrons, while an f subshell can have a maximum of 14 electrons. By limiting subshells to these maxima, we can distribute the available electrons to their shells and subshells.

Example 11.3.1: Carbon Atoms

How would the six electrons for C be assigned to the n and ℓ quantum numbers?

Solution

The first two electrons go into the 1s shell-subshell combination. Two additional electrons can go into the 2s shell-subshell, but now this subshell is filled with the maximum number of electrons. The n = 2 shell also has a p subshell, so the remaining two electrons can go into the 2p subshell. The 2p subshell is not completely full because it can hold a maximum of six electrons.

Exercise 11.3.1: Sodium Atoms

How would the 11 electrons for Na be assigned to the n and ℓ quantum numbers?

Answer

two 1s electrons, two 2s electrons, six 2p electrons, and one 3s electron

Now that we see how electrons are partitioned among the shells and subshells, we need a more concise way of communicating this partitioning. Chemists use an **electron configuration** to represent the organization of electrons in shells and subshells in an atom. An electron configuration simply lists the shell and subshell labels, with a right superscript giving the number of electrons in that subshell. The shells and subshells are listed in the order of filling.

For example, an H atom has a single electron in the 1s subshell. Its electron configuration is

$$\text{H: } 1s^1$$

The He atom has two electrons in the 1s subshell. Its electron configuration is

$$\text{He: } 1s^2$$

The three electrons for Li are arranged in the 1s subshell (two electrons) and the 2s subshell (one electron). The electron configuration of Li is

$$\text{Li: } 1s^2 2s^1$$

The Be atom has four electrons, two in the 1s subshell and two in the 2s subshell. Its electron configuration is

$$\text{Be: } 1s^2 2s^2$$

Now that the 2s subshell is filled, electrons in larger atoms must go into the 2p subshell, which can hold a maximum of six electrons. The next six elements progressively fill up the 2p subshell:

- B: $1s^2 2s^2 2p^1$
- 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: $1s^2 2s^2 2p^6$

Now that the 2p subshell is filled (all possible subshells in the n = 2 shell), the next electron for the next-larger atom must go into the n = 3 shell, s subshell.

Example 11.3.2: Sodium

What is the electron configuration for Na, which has 11 electrons?

Solution

The first two electrons occupy the 1s subshell. The next two occupy the 2s subshell, while the next six electrons occupy the 2p subshell. This gives us 10 electrons so far, with 1 electron left. This last electron goes into the n = 3 shell, s subshell. Thus, the electron configuration of Na is $1s^2 2s^2 2p^6 3s^1$.

Exercise 11.3.2: Magnesium

What is the electron configuration for Mg, which has 12 electrons?

Answer

$1s^2 2s^2 2p^6 3s^2$

For larger atoms, the electron arrangement becomes more complicated. This is because after the 3p subshell is filled, filling the 4s subshell first actually leads to a lesser overall energy than filling the 3d subshell. Recall that while the principal quantum number largely dictates the energy of an electron, the angular momentum quantum number also has an impact on energy; by the time we get to the 3d and 4s subshells, we see overlap in the filling of the shells. Thus, after the 3p subshell is completely filled (which occurs for Ar), the next electron for K occupies the 4s subshell, not the 3d subshell:

$$\text{K: } 1s^2 2s^2 2p^6 3s^2 3p^6 4s^1,$$

not

$$\text{K: } 1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$$

For larger and larger atoms, the order of filling the shells and subshells seems to become even more complicated. There are some useful ways to remember the order, like that shown in Figure **11.3.1**. If you follow the arrows in order, they pass through the subshells in the order that they are filled with electrons in larger atoms. Initially, the order is the same as the expected shell-subshell order, but for larger atoms, there is some shifting around of the principal quantum numbers. However, Figure **11.3.1** gives a valid ordering of filling subshells with electrons for most atoms.

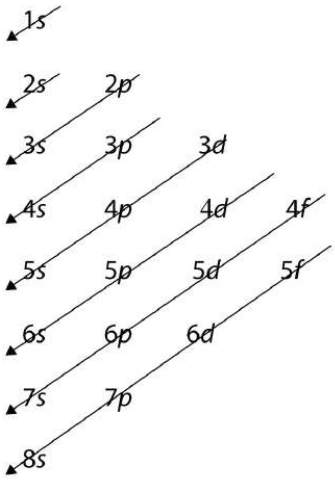


Figure **11.3.1** Electron Shell Filling Order. Starting with the top arrow, follow each arrow. The subshells you reach along each arrow give the ordering of filling of subshells in larger atoms. The n = 5 and higher shells have more subshells, but only those subshells that are needed to accommodate the electrons of the known elements are given.

The electron shell filling order goes as follows: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p, then 8s.

✔ Example 11.3.3: Tin

What is the predicted electron configuration for Sn, which has 50 electrons?

Solution

We will follow the chart in Figure 8.4., until we can accommodate 50 electrons in the subshells in the proper order: Sn: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^2$

Verify by adding the superscripts, which indicate the number of electrons: 2 + 2 + 6 + 2 + 6 + 2 + 10 + 6 + 2 + 10 + 2 = 50, so we have placed all 50 electrons in subshells in the proper order.

? Exercise 11.3.3: Barium

What is the electron configuration for Ba, which has 56 electrons?

Answer

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2$

As the previous example demonstrated, electron configurations can get fairly long. An **abbreviated electron configuration** uses one of the elements from the last column of the periodic table, which contains the noble gases, to represent the core of electrons up to that element. Then, the remaining electrons are listed explicitly. For example, the abbreviated electron configuration for Li, which has three electrons, would be

$$\text{Li: [He]}2s^1$$

where [He] represents the two-electron core that is equivalent to He's electron configuration. The square brackets represent the electron configuration of a noble gas. This is not much of an abbreviation. However, consider the abbreviated electron configuration for W, which has 74 electrons:

$$\text{W: [Xe]6s}^2\text{4f}^{14}\text{5d}^4$$

This is a significant simplification over an explicit listing of all 74 electrons. So for larger elements, the abbreviated electron configuration can be a very useful shorthand.

Example 11.3.4: Phosphorus

What is the abbreviated electron configuration for P, which has 15 electrons?

Solution

With 15 electrons, the electron configuration of P is

$$\text{P: } 1s^2 2s^2 2p^6 3s^2 3p^3$$

The first immediate noble gas is Ne, which has an electron configuration of $1s^2 2s^2 2p^6$. Using the electron configuration of Ne to represent the first 10 electrons, the abbreviated electron configuration of P is

$$\text{P: [Ne]}3s^2 3p^3$$

Exercise 11.3.4: Rubidium

What is the abbreviated electron configuration for Rb, which has 37 electrons?

Answer

$[\text{Kr}]5s^1$

There are some exceptions to the rigorous filling of subshells by electrons. In many cases, an electron goes from a higher-numbered shell to a lower-numbered, but later-filled, subshell to fill the later-filled subshell. One example is Ag. With 47 electrons, its electron configuration is predicted to be

$$\text{Ag: [Kr]}5s^2 4d^9$$

However, experiments have shown that the electron configuration is actually

$$\text{Ag: [Kr]}5s^1 4d^{10}$$

This, then, qualifies as an exception to our expectations. At this point, you do not need to memorize the exceptions; but if you come across one, understand that it is an exception to the normal rules of filling subshells with electrons, which can happen.

Summary

The Pauli exclusion principle limits the number of electrons in the subshells and shells. Electrons in larger atoms fill shells and subshells in a regular pattern that can be followed. Electron configurations are a shorthand method of indicating what subshells electrons occupy in atoms. Abbreviated electron configurations are a simpler way of representing electron configurations for larger atoms. Exceptions to the strict filling of subshells with electrons do occur.

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11.4: Electronic Structure and the Periodic Table

Learning Objectives

- Relate the electron configurations of the elements to the shape of the periodic table.
- Determine the expected electron configuration of an element by its place on the periodic table.

In Chapter 3, we introduced the periodic table as a tool for organizing the known chemical elements. A periodic table is shown in Figure **11.4.1**. The elements are listed by atomic number (the number of protons in the nucleus), and elements with similar chemical properties are grouped together in columns.

1 H 1.00794																	2 He 4.002602
3 Li 6.941	4 Be 9.012182											5 B 10.811	6 C 12.0107	7 N 14.00674	8 O 15.9994	9 F 18.9984032	10 Ne 20.1797
11 Na 22.989770	12 Mg 24.3050											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 196.56655	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.760	52 Te 127.60	53 I 126.90447	54 Xe 131.29
55 Cs 132.90545	56 Ba 137.327	57 La 138.9055	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 Tl 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)	89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 (269)	111 (272)	112 (277)		114 (289) (287)		116 (289)		118 (293)

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	71 Lu 174.967
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)	103 Lr (262)

Figure **11.4.1**: The Periodic Table

Why does the periodic table have the structure it does? The answer is rather simple, if you understand electron configurations, the shape of the periodic table mimics the filling of the subshells with electrons.

> *The shape of the periodic table mimics the filling of the subshells with electrons.*

Let us start with H and He. Their electron configurations are $1s^1$ and $1s^2$, respectively; with He, the $n = 1$ shell is filled. These two elements make up the first row of the periodic table (Figure **11.4.2**)

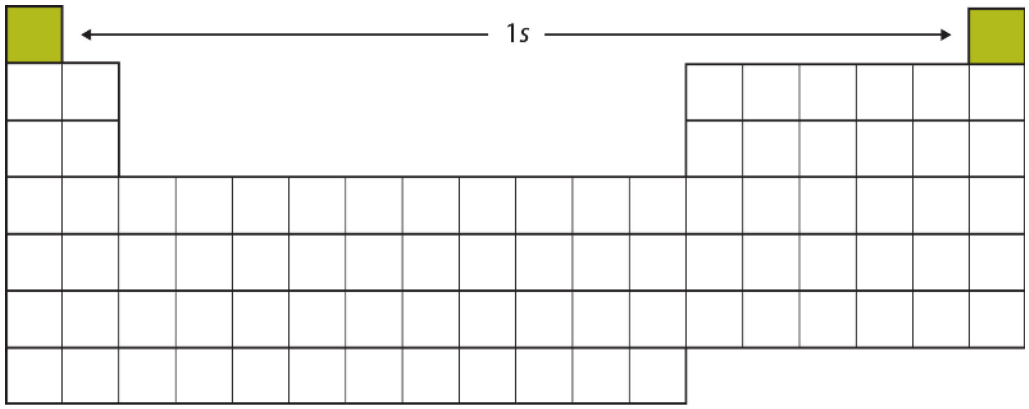


Figure **11.4.2**: The 1s Subshell. H and He represent the filling of the 1s subshell.

The next two electrons, for Li and Be, would go into the 2*s* subshell. Figure **11.4.3** shows that these two elements are adjacent on the periodic table.

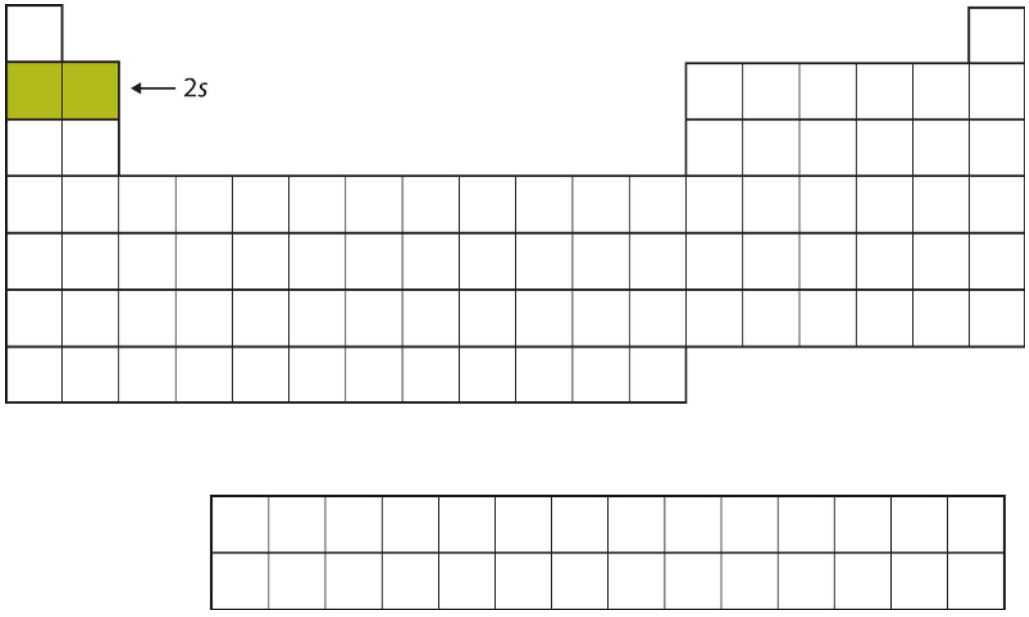


Figure **11.4.3**: The 2s Subshell. In Li and Be, the 2s subshell is being filled.

For the next six elements, the 2*p* subshell is being occupied with electrons. On the right side of the periodic table, these six elements (B through Ne) are grouped together (Figure **11.4.4**).

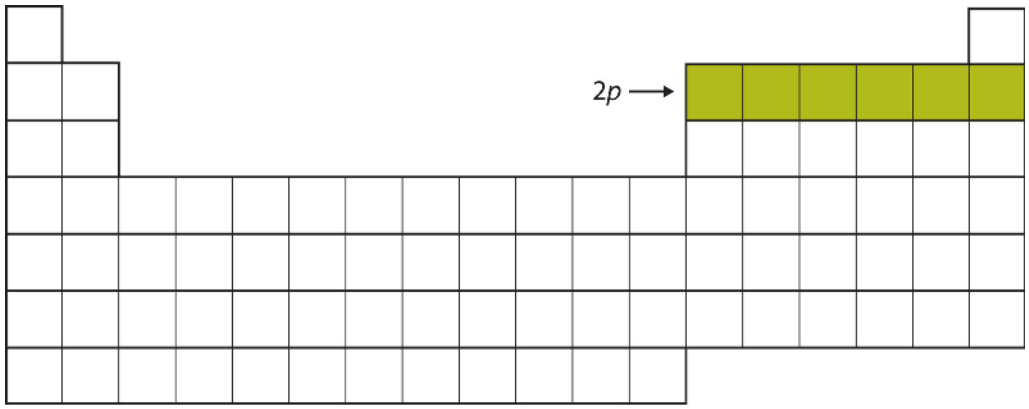


Figure 11.4.4: The 2p Subshell. For B through Ne, the 2p subshell is being occupied.

The next subshell to be filled is the 3*s* subshell. The elements coinciding this subshell being filled, Na and Mg, are back on the left side of the periodic table (Figure 11.4.5).

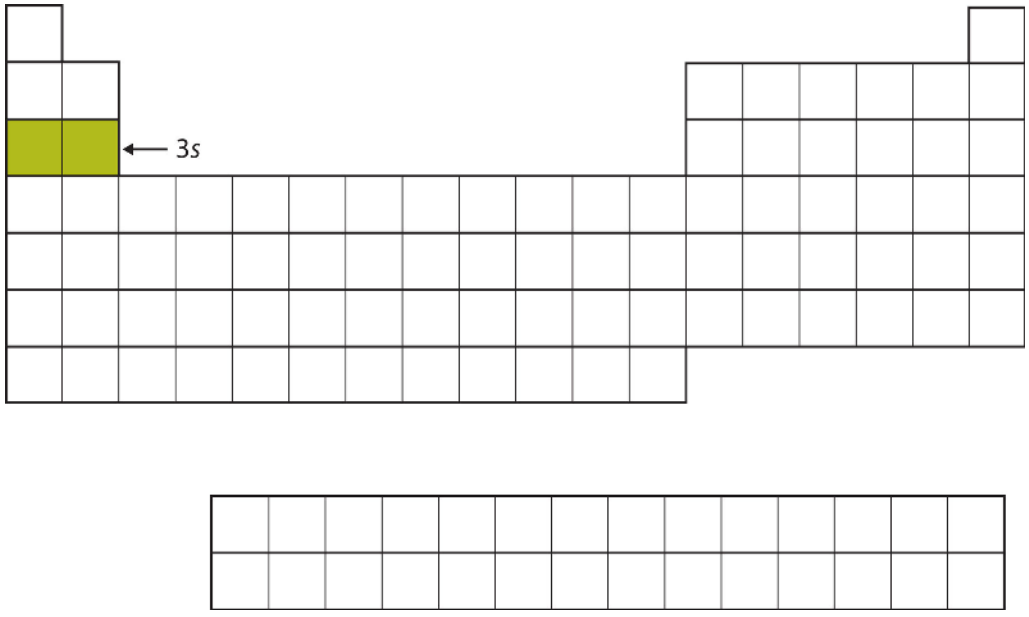


Figure 11.4.5: The 3s Subshell. Now the 3s subshell is being occupied.

Next, the 3*p* subshell is filled with the next six elements (Figure 11.4.6).

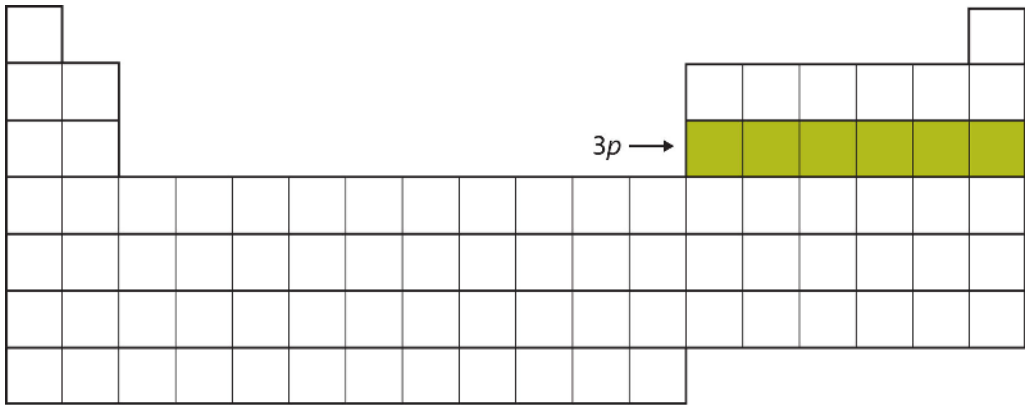


Figure8.5.6: The 3p Subshell. Next, the 3p subshell is filled with electrons.

Instead of filling the 3*d* subshell next, electrons go into the 4*s* subshell (Figure **11.4.7**).

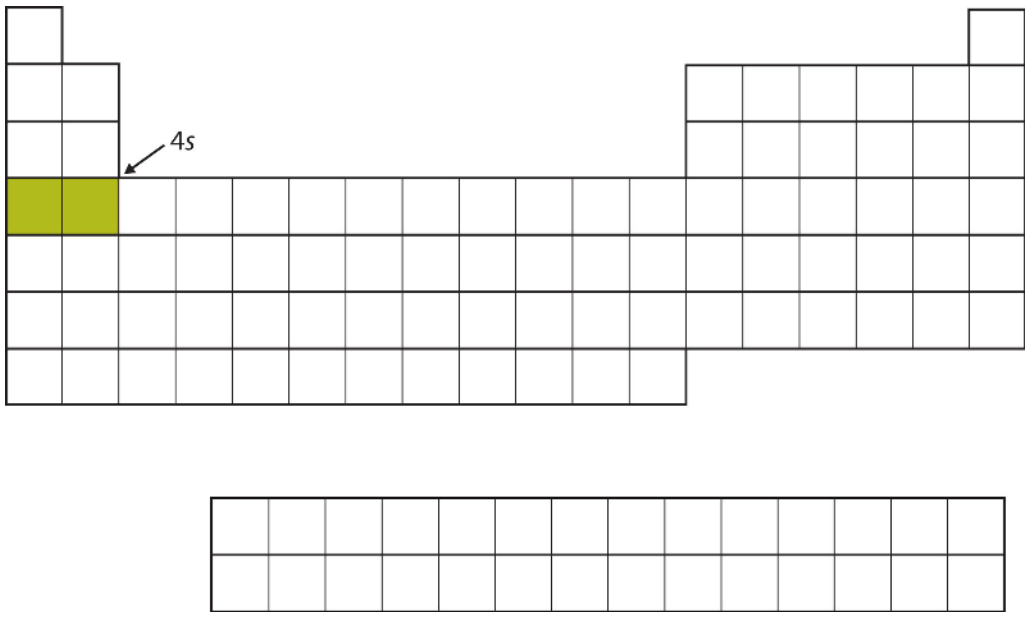


Figure **11.4.7**: The 4s Subshell. The 4s subshell is filled before the 3d subshell. This is reflected in the structure of the periodic table.

After the 4*s* subshell is filled, the 3*d* subshell is filled with up to 10 electrons. This explains the section of 10 elements in the middle of the periodic table (Figure **11.4.8**).

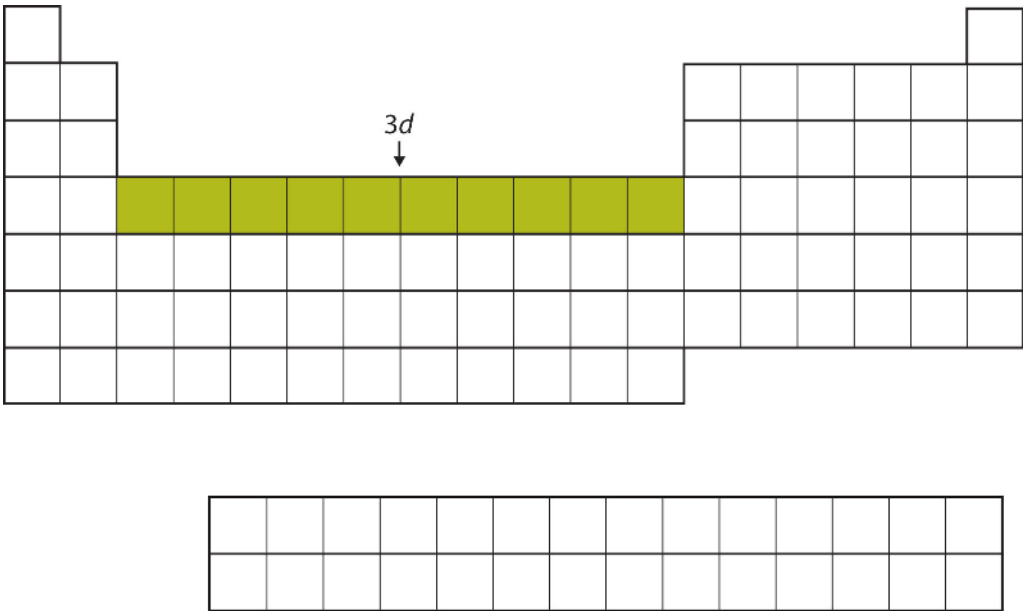


Figure 11.4.8: The 3d Subshell. The 3d subshell is filled in the middle section of the periodic table.

And so forth. As we go across the columns of the periodic table, the overall shape of the table outlines how the electrons are occupying the shells and subshells.

The first two columns on the left side of the periodic table are where the *s* subshells are being occupied. Because of this, the first two rows of the periodic table are labeled the **s block**. Similarly, the **p block** is the right-most six columns of the periodic table, the **d block** is the middle 10 columns of the periodic table, while the **f block** is the 14-column section that is normally depicted as detached from the main body of the periodic table. It could be part of the main body, but then the periodic table would be rather long and cumbersome. Figure 11.4.9 shows the blocks of the periodic table.

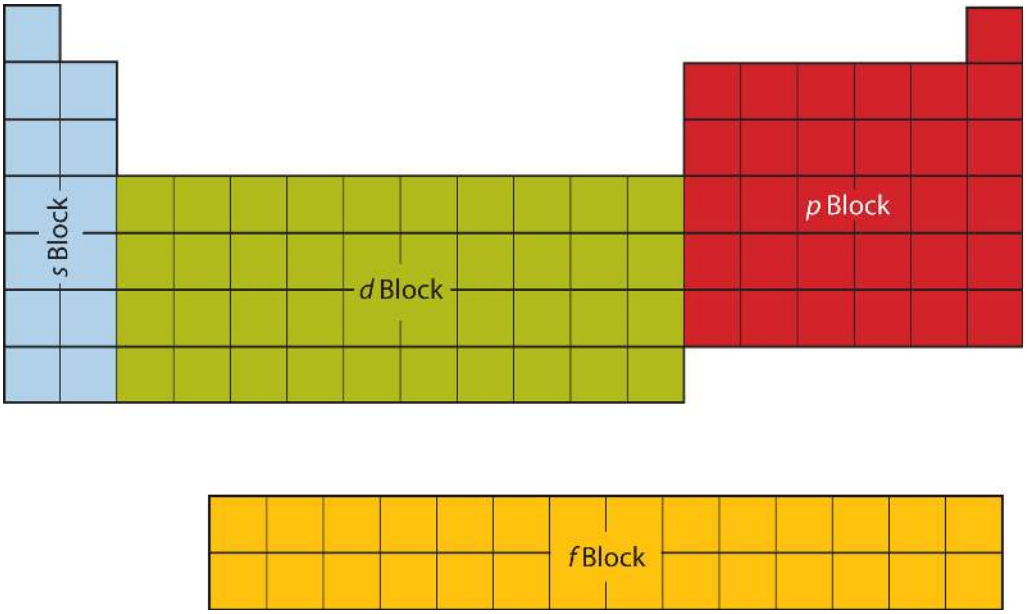


Figure 11.4.9: Blocks on the Periodic Table. The periodic table is separated into blocks depending on which subshell is being filled for the atoms that belong in that section.

Empty periodic table, separated into 4 different colored blocks. S block is blue, d block is green, p block is red and f block is orange.

The electrons in the highest-numbered shell, plus any electrons in the last unfilled subshell, are called **valence electrons**; the highest-numbered shell is called the **valence shell**. (The inner electrons are called *core electrons*.) The valence electrons largely control the chemistry of an atom. If we look at just the valence shell's electron configuration, we find that in each column, the

valence shell's electron configuration is the same. For example, take the elements in the first column of the periodic table: H, Li, Na, K, Rb, and Cs. Their electron configurations (abbreviated for the larger atoms) are as follows, with the valence shell electron configuration highlighted:

Table with two columns and 6 rows. The first column on the left has various elements in the rows underneath. The second column on the right has the different corresponding electron configurations for the specified element in the rows underneath.

H:	$1s^{\mathbf{1}}$
Li:	$1s^2 2s^{\mathbf{1}}$
Na:	$[Ne]3s^{\mathbf{1}}$
K:	$[Ar]4s^{\mathbf{1}}$
Rb:	$[Kr]5s^{\mathbf{1}}$
Cs:	$[Xe]6s^{\mathbf{1}}$

They all have a similar electron configuration in their valence shells: a single *s* electron. Because much of the chemistry of an element is influenced by valence electrons, we would expect that these elements would have similar chemistry—*and they do*. The organization of electrons in atoms explains not only the shape of the periodic table, but also the fact that elements in the same column of the periodic table have similar chemistry.

The same concept applies to the other columns of the periodic table. Elements in each column have the same valence shell electron configurations, and the elements have some similar chemical properties. This is strictly true for all elements in the *s* and *p* blocks. In the *d* and *f* blocks, because there are exceptions to the order of filling of subshells with electrons, similar valence shells are not absolute in these blocks. However, many similarities do exist in these blocks, so a similarity in chemical properties is expected.

Similarity of valence shell electron configuration implies that we can determine the electron configuration of an atom solely by its position on the periodic table. Consider Se, as shown in Figure **11.4.10**. It is in the fourth column of the *p* block. This means that its electron configuration should end in a p^4 electron configuration. Indeed, the electron configuration of Se is $[Ar]4s^2 3d^{10} 4p^4$, as expected.

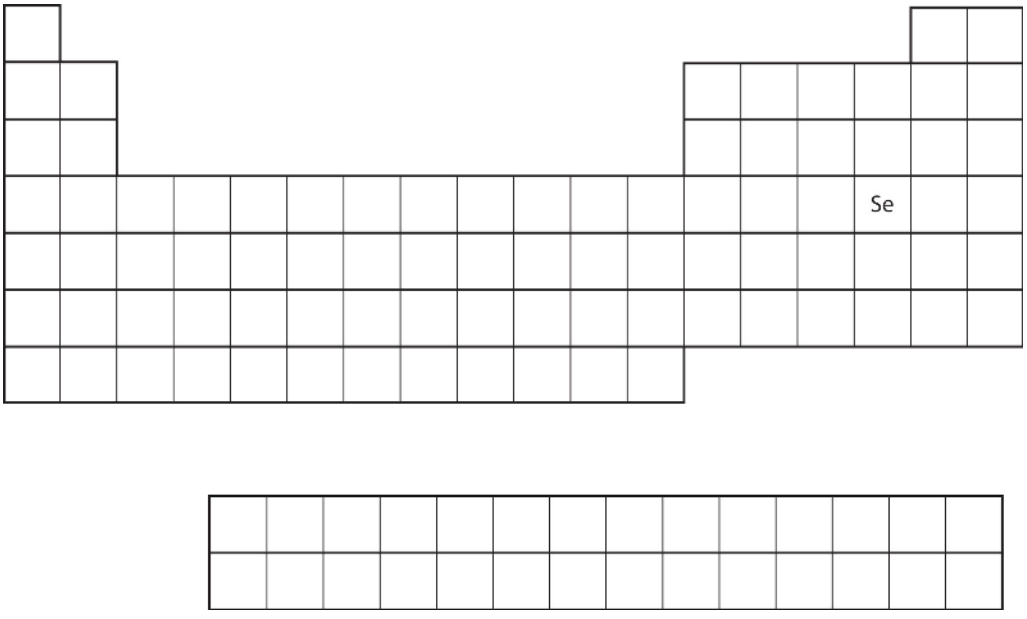


Figure **11.4.10**: Selenium on the Periodic Table

Example 11.4.1

From the element's position on the periodic table, predict the valence shell electron configuration for each atom (Figure **11.4.11**).

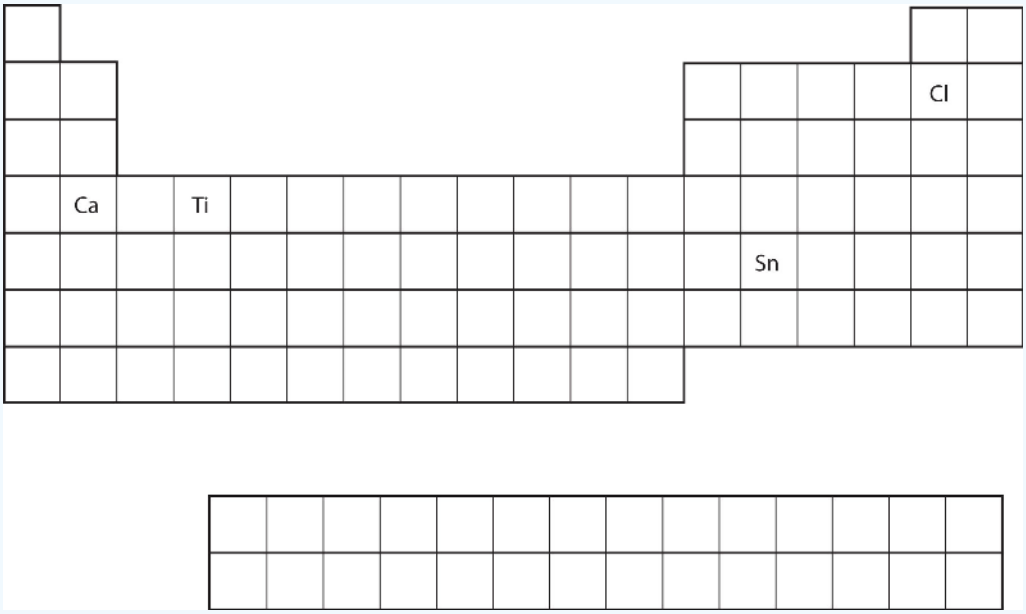


Figure **11.4.11**: Various Elements on the Periodic Table

1. Ca
2. Sn

Solution

1. Ca is located in the second column of the *s* block. We would expect that its electron configuration should end with s^2. Calcium's electron configuration is $[Ar]4s^2$.
2. Sn is located in the second column of the *p* block, so we expect that its electron configuration would end in p^2. Tin's electron configuration is $[Kr]5s^24d^{10}5p^2$.

Exercise 11.4.1

From the element's position on the periodic table, predict the valence shell electron configuration for each atom. Figure **11.4.11**.

a. Ti
b. Cl

Answer a

$[Ar]4s^23d^2$

Answer b

$[Ne]3s^23p^5$

Food and Drink Application: Artificial Colors

The color of objects comes from a different mechanism than the colors of neon and other discharge lights. Although colored lights produce their colors, objects are colored because they preferentially reflect a certain color from the white light that shines on them. A red tomato, for example, is bright red because it reflects red light while absorbing all the other colors of the rainbow.

Many foods, such as tomatoes, are highly colored; in fact, the common statement "you eat with your eyes first" is an implicit recognition that the visual appeal of food is just as important as its taste. But what about processed foods?

Many processed foods have food colorings added to them. There are two types of food colorings: natural and artificial. Natural food colorings include caramelized sugar for brown; annatto, turmeric, and saffron for various shades of orange or yellow; betanin from beets for purple; and even carmine, a deep red dye that is extracted from the cochineal, a small insect that is a parasite on cacti in Central and South America. (That's right—you may be eating bug juice!)

Some colorings are artificial. In the United States, the Food and Drug Administration currently approves only seven compounds as artificial colorings in food, beverages, and cosmetics:

- FD&C Blue #1: Brilliant Blue FCF
- FD&C Blue #2: Indigotine
- FD&C Green #3: Fast Green FCF
- RD&C Red #3: Erythrosine
- FD&C Red #40: Allura Red AC
- FD&C Yellow #5: Tartrazine
- FD&C Yellow #6: Sunset Yellow FCF

Lower-numbered colors are no longer on the market or have been removed for various reasons. Typically, these artificial colorings are large molecules that absorb certain colors of light very strongly, making them useful even at very low concentrations in foods and cosmetics. Even at such low amounts, some critics claim that a small portion of the population (especially children) is sensitive to artificial colorings and urge that their use be curtailed or halted. However, formal studies of artificial colorings and their effects on behavior have been inconclusive or contradictory. Many people continue to enjoy processed foods with artificial coloring (like those shown in the accompanying figure).



Artificial food colorings. Artificial food colorings are found in a variety of food products, such as processed foods, candies, and egg dyes. Even pet foods have artificial food coloring in them. (CC by 2.0, Matthew Bland via Flickr.)

Summary

The arrangement of electrons in atoms is responsible for the shape of the periodic table. Electron configurations can be predicted by the position of an atom on the periodic table.

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11.5: Periodic Trends

Learning Objective

- Be able to state how certain properties of atoms vary based on their relative position on the periodic table.

One reason the periodic table is so useful is that its structure allows us to qualitatively determine how some properties of the elements vary according to their position on the periodic table. The variations of properties according to positions on the periodic table are called **periodic trends**. There is no other tool in science that allows us to judge relative properties of a class of objects like this, which makes the periodic table a very useful tool. Many periodic trends are general. There may be a few points where an opposite trend is seen, but there is an overall trend when considered across a whole row, or down an entire column of the periodic table.

The first periodic trend we will consider is atomic radius. The **atomic radius** is an indication of the size of an atom. Although the concept of a definite radius of an atom is a bit fuzzy, atoms behave as if they have a certain radius. Such radii can be estimated from various experimental techniques, such as the x-ray crystallography of crystals.

As you go down a column of the periodic table, the atomic radii increase. This is because the valence electron shell is getting larger and there is a larger principal quantum number, so the valence shell lies physically farther away from the nucleus. This trend can be summarized as follows:

\[as\downarrow PT,atomic\; radius \uparrow\nonumber \]

where PT stands for periodic table. Going across a row on the periodic table, left to right, the trend is different. This is because although the valence shell maintains the same principal quantum number, the number of protons—and hence the nuclear charge—is increasing as you go across the row. The increasing positive charge casts a tighter grip on the valence electrons, so as you go across the periodic table, the atomic radii decrease. Again, we can summarize this trend as follows:

$$as \rightarrow PT, atomic\ radius \downarrow$$

Figure **11.5.1** shows spheres representing the atoms of the *s* and *p* blocks from the periodic table to scale, showing the two trends for the atomic radius.

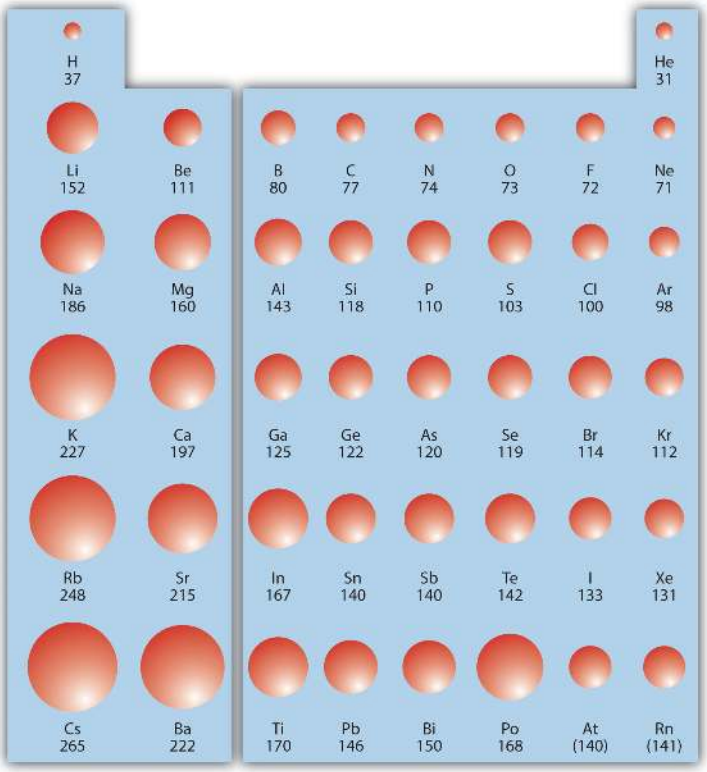


Figure 11.5.1: Atomic Radii Trends on the Periodic Table. Although there are some reversals in the trend (e.g., see Po in the bottom row), atoms generally get smaller as you go across the periodic table and larger as you go down any one column. Numbers are the radii in pm.

Example 11.5.1: Atomic Radii

Referring only to a periodic table and not to Figure **11.5.1**, which atom is larger in each pair?

a. Si or S
b. S or Te

Solution

a. Si is to the left of S on the periodic table, so it is larger because as you go across the row, the atoms get smaller.
b. S is above Te on the periodic table, so Te is larger because as you go down the column, the atoms get larger.

Exercise 11.5.1: Atomic Radii

Referring only to a periodic table and not to Figure **11.5.1**, which atom is smaller, Ca or Br?

Answer

Br

Ionization energy (IE) is the amount of energy required to remove an electron from an atom in the gas phase:

$$A(g) \rightarrow A^{+}(g) + e^{-} \quad \Delta H \equiv IE$$

IE is usually expressed in kJ/mol of atoms. It is always positive because the removal of an electron always requires that energy be put in (i.e., it is endothermic). IE also shows periodic trends. As you go down the periodic table, it becomes easier to remove an electron from an atom (i.e., IE decreases) because the valence electron is farther away from the nucleus. Thus,

$$as \downarrow PT,\ IE \downarrow$$

However, as you go across the periodic table and the electrons get drawn closer in, it takes more energy to remove an electron. As a result, IE increases:

$$as \rightarrow PT,\ IE \uparrow$$

Figure 11.5.2 shows values of IE versus position on the periodic table. Again, the trend isn't absolute, but the general trends going across and down the periodic table should be obvious.

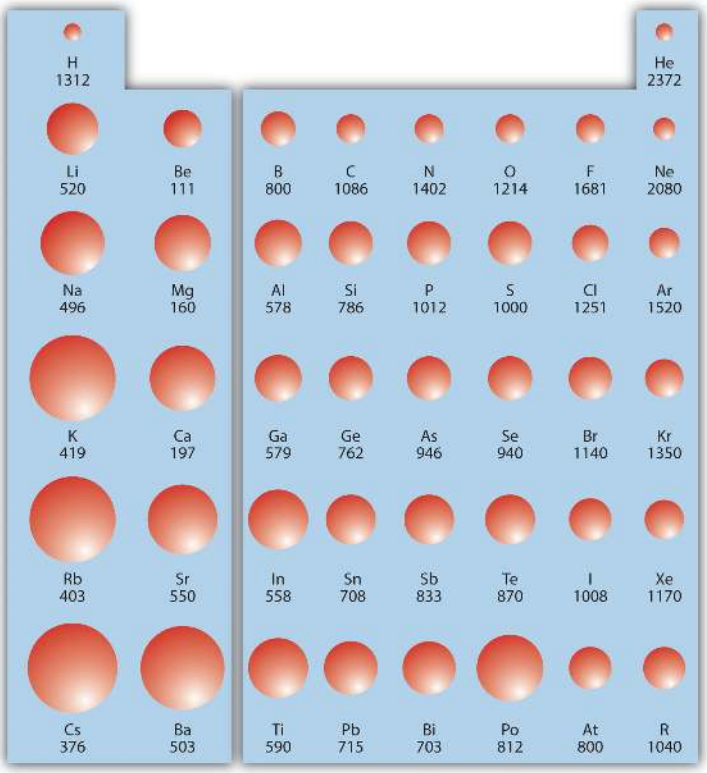


Figure 11.5.2: Ionization Energy on the Periodic Table. Values are in kJ/mol.

IE also shows an interesting trend within a given atom. This is because more than one IE can be defined by removing successive electrons (if the atom has them to begin with):

- First Ionization Energy (IE_1):

$$A(g) \rightarrow A^+(g) + e^-$$

- Second Ionization Energy (IE_2):

$$A^+(g) \rightarrow A^{2+}(g) + e^-$$

- Third Ionization Energy (IE_3):

$$A^{2+}(g) \rightarrow A^{3+}(g) + e^-$$

and so forth.

Each successive IE is larger than the previous because an electron is being removed from an atom with a progressively larger positive charge. However, IE takes a large jump when a successive ionization goes down into a new shell. For example, the following are the first three IEs for Mg, whose electron configuration is $1s^2 2s^2 2p^6 3s^2$:

First Ionization Energy (IE_1) = 738 kJ/mol:

$$Mg(g) \rightarrow Mg^+(g) + e^-$$

Second Ionization Energy (IE_2) = 1,450 kJ/mol:

$$Mg^{+}(g) \rightarrow Mg^{2+}(g) + e^{-}$$

Third Ionization Energy (IE_3) = 7,734 kJ/mol:

$$Mg^{2+}(g) \rightarrow Mg^{3+}(g) + e^{-}$$

The second IE is twice the first, which is not a surprise: the first IE involves removing an electron from a neutral atom, while the second one involves removing an electron from a positive ion. The third IE, however, is over *five times* the previous one. Why is it so much larger? Because the first two electrons are removed from the 3*s* subshell, but the third electron has to be removed from the n = 2 shell (specifically, the 2*p* subshell, which is lower in energy than the n = 3 shell). Thus, it takes much more energy than just overcoming a larger ionic charge would suggest. Trends like this one demonstrate that electrons within atoms are organized in groups.

Example 11.5.2: Ionization Energies

Which atom in each pair has the larger first ionization energy?

a. Ca or Sr
b. K or K^+

Solution

a. Because Sr is below Ca on the periodic table, it is easier to remove an electron from it; thus, Ca has the higher IE.
b. Because K^+ has a positive charge, it will be harder to remove another electron from it, so its IE is larger than that of K. Indeed, it will be significantly larger because the next electron in K^+ to be removed comes from another shell.

Exercise 11.5.2: Ionization Energies

Which atom has the lower ionization energy, C or F?

Answer

C

The opposite of IE is described by **electron affinity (EA),** which is the energy change when a gas-phase atom accepts an electron:

$$A(g) + e^{-} \rightarrow A^{-}(g) \quad \Delta H \equiv EA$$

EA is also usually expressed in kJ/mol. EA also demonstrates some periodic trends, although they are less obvious than the other periodic trends discussed previously. Generally, as you go across the periodic table, EA increases its magnitude:

$$as \rightarrow PT,\ EA \uparrow$$

There is not a definitive trend as you go down the periodic table; sometimes EA increases, sometimes it decreases. Figure **11.5.3** shows EA values versus position on the periodic table for the *s*- and *p*-block elements. The trend isn't absolute, especially considering the large positive EA values for the second column. However, the general trend going across the periodic table should be obvious.

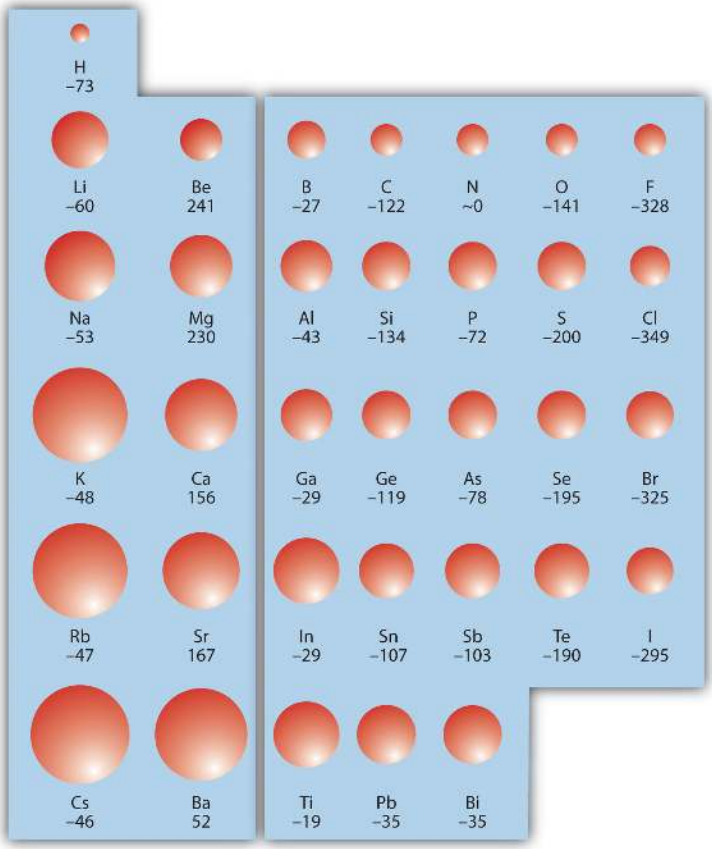


Figure **11.5.3**: Electron Affinity on the Periodic Table. Values are in kJ/mol.

Example 11.5.3: Electron Affinities

Predict which atom in each pair will have the highest magnitude of Electron Affinity.

a. C or F
b. Na or S

Solution

a. C and F are in the same row on the periodic table, but F is farther to the right. Therefore, F should have the larger magnitude of EA.
b. Na and S are in the same row on the periodic table, but S is farther to the right. Therefore, S should have the larger magnitude of EA.

Exercise 11.5.3: Electron Affinities

Predict which atom will have the highest magnitude of Electron Affinity: As or Br.

Answer

Br

Summary

Certain properties—notably atomic radius, ionization energies, and electron affinities—can be qualitatively understood by the positions of the elements on the periodic table.

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CHAPTER OVERVIEW

12: Chemical Bonds

How do atoms make compounds? Typically they join together in such a way that they lose their identities as elements and adopt a new identity as a compound. These joins are called *chemical bonds*. But how do atoms join together? Ultimately, it all comes down to electrons. Before we discuss how electrons interact, we need to introduce a tool to simply illustrate electrons in an atom.

12.1 Lewis Electron Dot Diagrams
12.2: Ionic and Covalent Bonds
12.3: Bond Polarity
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12.5: Electron Transfer - Ionic Bonds
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12.8: Molecular Shapes
12.9: Polar Molecules

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12.1 Lewis Electron Dot Diagrams

Learning Objective

- Draw a Lewis electron dot diagram for an atom or a monatomic ion.

In almost all cases, chemical bonds are formed by interactions of valence electrons in atoms. To facilitate our understanding of how valence electrons interact, a simple way of representing those valence electrons would be useful.

A **Lewis electron dot diagram** (or electron dot diagram or a Lewis diagram or a Lewis structure) is a representation of the valence electrons of an atom that uses dots around the symbol of the element. The number of dots equals the number of valence electrons in the atom. These dots are arranged to the right and left and above and below the symbol, with no more than two dots on a side. (It does not matter what order the positions are used.) For example, the Lewis electron dot diagram for hydrogen is simply

$$\mathbf{H}\cdot \tag{1}$$

Because the side is not important, the Lewis electron dot diagram could also be drawn as follows:

$$\dot{\mathbf{H}} \quad or \quad \cdot\mathbf{H} \quad or \quad \underset{\cdot}{\mathbf{H}} \tag{2}$$

The electron dot diagram for helium, with two valence electrons, is as follows:

$$\mathbf{He:} \tag{3}$$

By putting the two electrons together on the same side, we emphasize the fact that these two electrons are both in the 1*s* subshell; this is the common convention we will adopt, although there will be exceptions later. The next atom, lithium, has an electron configuration of $1s^2 2s^1$, so it has only one electron in its valence shell. Its electron dot diagram resembles that of hydrogen, except the symbol for lithium is used:

$$\mathbf{Li}\cdot \tag{4}$$

Beryllium has two valence electrons in its 2*s* shell, so its electron dot diagram is like that of helium:

$$\mathbf{Be:} \tag{5}$$

The next atom is boron. Its valence electron shell is $2s^2 2p^1$, so it has three valence electrons. The third electron will go on another side of the symbol:

$$\dot{\mathbf{B}}\mathbf{e:} \tag{6}$$

Again, it does not matter on which sides of the symbol the electron dots are positioned.

For carbon, there are four valence electrons, two in the 2*s* subshell and two in the 2*p* subshell. As usual, we will draw two dots together on one side, to represent the 2*s* electrons. However, conventionally, we draw the dots for the two *p* electrons on different sides. As such, the electron dot diagram for carbon is as follows:

$$\cdot\dot{\mathbf{C}}\mathbf{:} \tag{7}$$

With N, which has three *p* electrons, we put a single dot on each of the three remaining sides:

$$\cdot\underset{\cdot}{\dot{\mathbf{N}}}\mathbf{:} \tag{8}$$

For oxygen, which has four *p* electrons, we now have to start doubling up on the dots on one other side of the symbol. When doubling up electrons, make sure that a side has no more than two electrons.

$$\cdot\underset{\cdot}{\ddot{\mathbf{O}}}\mathbf{:} \tag{9}$$

Fluorine and neon have seven and eight dots, respectively:

$$:\underset{\cdot}{\ddot{\mathbf{F}}}\mathbf{:} \tag{10}$$

$$:\ddot{\underset{\cdot\cdot}{\mathrm{N}}}\mathrm{e}: \tag{11}$$

With the next element, sodium, the process starts over with a single electron because sodium has a single electron in its highest-numbered shell, the n = 3 shell. By going through the periodic table, we see that the Lewis electron dot diagrams of atoms will never have more than eight dots around the atomic symbol.

Example 1:

What is the Lewis electron dot diagram for each element?

a. aluminum
b. selenium

Solution

a. The valence electron configuration for aluminum is $3s^2 3p^1$. So it would have three dots around the symbol for aluminum, two of them paired to represent the 3*s* electrons:

$$\mathrm{Al}: \tag{12}$$

2. The valence electron configuration for selenium is $4s^2 4p^4$. In the highest-numbered shell, the n = 4 shell, there are six electrons. Its electron dot diagram is as follows:

$$\cdot\ddot{\underset{\cdot\cdot}{\mathrm{S}}}\mathrm{e}: \tag{13}$$

Exercise 1

What is the Lewis electron dot diagram for each element?

a. phosphorus
b. argon

Answer

$$\cdot\dot{\underset{\cdot}{\mathrm{P}}}: \tag{14}$$

$$:\ddot{\underset{\cdot\cdot}{\mathrm{Ar}}}: \tag{15}$$

For atoms with partially filled *d* or *f* subshells, these electrons are typically omitted from Lewis electron dot diagrams. For example, the electron dot diagram for iron (valence shell configuration $4s^2 3d^6$) is as follows:

$$\mathrm{Fe}: \tag{16}$$

Elements in the same column of the periodic table have similar Lewis electron dot diagrams because they have the same valence shell electron configuration. Thus the electron dot diagrams for the first column of elements are as follows:

$$\mathrm{H}\cdot\ \ \mathrm{Li}\cdot\ \ \mathrm{Na}\cdot\ \ \mathrm{K}\cdot\ \ \mathrm{Rb}\cdot\ \ \mathrm{Cs}\cdot \tag{17}$$

Monatomic ions are atoms that have either lost (for cations) or gained (for anions) electrons. Electron dot diagrams for ions are the same as for atoms, except that some electrons have been removed for cations, while some electrons have been added for anions. Thus in comparing the electron configurations and electron dot diagrams for the Na atom and the Na^+ ion, we note that the Na atom has a single valence electron in its Lewis diagram, while the Na^+ ion has lost that one valence electron:

$$\textit{Lewis dot diagram}: \quad \mathrm{Na}\cdot \quad Na^+ \tag{18}$$

$$\textit{Electron configuration}: \quad [Ne]\,3s^1 \quad [Ne] \tag{19}$$

Technically, the valence shell of the Na^+ ion is now the n = 2 shell, which has eight electrons in it. So why do we not put eight dots around Na^+? Conventionally, when we show electron dot diagrams for ions, we show the original valence shell of the atom, which in this case is the n = 3 shell and empty in the Na^+ ion.

In making cations, electrons are first lost from the *highest numbered shell*, not necessarily the last subshell filled. For example, in going from the neutral Fe atom to the Fe^{2+} ion, the Fe atom loses its two 4*s* electrons first, not its 3*d* electrons, despite the fact that the 3*d* subshell is the last subshell being filled. Thus we have

$$\textit{Lewis dot diagram}: \quad \mathbf{Fe}: \quad Fe^{2+} \tag{20}$$

$$\textit{Electron configuration}: \quad [Ar]\,4s^2 3d^6 \quad [Ar]\,3d^6 \tag{21}$$

Anions have extra electrons when compared to the original atom. Here is a comparison of the Cl atom with the Cl^- ion:

$$\textit{Lewis dot diagram}: \quad :\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}\cdot \quad :\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}:^- \tag{22}$$

$$\textit{Electron configuration}: \quad [Ne]\,3s^2 3p^5 \quad [Ne]\,3s^2 3p^6 \tag{23}$$

Example 2:

What is the Lewis electron dot diagram for each ion?

a. Ca^{2+}
b. O^{2-}

Solution

a. Having lost its two original valence electrons, the Lewis electron dot diagram is just Ca^{2+}.

Ca^{2+}

b. The O^{2-} ion has gained two electrons in its valence shell, so its Lewis electron dot diagram is as follows:

$$:\ddot{\underset{\cdot\cdot}{\mathrm{O}}}:^{2-} \tag{24}$$

Exercise 2

Neutral Tl has the electron configuration: $6s^2 5d^{10} 6p^1$. What is the Lewis electron dot diagram for the Tl^+ ion?

Answer

$$\mathbf{Tl}:^+ \tag{25}$$

Summary

- Lewis electron dot diagrams use dots to represent valence electrons around an atomic symbol.
- Lewis electron dot diagrams for ions have less (for cations) or more (for anions) dots than the corresponding atom.

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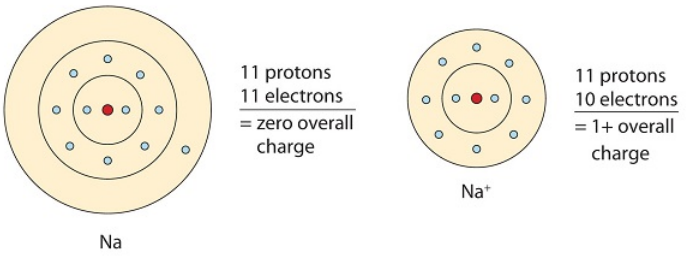
12.2: Ionic and Covalent Bonds

There are many types of chemical bonds and forces that bind molecules together. The two most basic types of bonds are characterized as either ionic or covalent. In ionic bonding, atoms transfer electrons to each other. Ionic bonds require at least one electron donor and one electron acceptor. In contrast, atoms with the same electronegativity share electrons in covalent bonds, because neither atom preferentially attracts or repels the shared electrons.

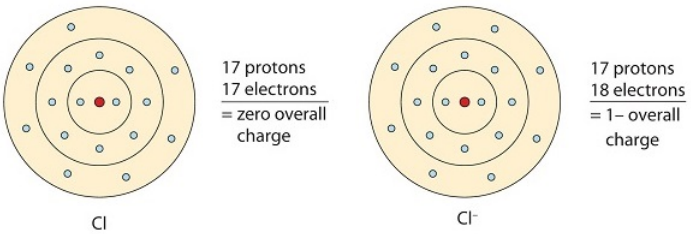
Introduction

Ionic bonding is the complete transfer of valence electron(s) between atoms. It is a type of chemical bond that generates two oppositely charged ions. In ionic bonds, the metal loses electrons to become a positively charged cation, whereas the nonmetal accepts those electrons to become a negatively charged anion. Ionic bonds require an electron donor, often a metal, and an electron acceptor, a nonmetal.

Ionic bonding is observed because metals have few electrons in their outer-most orbitals. By losing those electrons, these metals can achieve noble gas configuration and satisfy the octet rule. Similarly, nonmetals that have close to 8 electrons in their valence shells tend to readily accept electrons to achieve noble gas configuration. In ionic bonding, more than 1 electron can be donated or received to satisfy the octet rule. The charges on the anion and cation correspond to the number of electrons donated or received. In ionic bonds, the net charge of the compound must be zero.



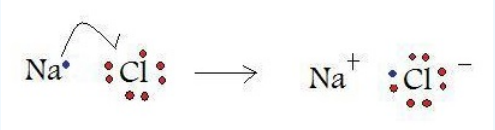
This sodium molecule donates the lone electron in its valence orbital in order to achieve octet configuration. This creates a positively charged cation due to the loss of electron.



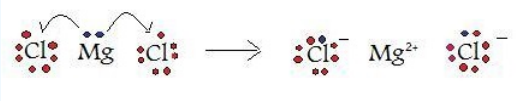
This chlorine atom receives one electron to achieve its octet configuration, which creates a negatively charged anion.

The predicted overall energy of the ionic bonding process, which includes the ionization energy of the metal and electron affinity of the nonmetal, is usually positive, indicating that the reaction is endothermic and unfavorable. However, this reaction is highly favorable because of the electrostatic attraction between the particles. At the ideal interatomic distance, attraction between these particles releases enough energy to facilitate the reaction. Most ionic compounds tend to dissociate in polar solvents because they are often polar. This phenomenon is due to the opposite charges on each ion.

Example 12.2.1: Chloride Salts



In this example, the sodium atom is donating its 1 valence electron to the chlorine atom. This creates a sodium cation and a chlorine anion. Notice that the net charge of the resulting compound is 0.



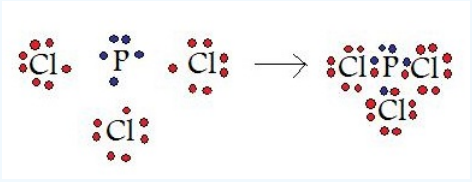
In this example, the magnesium atom is donating both of its valence electrons to chlorine atoms. Each chlorine atom can only accept 1 electron before it can achieve its noble gas configuration; therefore, 2 atoms of chlorine are required to accept the 2 electrons donated by the magnesium. Notice that the net charge of the compound is 0.

Covalent Bonding

Covalent bonding is the sharing of electrons between atoms. This type of bonding occurs between two atoms of the same element or of elements close to each other in the periodic table. This bonding occurs primarily between nonmetals; however, it can also be observed between nonmetals and metals.

If atoms have similar electronegativities (the same affinity for electrons), covalent bonds are most likely to occur. Because both atoms have the same affinity for electrons and neither has a tendency to donate them, they share electrons in order to achieve octet configuration and become more stable. In addition, the ionization energy of the atom is too large and the electron affinity of the atom is too small for ionic bonding to occur. For example: carbon does not form ionic bonds because it has 4 valence electrons, half of an octet. To form ionic bonds, Carbon molecules must either gain or lose 4 electrons. This is highly unfavorable; therefore, carbon molecules share their 4 valence electrons through single, double, and triple bonds so that each atom can achieve noble gas configurations. Covalent bonds include interactions of the sigma and pi orbitals; therefore, covalent bonds lead to formation of single, double, triple, and quadruple bonds.

✔ Example 12.2.2: PCl_3



In this example, a phosphorous atom is sharing its three unpaired electrons with three chlorine atoms. In the end product, all four of these molecules have 8 valence electrons and satisfy the octet rule.

Bonding in Organic Chemistry

Ionic and covalent bonds are the two extremes of bonding. Polar covalent is the intermediate type of bonding between the two extremes. Some ionic bonds contain covalent characteristics and some covalent bonds are partially ionic. For example, most carbon-based compounds are covalently bonded but can also be partially ionic. Polarity is a measure of the separation of charge in a compound. A compound's polarity is dependent on the symmetry of the compound and on differences in electronegativity between atoms. Polarity occurs when the electron pushing elements, found on the left side of the periodic table, exchanges electrons with the electron pulling elements, on the right side of the table. This creates a spectrum of polarity, with ionic (polar) at one extreme, covalent (nonpolar) at another, and polar covalent in the middle.

Both of these bonds are important in organic chemistry. Ionic bonds are important because they allow the synthesis of specific organic compounds. Scientists can manipulate ionic properties and these interactions in order to form desired products. Covalent bonds are especially important since most carbon molecules interact primarily through covalent bonding. Covalent bonding allows molecules to share electrons with other molecules, creating long chains of compounds and allowing more complexity in life.

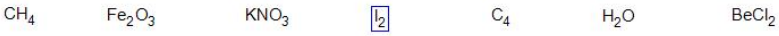
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2. Petrucci, Ralph H. General Chemistry: Principles and Modern Applications. Upper Saddle River, NJ: Pearson Education, 2007.

3. Brown, Theodore L., Eugene H. Lemay, and Bruce E. Bursten. Chemistry: The Central Science. 6th ed. Englewood Cliffs, NJ: Prentice Hall, 1994.

Problems

1. Are these compounds ionic or covalent?

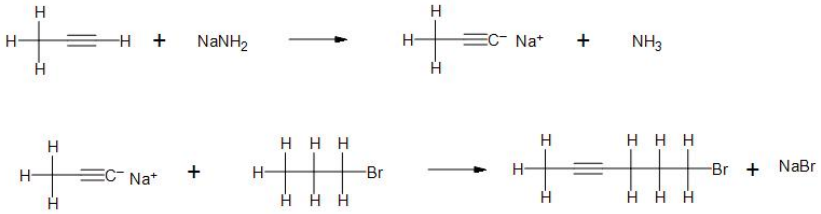


2. In the following reactions, indicate whether the reactants and products are ionic or covalently bonded.

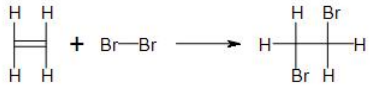
a)



b) Clarification: What is the nature of the bond between sodium and amide? What kind of bond forms between the anion carbon chain and sodium?



c)



Solutions

- 1) From left to right: Covalent, Ionic, Ionic, Covalent, Covalent, Covalent, Ionic.
- 2a) All products and reactants are ionic.
- 2b) From left to right: Covalent, Ionic, Ionic, Covalent, Ionic, Covalent, Covalent, Ionic.
- 2c) All products and reactants are covalent.

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12.3: Bond Polarity

Have you ever spent time with someone you really didn't like? You had nothing in common with them and did not want to have anything to do with them. On the other hand, there are people you enjoy being with. You have a lot in common and like to share with them. Atoms work the same way. If there are strong differences in their attraction of electrons, on atom gets the electrons and the other atom loses them. If they are similar, they share electrons to form a covalent bond.

Bond Polarity

Electronegativity is defined as the ability of an atom to attract electrons when the atoms are in a compound. Electronegativities of elements are shown in the periodic table below.

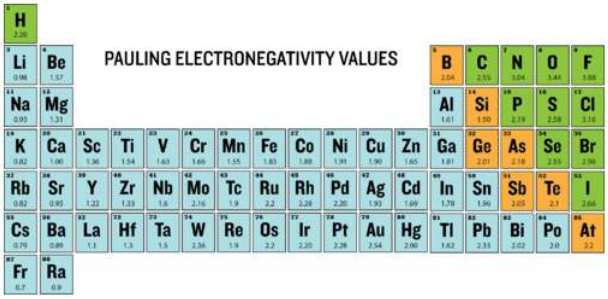


Figure 9.13.1: *Electronegativities of elements.*

The degree to which a given bond is ionic or covalent is determined by calculating the difference in electronegativity between the two atoms involved in the bond.

As an example, consider the bond that occurs between an atom of potassium and an atom of fluorine. Using the table, the difference in electronegativity is equal to $4.0 - 0.8 = 3.2$. Since the difference in electronegativity is relatively large, the bond between the two atoms is ionic. Since the fluorine atom has a much larger attraction for electrons than the potassium atom does, the valence electron from the potassium atom is completely transferred to the fluorine atom. The diagram below shows how difference in electronegativity relates to the ionic or covalent character of a chemical bond.

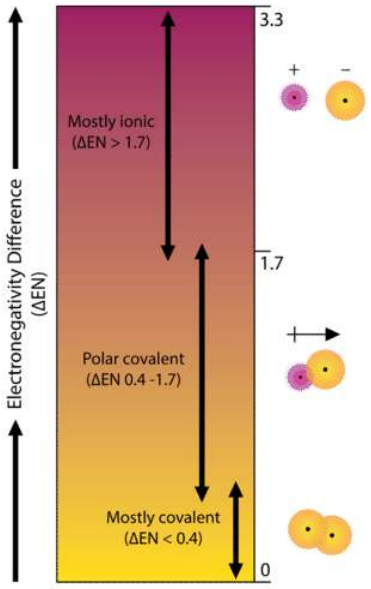


Figure 9.13.2: *Bond type is predicted on the difference in electronegativity of the two elements involved in the bond.*

The polarity of a covalent bond can be judged by determining the *difference* of the electronegativities of the two atoms involved in the covalent bond, as summarized in the following table:

Electronegativity Difference	Bond Type
0	nonpolar covalent
0–0.4	slightly polar covalent
0.4–1.9	definitely polar covalent
>1.9	likely ionic

Nonpolar Covalent Bonds

A bond in which the electronegativity difference is less than 1.7 is considered to be mostly covalent in character. However, at this point we need to distinguish between two general types of covalent bonds. A **nonpolar covalent bond** is a covalent bond in which the bonding electrons are shared equally between the two atoms. In a nonpolar covalent bond, the distribution of electrical charge is balanced between the two atoms.

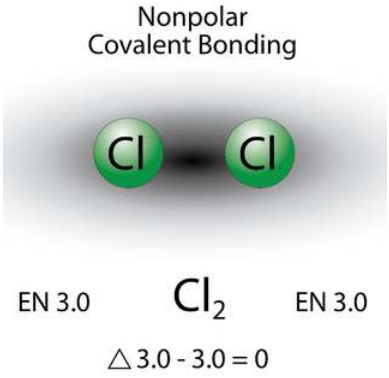


Figure 9.13.3: *A nonpolar covalent bond is one in which the distribution of electron density between the two atoms is equal.*

The two chlorine atoms share the pair of electrons in the single covalent bond equally, and the electron density surrounding the $\mathbf{Cl_2}$ molecule is symmetrical. Also note that molecules in which the electronegativity difference is very small (<0.4) are also considered nonpolar covalent. An example would be a bond between chlorine and bromine ($\Delta\text{EN} = 3.0 - 2.8 = 0.2$).

Polar Covalent Bonds

A bond in which the electronegativity difference between the atoms is between 0.4 and 1.7 is called a polar covalent bond. A **polar covalent bond** is a covalent bond in which the atoms have an unequal attraction for electrons and so the sharing is unequal. In a polar covalent bond, sometimes simply called a polar bond, the distribution of electrons around the molecule is no longer symmetrical.

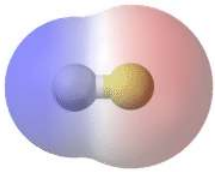


Figure 9.13.4: *In the polar covalent bond of* $\mathbf{HF}$*, the electron density is unevenly distributed. There is a higher density (red) near the fluorine atom, and a lower density (blue) near the hydrogen atom.*

An easy way to illustrate the uneven electron distribution in a polar covalent bond is to use the Greek letter delta (δ).

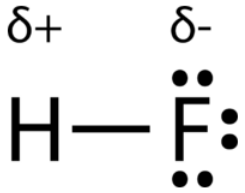


Figure 9.13.5: *Use of δ to indicate partial charge.*

The atom with the greater electronegativity acquires a partial negative charge, while the atom with the lesser electronegativity acquires a partial positive charge. The delta symbol is used to indicate that the quantity of charge is less than one. A crossed arrow can also be used to indicate the direction of greater electron density.

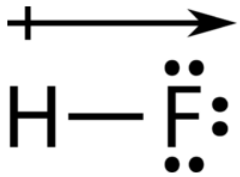


Figure 9.13.6: *Use of crossed arrow to indicate polarity.*

Summary

- The electronegativity of an atom determines how strongly it attracts electrons to itself.
- The polarity of a bond is affected by the electronegativity values of the two atoms involved in that bond.

Contributors

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12.4: Covalent Bonds and Lewis Structures

Learning Objectives

- Define *covalent bond*.
- Illustrate covalent bond formation with Lewis electron dot diagrams.

Ionic bonding typically occurs when it is easy for one atom to lose one or more electrons, and for another atom to gain one or more electrons. However, some atoms will not give up or gain electrons easily. Yet they still participate in compound formation. How? There is another mechanism for obtaining a complete valence shell: *sharing* electrons. When electrons are shared between two atoms, they form a **covalent bond**.

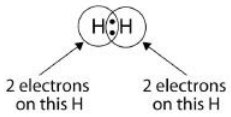
Let us illustrate a covalent bond by using H atoms, with the understanding that H atoms need only two electrons to fill the 1*s* subshell. Each H atom starts with a single electron in its valence shell:

$$\mathbf{H}\cdot \quad \cdot\mathbf{H}$$

The two H atoms can share their electrons:

$$\mathbf{H:H}$$

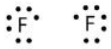
We can use circles to show that each H atom has two electrons around the nucleus, completely filling each atom's valence shell:



Because each H atom has a filled valence shell, this bond is stable, and we have made a diatomic hydrogen molecule. (This explains why hydrogen is one of the diatomic elements.) For simplicity's sake, it is not unusual to represent the covalent bond with a dash, instead of with two dots:

H–H

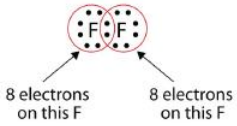
Because two atoms are sharing one pair of electrons, this covalent bond is called a **single bond**. As another example, consider fluorine. F atoms have seven electrons in their valence shell:



These two atoms can do the same thing that the H atoms did; they share their unpaired electrons to make a covalent bond.



Note that each F atom has a complete octet around it now:



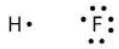
We can also write this using a dash to represent the shared electron pair:



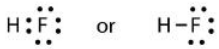
There are two different types of electrons in the fluorine diatomic molecule. The **bonding electron pair** makes the covalent bond. Each F atom has three other pairs of electrons that do not participate in the bonding; they are called **lone pair electrons**. Each F

atom has one bonding pair and three lone pairs of electrons.

Covalent bonds can be made between different elements as well. One example is HF. Each atom starts out with an odd number of electrons in its valence shell:



The two atoms can share their unpaired electrons to make a covalent bond:



Note that the H atom has a full valence shell with two electrons, while the F atom has a complete octet of electrons.

Example 12.4.1

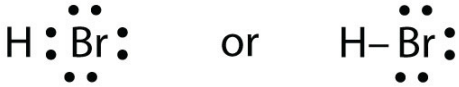
Use Lewis electron dot diagrams to illustrate the covalent bond formation in HBr.

Solution

HBr is very similar to HF, except that it has Br instead of F. The atoms are as follows:



The two atoms can share their unpaired electron:



Exercise 12.4.1

Use Lewis electron dot diagrams to illustrate the covalent bond formation in Cl_2.

Answer



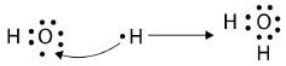
More than two atoms can participate in covalent bonding, although any given covalent bond will be between two atoms only. Consider H and O atoms:



The H and O atoms can share an electron to form a covalent bond:



The H atom has a complete valence shell. However, the O atom has only seven electrons around it, which is not a complete octet. This can be fixed by including a second H atom, whose single electron will make a second covalent bond with the O atom:



(It does not matter what side the second H atom is positioned on.) Now the O atom has a complete octet around it, and each H atom has two electrons, filling its valence shell. This is how a water molecule, H_2O, is made.

Example 12.4.2

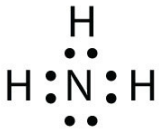
Use a Lewis electron dot diagram to show the covalent bonding in NH_3.

Solution

The N atom has the following Lewis electron dot diagram:



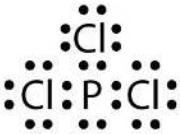
It has three unpaired electrons, each of which can make a covalent bond by sharing electrons with an H atom. The electron dot diagram of NH_3 is as follows:



Exercise 12.4.2

Use a Lewis electron dot diagram to show the covalent bonding in PCl_3.

Answer



There is a simple set of steps for determining the Lewis electron dot diagram of a simple molecule. First, you must identify the central atom and the surrounding atoms. The **central atom** is the atom in the center of the molecule, while the **surrounding atoms** are the atoms making bonds to the central atom. The central atom is usually written first in the formula of the compound (H_2O is the notable exception). After the central and surrounding atoms have been identified, follow these steps:

1. Count the total number of valence electrons. Add extra if the species has negative charges and remove some for every positive charge on the species.
2. Write the central atom and surround it with the surrounding atoms.
3. Put a pair of electrons between the central atom and each surrounding atom.
4. Complete the octets around the surrounding atoms (except for H).
5. Put remaining electrons, if any, around the central atom.
6. Check that every atom has a full valence shell.

Let us try these steps to determine the electron dot diagram for BF_4^-. The B atom is the central atom, and the F atoms are the surrounding atoms. There is a negative sign on the species, so we have an extra electron to consider.

1. **Count the total number of electrons.** B has 3, each F has 7, and there is one extra electron: 3 + 7 + 7 + 7 + 7 + 1 = 32.

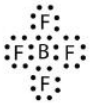
2. **Write the central atom surrounded by surrounding atoms.**



3. **Put a pair of electrons between the central atom and each surrounding atom.** This uses up eight electrons, so we have 32 − 8 = 24 electrons left.



4. **Complete the octets around the surrounding atoms (except for H).** This uses up 24 more electrons, leaving 24 − 24 = 0 electrons left.



5. **Put remaining electrons, if any, around the central atom.** There are no additional electrons to add to the central atom.

6. **Check.** The B atom has eight electrons around it, as does each F atom. Each atom has a complete octet. This is a good Lewis electron dot diagram for BF_4^-.

Sometimes, however, these steps do not work. If we were to follow these steps for the compound formaldehyde (CH_2O), we would get the following:



The H and O atoms have the proper number of electrons, but the C atom only has six electrons around it, not the eight electrons for an octet. How do we fix this?

We fix this by recognizing that two atoms can share more than one pair of electrons. In the case of CH_2O, the O and C atoms share two pairs of electrons, with the following Lewis electron dot diagram as a result:



By circling the electrons around each atom, we can now see that the O and C atoms have octets, while each H atom has two electrons:



Each valence shell is full, so this is an acceptable Lewis electron dot diagram. If we were to use lines to represent the bonds, we would use two lines between the C and O atoms:



The bond between the C and O atoms is a **double bond** and represents two bonding pairs of electrons between the atoms. If the rules for drawing Lewis electron dot diagrams do not work as written, a double bond may be required.

Example 12.4.3: Carbon Dioxide

What is the proper Lewis electron dot diagram for CO_2?

Solution

The central atom is a C atom, with O atoms as surrounding atoms. We have a total of 4 + 6 + 6 = 16 valence electrons. Following the rules for Lewis electron dot diagrams for compounds gives us



The O atoms have complete octets around them, but the C atom only has four electrons around it. The way to solve this dilemma is to make a double bond between carbon and *each* O atom:



Each O atom still has eight electrons around it, but now the C atom also has a complete octet. This is an acceptable Lewis electron dot diagram for CO_2.

Exercise 12.4.3

What is the proper Lewis electron dot diagram for carbonyl sulfide (COS)?

Answer



It is also possible to have a **triple bond,** in which there are three pairs of electrons between two atoms. Good examples of this are elemental nitrogen (N_2) and acetylene (C_2H_2):



Acetylene is an interesting example of a molecule with two central atoms, which are both C atoms. Polyatomic ions are bonded together with covalent bonds. Because they are ions, however, they participate in ionic bonding with other ions. So both major types of bonding can occur at the same time.

Food and Drink Application: Vitamins and Minerals

Vitamins are nutrients that our bodies need in small amounts but cannot synthesize; therefore, they must be obtained from the diet. The word *vitamin* comes from "vital amine" because it was once thought that all these compounds had an amine group (NH_2) in it. This is not actually true, but the name stuck anyway.

All vitamins are covalently bonded molecules. Most of them are commonly named with a letter, although all of them also have formal chemical names. Thus vitamin A is also called retinol, vitamin C is called ascorbic acid, and vitamin E is called tocopherol. There is no single vitamin B; there is a group of substances called the *B complex vitamins* that are all water soluble and participate in cell metabolism. If a diet is lacking in a vitamin, diseases such as scurvy or rickets develop. Luckily, all vitamins are available as supplements, so any dietary deficiency in a vitamin can be easily corrected.

A mineral is any chemical element other than carbon, hydrogen, oxygen, or nitrogen that is needed by the body. Minerals that the body needs in quantity include sodium, potassium, magnesium, calcium, phosphorus, sulfur, and chlorine. Essential minerals that the body needs in tiny quantities (so-called *trace elements*) include manganese, iron, cobalt, nickel, copper, zinc, molybdenum, selenium, and iodine. Minerals are also obtained from the diet. Interestingly, most minerals are consumed in ionic form, rather than as elements or from covalent molecules. Like vitamins, most minerals are available in pill form, so any deficiency can be compensated for by taking supplements.



Supplement Facts

Serving Size 1 Tablet

Each Tablet Contains	% Daily Value
Vitamin A 5000 I.U (50% as Beta Carotene)	100%
Vitamin C 60 mg	100%
Vitamin D 400 I.U.	100%
Vitamin E 30 I.U.	100%
Vitamin K 25 mcg	31%
Thiamin (Vitamin B1) 1.5 mg	100%
Riboflavin (Vitamin B2) 1.7 mg	100%
Niacin 20 mg	100%
Vitamin B6 2 mg	100%
Folic Acid 400 mcg	100%
Vitamin B12 6 mcg	100%
Biotin 30 mcg	10%
Pantothenic Acid 10 mg	100%
Calcium 160 mg	16%
Iron 18 mg	100%
Phosphorus 110 mg	11%
Iodine 150 mcg	100%
Magnesium 100 mg	25%
Zinc 15 mg	100%
Selenium 20 mcg	29%
Copper 2 mg	100%
Manganese 2 mg	100%
Chromium 120 mcg	100%
Molybdenum 75 mcg	100%
Chloride 72 mg	2%
Potassium 80 mg	2%
Boron 150 mcg	*
Nickel 5 mcg	*
Silicon 2 mg	*
Tin 10 mcg	*
Vanadium 10 mcg	*
Lutein 250 mcg	*

* Daily Value (DV) not stablished

Figure **12.4.1**: Vitamin and Mineral supplements. Every entry down through pantothenic acid is a vitamin, and everything from calcium and below is a mineral.

Summary

- Covalent bonds are formed when atoms share electrons.
- Lewis electron dot diagrams can be drawn to illustrate covalent bond formation.
- Double bonds or triple bonds between atoms may be necessary to properly illustrate the bonding in some molecules.

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12.5: Electron Transfer - Ionic Bonds

Learning Objectives

- State the octet rule.
- Define *ionic bond*.
- Demonstrate electron transfer between atoms to form ionic bonds.

In Section 9.2, we saw how ions are formed by losing electrons to make cations or by gaining electrons to form anions. The astute reader may have noticed something: Many of the ions that form have eight electrons in their valence shell. Either atoms gain enough electrons to have eight electrons in the valence shell and become the appropriately charged anion, or they lose the electrons in their original valence shell; the *lower* shell, now the valence shell, has eight electrons in it, so the atom becomes positively charged. For whatever reason, having eight electrons in a valence shell is a particularly energetically stable arrangement of electrons. The trend that atoms like to have eight electrons in their valence shell is called the **octet rule**. When atoms form compounds, the octet rule is not always satisfied for all atoms at all times, but it is a very good rule of thumb for understanding the kinds of bonding arrangements that atoms can make.

It is not impossible to violate the octet rule. Consider sodium: in its elemental form, it has one valence electron and is stable. It is rather reactive, however, and does not require a lot of energy to remove that electron to make the Na^+ ion. We *could* remove another electron by adding even more energy to the ion, to make the Na^{2+} ion. However, that requires much more energy than is normally available in chemical reactions, so sodium stops at a 1+ charge after losing a single electron. It turns out that the Na^+ ion has a complete octet in its new valence shell, the $n = 2$ shell, which satisfies the octet rule. The octet rule is a result of trends in energies and is useful in explaining why atoms form the ions that they do.

Now consider an Na atom in the presence of a Cl atom. The two atoms have these Lewis electron dot diagrams and electron configurations:

$$\mathbf{Na}\cdot \qquad \cdot\ddot{\underset{\cdot\cdot}{\mathbf{Cl}}}\mathbf{:} \tag{12.5.1}$$

$$[Ne]\,3s^1 \qquad [Ne]\,3s^2 3p^5 \tag{12.5.2}$$

For the Na atom to obtain an octet, it must lose an electron; for the Cl atom to gain an octet, it must gain an electron. An electron transfers from the Na atom to the Cl atom:

$$\mathbf{Na}\cdot \rightsquigarrow \cdot\ddot{\underset{\cdot\cdot}{\mathbf{Cl}}}\mathbf{:} \tag{12.5.3}$$

resulting in two ions—the Na^+ ion and the Cl^- ion:

$$\mathbf{Na^+} \qquad \mathbf{:}\ddot{\underset{\cdot\cdot}{\mathbf{Cl}}}\mathbf{:^-} \tag{12.5.4}$$

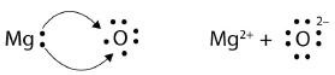
$$[Ne] \qquad [Ne]\,3s^2 3p^6 \tag{12.5.5}$$

Both species now have complete octets, and the electron shells are energetically stable. From basic physics, we know that opposite charges attract. This is what happens to the Na^+ and Cl^- ions:

$$\mathbf{Na^+ + :}\ddot{\underset{\cdot\cdot}{\mathbf{Cl}}}\mathbf{:^-} \rightarrow Na^+Cl^- \;\; or \;\; NaCl \tag{12.5.6}$$

where we have written the final formula (the formula for sodium chloride) as per the convention for ionic compounds, without listing the charges explicitly. The attraction between oppositely charged ions is called an **ionic bond,** and it is one of the main types of chemical bonds in chemistry. Ionic bonds are caused by electrons *transferring* from one atom to another.

In electron transfer, the number of electrons lost must equal the number of electrons gained. We saw this in the formation of NaCl. A similar process occurs between Mg atoms and O atoms, except in this case two electrons are transferred:



The two ions each have octets as their valence shell, and the two oppositely charged particles attract, making an ionic bond:

$$\mathbf{Mg^{2+} + :\ddot{O}:^{2-}} \quad Mg^{2+}O^{2-} \text{ or } MgO \tag{12.5.7}$$

Remember, in the final formula for the ionic compound, we do not write the charges on the ions.

What about when an Na atom interacts with an O atom? The O atom needs two electrons to complete its valence octet, but the Na atom supplies only one electron:

$$\mathbf{Na\cdot \sim \cdot\ddot{O}:} \tag{12.5.8}$$

The O atom still does not have an octet of electrons. What we need is a second Na atom to donate a second electron to the O atom:



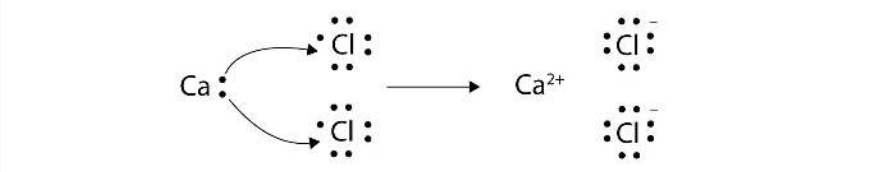
These three ions attract each other to give an overall neutral-charged ionic compound, which we write as Na_2O. The need for the number of electrons lost being equal to the number of electrons gained explains why ionic compounds have the ratio of cations to anions that they do. This is required by the law of conservation of matter as well.

Example 12.5.1:

With arrows, illustrate the transfer of electrons to form calcium chloride from Ca atoms and Cl atoms.

Solution

A Ca atom has two valence electrons, while a Cl atom has seven electrons. A Cl atom needs only one more to complete its octet, while Ca atoms have two electrons to lose. Thus we need two Cl atoms to accept the two electrons from one Ca atom. The transfer process looks as follows:

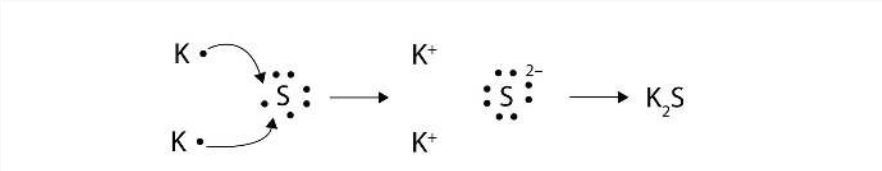


The oppositely charged ions attract each other to make $CaCl_2$.

Exercise 12.5.1

With arrows, illustrate the transfer of electrons to form potassium sulfide from K atoms and S atoms.

Answer



The strength of ionic bonding depends on two major characteristics: the magnitude of the charges and the size of the ion. The greater the magnitude of the charge, the stronger the ionic bond. The smaller the ion, the stronger the ionic bond (because a smaller ion size allows the ions to get closer together). The measured strength of ionic bonding is called the **lattice energy**. Some lattice energies are given in Table 12.5.1 - Lattice Energies of Some Ionic Compounds.

Table* 12.5.1*: *Lattice Energies of Some Ionic Compounds*

https://chem.libretexts.org/@go/page/177405

Compound	Lattice Energy (kJ/mol)
LiF	1,036
LiCl	853
NaCl	786
NaBr	747
MgF_2	2,957
Na_2O	2,481
MgO	3,791

Chemistry Is Everywhere: Salt

The element sodium (part [a] in the accompanying figure) is a very reactive metal; given the opportunity, it will react with the sweat on your hands and form sodium hydroxide, which is a very corrosive substance. The element chlorine (part [b] in the accompanying figure) is a pale yellow, corrosive gas that should not be inhaled due to its poisonous nature. Bring these two hazardous substances together, however, and they react to make the ionic compound sodium chloride (part [c] in the accompanying figure), known simply as salt.

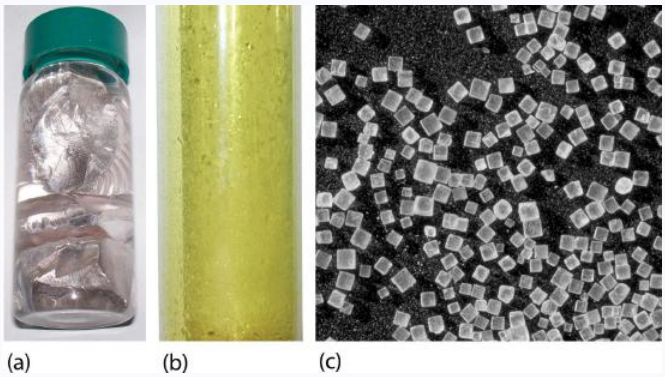


Figure 12.5.1*: Sodium + Chlorine = Sodium Chloride (a) Sodium is a very reactive metal. (b) Chlorine is a pale yellow, noxious gas. (c) Together, sodium and chlorine make sodium chloride—salt—which is necessary for our survival. Source: Photo on the left courtesy of Greenhorn1. Photo in the center courtesy of Benjah-bmm27, . Photo on the right © Thinkstock.*

Salt is necessary for life. Na^+ ions are one of the main ions in the human body and are necessary to regulate the fluid balance in the body. Cl^- ions are necessary for proper nerve function and respiration. Both of these ions are supplied by salt. The taste of salt is one of the fundamental tastes; salt is probably the most ancient flavoring known, and one of the few rocks we eat.

The health effects of too much salt are still under debate, although a 2010 report by the US Department of Agriculture concluded that “excessive sodium intake…raises blood pressure, a well-accepted and extraordinarily common risk factor for stroke, coronary heart disease, and kidney disease.”US Department of Agriculture Committee for Nutrition Policy and Promotion, Report of the Dietary Guidelines Advisory Committee on the Dietary Guidelines for Americans, accessed January 5, 2010. It is clear that most people ingest more salt than their bodies need, and most nutritionists recommend curbing salt intake. Curiously, people who suffer from low salt (called *hyponatria*) do so not because they ingest too little salt but because they drink too much water. Endurance athletes and others involved in extended strenuous exercise need to watch their water intake so their body’s salt content is not diluted to dangerous levels.

- The tendency to form species that have eight electrons in the valence shell is called the octet rule.
- The attraction of oppositely charged ions caused by electron transfer is called an ionic bond.
- The strength of ionic bonding depends on the magnitude of the charges and the sizes of the ions.

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12.6: Lewis Structures

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12.7: Violations of the Octet Rule

Learning Objective

- Recognize the three major types of violations of the octet rule.

As important and useful as the octet rule is in chemical bonding, there are some well-known violations. This does not mean that the octet rule is useless—quite the contrary. As with many rules, there are exceptions, or violations.

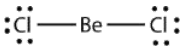
There are three violations to the octet rule. **Odd-electron molecules** are the first violation to the octet rule. Although they are few, some stable compounds have an odd number of electrons in their valence shells. With an odd number of electrons, at least one atom in the molecule will have to violate the octet rule. Examples of stable odd-electron molecules are **NO**, $\mathbf{NO_2}$, and $\mathbf{ClO_2}$. The Lewis electron dot diagram for **NO** is as follows:



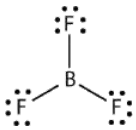
Nitrogen and oxygen share four electrons between them. Oxygen has two lone pairs while nitrogen has one full lone pair and one additional electron.

Although the **O** atom has an octet of electrons, the **N** atom has only seven electrons in its valence shell. Although **NO** is a stable compound, it is very chemically reactive, as are most other odd-electron compounds.

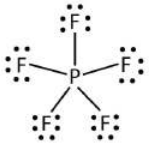
Electron-deficient molecules are the second violation to the octet rule. These stable compounds have less than eight electrons around an atom in the molecule. The most common examples are the covalent compounds of beryllium and boron. For example, beryllium can form two covalent bonds, resulting in only four electrons in its valence shell:



Boron commonly makes only three covalent bonds, resulting in only six valence electrons around the **B** atom. A well-known example is $\mathbf{BF_3}$:



The third violation to the octet rule is found in those compounds with more than eight electrons assigned to their valence shell. These are called **expanded valence shell molecules**. Such compounds are formed only by central atoms in the third row of the periodic table or beyond that have empty *d* orbitals in their valence shells that can participate in covalent bonding. One such compound is $\mathbf{PF_5}$. The only reasonable Lewis electron dot diagram for this compound has the **P** atom making five covalent bonds:



Formally, the **P** atom has 10 electrons in its valence shell.

Example 12.7.1

Identify each violation to the octet rule by drawing a Lewis electron dot diagram.

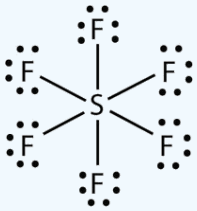
a. **ClO**
b. $\mathbf{SF_6}$

Solution

1. With one Cl atom and one O atom, this molecule has 6 + 7 = 13 valence electrons, so it is an odd-electron molecule. A Lewis electron dot diagram for this molecule is as follows:



2. In $\mathbf{SF_6}$, the central S atom makes six covalent bonds to the six surrounding F atoms, so it is an expanded valence shell molecule. Its Lewis electron dot diagram is as follows:

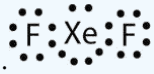


? Exercise 12.7.1: Xenon Difluoride

Identify the violation to the octet rule in $\mathbf{XeF_2}$ by drawing a Lewis electron dot diagram.

Answer

The Xe atom has an expanded valence shell with more than eight electrons around it.



Summary

There are three violations to the octet rule: odd-electron molecules, electron-deficient molecules, and expanded valence shell molecules.

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12.8: Molecular Shapes

Learning Objective

- Determine the shape of simple molecules.

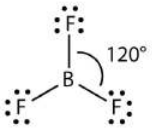
Molecules have shapes. There is an abundance of experimental evidence to that effect—from their physical properties to their chemical reactivity. Small molecules—molecules with a single central atom—have shapes that can be easily predicted. The basic idea in molecular shapes is **called valence shell electron pair repulsion (VSEPR).** It basically says that electron pairs, being composed of negatively charged particles, repel each other to get as far away from each other as possible. VSEPR makes a distinction between *electron group geometry*, which expresses how electron groups (bonds and nonbonding electron pairs) are arranged, and *molecular geometry*, which expresses how the atoms in a molecule are arranged. However, the two geometries are related.

There are two types of **electron groups**: any type of bond—single, double, or triple—and lone electron pairs. When applying VSEPR to simple molecules, the first thing to do is to count the number of electron groups around the central atom. Remember that a multiple bond counts as only *one* electron group.

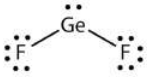
Any molecule with only two atoms is linear. A molecule whose central atom contains only two electron groups orients those two groups as far apart from each other as possible—180° apart. When the two electron groups are 180° apart, the atoms attached to those electron groups are also 180° apart, so the overall molecular shape is linear. Examples include BeH_2 and CO_2:



A molecule with three electron groups orients the three groups as far apart as possible. They adopt the positions of an equilateral triangle—120° apart and in a plane. The shape of such molecules is *trigonal planar*. An example is BF_3:



Some substances have a trigonal planar electron group distribution but have atoms bonded to only two of the three electron groups. An example is GeF_2:



From an electron group geometry perspective, GeF_2 has a trigonal planar shape, but its real shape is dictated by the positions of the atoms. This shape is called *bent* or *angular*.

A molecule with four electron groups about the central atom orients the four groups in the direction of a tetrahedron, as shown in Figure **12.8.1** Tetrahedral Geometry. If there are four atoms attached to these electron groups, then the molecular shape is also *tetrahedral*. Methane (CH_4) is an example.

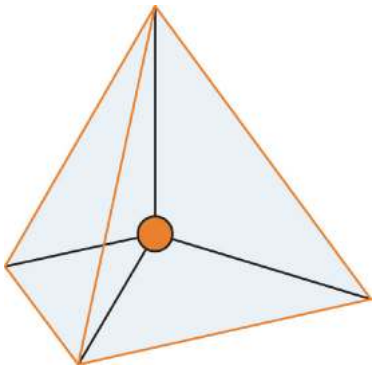
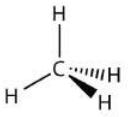
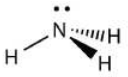


Figure* 12.8.1*: *Tetrahedral Geometry. Four electron groups orient themselves in the shape of a tetrahedron.*

This diagram of CH_4 illustrates the standard convention of displaying a three-dimensional molecule on a two-dimensional surface. The straight lines are in the plane of the page, the solid wedged line is coming out of the plane toward the reader, and the dashed wedged line is going out of the plane away from the reader.



NH_3 is an example of a molecule whose central atom has four electron groups but only three of them are bonded to surrounding atoms.



Although the electron groups are oriented in the shape of a tetrahedron, from a molecular geometry perspective, the shape of NH_3 is *trigonal pyramidal*.

H_2O is an example of a molecule whose central atom has four electron groups but only two of them are bonded to surrounding atoms.

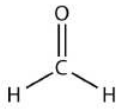


Although the electron groups are oriented in the shape of a tetrahedron, the shape of the molecule is *bent* or *angular*. A molecule with four electron groups about the central atom but only one electron group bonded to another atom is linear because there are only two atoms in the molecule.

Double or triple bonds count as a single electron group. CH_2O has the following Lewis electron dot diagram.



The central C atom has three electron groups around it because the double bond counts as one electron group. The three electron groups repel each other to adopt a trigonal planar shape:



(The lone electron pairs on the O atom are omitted for clarity.) The molecule will not be a perfect equilateral triangle because the C–O double bond is different from the two C–H bonds, but both planar and triangular describe the appropriate approximate shape of this molecule.

Example 12.8.1:

What is the approximate shape of each molecule?

a. PCl_3
b. NOF

Solution

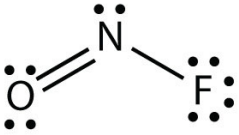
The first step is to draw the Lewis electron dot diagram of the molecule.

1. For PCl_3, the electron dot diagram is as follows:



The lone electron pairs on the Cl atoms are omitted for clarity. The P atom has four electron groups with three of them bonded to surrounding atoms, so the molecular shape is trigonal pyramidal.

2. The electron dot diagram for NOF is as follows:



The N atom has three electron groups on it, two of which are bonded to other atoms. The molecular shape is bent.

Exercise 12.8.1

What is the approximate molecular shape of CH_2Cl_2?

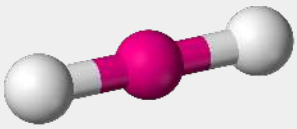
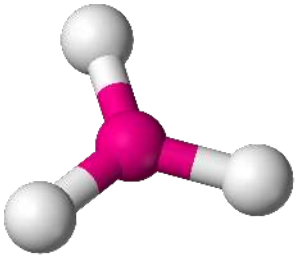
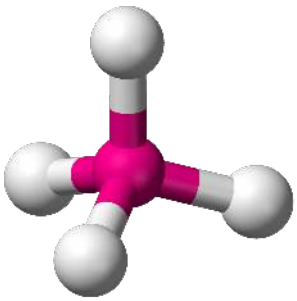
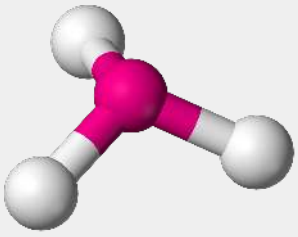
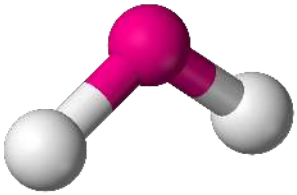
Answer

Tetrahedral

Table 12.8.1 summarizes the shapes of molecules based on their number of electron groups and surrounding atoms.

Table* 12.8.1*: *Summary of Molecular Shapes*

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Number of Electron Groups on Central Atom	Number of Surrounding Atoms	Molecular Shape	
any	1	linear	
2	2	linear	
3	3	trigonal planar	
3	2	bent	
4	4	tetrahedral	
4	3	trigonal pyramidal	
4	2	bent	

Images:Public Domain, Link

Summary

The approximate shape of a molecule can be predicted from the number of electron groups and the number of surrounding atoms.

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12.9: Polar Molecules

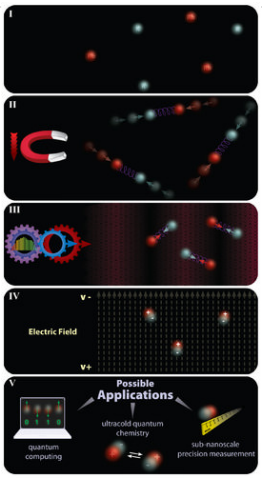


Figure 12.9.1 (Public Domain; G. Kuebler/JILA and the NIST via Patapsco Image Gallery [patapsco.nist.gov])

How cold are ultracold polar molecules?

Ultracold polar molecules have been created by research scientists. These "molecules" consist of **Rb** and **K** atoms excited by lasers to form a type of **Rb–K** compound where the **Rb** has a positive charge and the **K** has a negative charge. The material is formed at temperatures extremely close to absolute zero. The researchers believe these techniques will help them make new reactions and new materials.

Polar Molecules

A **polar molecule** is a molecule in which one end of the molecule is slightly positive, while the other end is slightly negative. A diatomic molecule that consists of a polar covalent bond, such as **HF**, is a polar molecule. The two electrically charged regions on either end of the molecule are called poles, similar to a magnet having a north and a south pole. A molecule with two poles is called a **dipole** (see figure below). Hydrogen fluoride is a dipole.



Figure 12.9.2: A dipole is any molecule with a positive end and a negative end, resulting from unequal distribution of electron density throughout the molecule. (CC BY-NC 3.0; Christopher Auyeung via CK-12 Foundation)

Polar molecules orient themselves in the presence of an electric field with the positive ends of the molecule being attracted to the negative plate, while the negative ends of the molecules are attracted to the positive plate (see figure below).

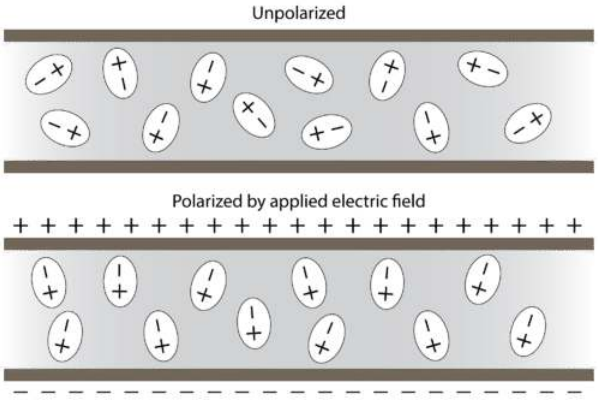


Figure 12.9.3: Polar molecules are randomly oriented in the absence of an applied electric field (top). In an electric field, the molecules orient themselves because of the attraction of opposite charges (bottom). (CC BY-NC 3.0; Zachary Wilson via CK-12 Foundation)

For molecules with more than two atoms, the molecular geometry must also be taken into account when determining if the molecule is polar or nonpolar. The figure below shows a comparison between carbon dioxide and water. Carbon dioxide (CO_2) is a linear molecule. The oxygen atoms are more electronegative than the carbon atom, so there are two individual dipoles pointing outward from the C atom to each O atom. However, since the dipoles are of equal strength and are oriented this way, they cancel out, and the overall molecular polarity of CO_2 is zero.

Water is a bent molecule because of the two lone pairs on the central oxygen atom. The individual dipoles point from the H atoms toward the O atom. Because of the shape, the dipoles do not cancel each other out, and the water molecule is polar. In the figure below, the net dipole is shown in blue and points upward.

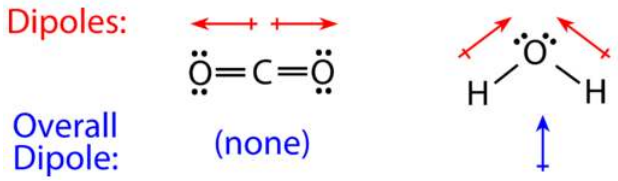


Figure 12.9.4: The molecular geometry of a molecule affects its polarity. (CC BY-NC 3.0; Joy Sheng via CK-12 Foundation)

Some other molecules are shown in the figure below. Notice that a tetrahedral molecule such as CH_4 is nonpolar. However, if one of the peripheral H atoms is replaced with another atom that has a different electronegativity, the molecule becomes polar. A trigonal planar molecule (BF_3) may be nonpolar if all three peripheral atoms are the same, but a trigonal pyramidal molecule (NH_3) is polar.

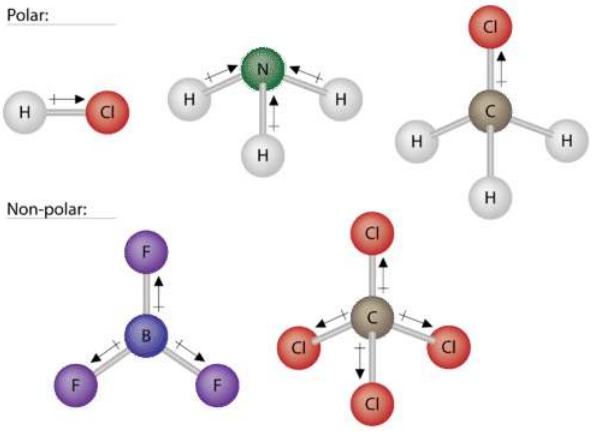


Figure 12.9.5: Some examples of polar and nonpolar molecules based on molecular geometry. (CC BY-NC 3.0; Joy Sheng via CK-12 Foundation)



Summary

- Polar molecules result from differences in the electronegativity of the atoms in the molecule.
- Dipoles that are directly opposite one another cancel each other out.

Review

1. Why is a polar molecule called a dipole?
2. The molecular geometry of NH_3 is trigonal pyramidal. What about the molecular geometry of NH_3 makes it a polar molecule?
3. What happens to polar molecules when an electric field is applied?

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CHAPTER OVERVIEW

15: Solutions

A solution is a *homogeneous mixture*—a mixture of two or more substances that are so intimately mixed that the mixture behaves in many ways like a single substance. Many chemical reactions occur when the reactants are dissolved in solution. In this chapter, we will introduce concepts that are applicable to solutions and the chemical reactions that occur in them.

15.1: Definitions
15.2: Quantitative Units of Concentration
15.3: Solution Concentration - Molality, Mass Percent, ppm and ppb
15.3: Solution Concentration - Molarity
15.4: Solution Concentration - Molality, Mass Percent, ppm and ppb
15.5: Dilutions and Concentrations
15.6: Concentrations as Conversion Factors
15.7: Acid-Base Titrations
15.8: Normality

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15.1: Definitions

Learning Objective

- Learn some terminology involving solutions.
- Recognize which terminology is qualitative and which terminology is quantitative.
- Explain why certain substances dissolve in other substances.

The major component of a solution is called the **solvent.** The minor component of a solution is called the **solute**. "Major" and "minor" indicate which component has the greater or lesser presence by mass or moles, respectively. Sometimes this becomes confusing, especially when considering substances with very different molar masses. We will confine the discussion here to solutions for which the major component and the minor component are obvious.

Solutions exist for every possible phase of the solute and the solvent. Salt water, for example, is a solution of solid NaCl in liquid water; soda water is a solution of gaseous CO_2 in liquid water, while air is a solution of a gaseous solute (O_2) in a gaseous solvent (N_2). In all cases, however, the overall phase of the solution is the same phase as the solvent.

Example 15.1.1: Sugar Water

A solution is made by dissolving 1.00 g of sucrose ($C_{12}H_{22}O_{11}$) in 100.0 g of liquid water. Identify the solvent and solute in the resulting solution.

Solution

Either by mass or by moles, the obvious minor component is sucrose, so it is the solute. Water—the majority component—is the solvent. The fact that the resulting solution is the same phase as water also suggests that water is the solvent.

Exercise 15.1.1

A solution is made by dissolving 3.33 g of HCl(g) in 40.0 g of liquid methyl alcohol (CH_3OH). Identify the solvent and solute in the resulting solution.

Answer

solute: HCl(g); solvent: CH_3OH

One important concept of solutions is in defining how much solute is dissolved in a given amount of solvent. This concept is called **concentration**. Various words are used to describe the relative amounts of solute. **Dilute** describes a solution that has very little solute, while **concentrated** describes a solution that has a lot of solute. One problem is that these terms are qualitative; they describe more or less but not exactly how much.

In most cases, only a certain maximum amount of solute can be dissolved in a given amount of solvent. This maximum amount is called the **solubility** of the solute. It is usually expressed in terms of the amount of solute that can dissolve in 100 g of the solvent at a given temperature. Table **15.1.1** lists the solubilities of some simple ionic compounds. These solubilities vary widely: NaCl can dissolve up to 31.6 g per 100 g of H_2O, while AgCl can dissolve only 0.00019 g per 100 g of H_2O.

Table **15.1.1**: Solubilities of Some Ionic Compounds

Solute	Solubility (g per 100 g of H_2O at 25°C)
AgCl	0.00019
$CaCO_3$	0.0006
KBr	70.7
NaCl	36.1
$NaNO_3$	94.6

When the maximum amount of solute has been dissolved in a given amount of solvent, we say that the solution is **saturated** with solute. When less than the maximum amount of solute is dissolved in a given amount of solute, the solution is **unsaturated**. These terms are also qualitative terms because each solute has its own solubility. A solution of 0.00019 g of AgCl per 100 g of H_2O may be saturated, but with so little solute dissolved, it is also rather dilute. A solution of 36.1 g of NaCl in 100 g of H_2O is also saturated but rather concentrated. Ideally, we need more precise ways of specifying the amount of solute in a solution. We will introduce such ways in Section 11.3.

In some circumstances, it is possible to dissolve more than the maximum amount of a solute in a solution. Usually, this happens by heating the solvent, dissolving more solute than would normally dissolve at regular temperatures, and letting the solution cool down slowly and carefully. Such solutions are called **supersaturated** solutions and are not stable; given an opportunity (such as dropping a crystal of solute in the solution), the excess solute will precipitate from the solution.

It should be obvious that some solutes dissolve in certain solvents but not others. NaCl, for example, dissolves in water but not in vegetable oil. Beeswax dissolves in liquid hexane but not water. What is it that makes a solute soluble in some solvents but not others?

The answer is intermolecular interactions. The intermolecular interactions include London dispersion forces, dipole-dipole interactions, and hydrogen bonding (as described in Chapter 10). From experimental studies, it has been determined that if molecules of a solute experience the same intermolecular forces that the solvent does, the solute will likely dissolve in that solvent. So, NaCl—a very polar substance because it is composed of ions—dissolves in water, which is very polar, but not in oil, which is generally nonpolar. Nonpolar wax dissolves in nonpolar hexane but not in polar water. This concept leads to the general rule that "like dissolves like" for predicting whether a solute is soluble in a given solvent. However, this is a general rule, not an absolute statement, so it must be applied with care.

✔ Example 15.1.2: Polar and Nonpolar Solvents

Would I_2 be more soluble in CCl_4 or H_2O? Explain your answer.

Solution

I_2 is nonpolar. Of the two solvents, CCl_4 is nonpolar and H_2O is polar, so I_2 would be expected to be more soluble in CCl_4.

? Exercise 15.1.2

Would C_3H_7OH be more soluble in CCl_4 or H_2O? Explain your answer.

Answer

H_2O because both experience hydrogen bonding

Summary

- Solutions are composed of a solvent (major component) and a solute (minor component).
- Concentration is the expression of the amount of solute in a given amount of solvent and can be described by several qualitative terms.
- Solubility is a specific amount of solute that can dissolve in a given amount of solvent.

- "Like dissolves like" is a useful rule for deciding if a solute will be soluble in a solvent.

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15.2: Quantitative Units of Concentration

Learning Objective

- Learn to determine specific concentrations with several common units.

Rather than qualitative terms (Section 11.2 - Definitions) we need quantitative ways to express the amount of solute in a solution; that is, we need specific units of concentration. In this section, we will introduce several common and useful units of concentration.

Molarity (M) is defined as the number of moles of solute divided by the number of liters of solution:

$$molarity = \frac{moles\ of\ solute}{liters\ of\ solution} \tag{15.2.1}$$

which can be simplified as

$$M = \frac{mol}{L},\ or\ mol/L \tag{15.2.2}$$

As with any mathematical equation, if you know any two quantities, you can calculate the third, unknown, quantity.

For example, suppose you have 0.500 L of solution that has 0.24 mol of NaOH dissolved in it. The concentration of the solution can be calculated as follows:

$$molarity = \frac{0.24\ mol\ NaOH}{0.500\ L} = 0.48\ M\ NaOH \tag{15.2.3}$$

The concentration of the solution is 0.48 M, which is spoken as “zero point forty-eight molarity” or “zero point forty-eight molar.” If the quantity of the solute is given in mass units, you must convert mass units to mole units before using the definition of molarity to calculate concentration. For example, what is the molar concentration of a solution of 22.4 g of HCl dissolved in 1.56 L? First, convert the mass of solute to moles using the molar mass of HCl (36.5 g/mol):

$$22.4\ \cancel{g\ HCl} \times \frac{1\ mol\ HCl}{36.5\ \cancel{g\ HCl}} = 0.614\ M\ HCl \tag{15.2.4}$$

Now we can use the definition of molarity to determine a concentration:

$$M = \frac{0.614\ mol\ HCl}{1.56\ L} = 0.394\ M \tag{15.2.5}$$

Example 15.2.1:

What is the molarity of a solution made when 32.7 g of NaOH are dissolved to make 445 mL of solution?

Solution

To use the definition of molarity, both quantities must be converted to the proper units. First, convert the volume units from milliliters to liters:

$$445\ \cancel{mL} \times \frac{1\ L}{1000\ \cancel{mL}} = 0.445\ L \tag{15.2.6}$$

Now we convert the amount of solute to moles, using the molar mass of NaOH, which is 40.0 g/mol:

$$32.7\ \cancel{g\ NaOH} \times \frac{1\ mol\ NaOH}{40.0\ \cancel{g\ NaOH}} = 0.818\ mol\ NaOH \tag{15.2.7}$$

Now we can use the definition of molarity to determine the molar concentration:

$$M = \frac{0.818\ mol\ NaOH}{0.445\ L} = 1.84\ M\ NaOH \tag{15.2.8}$$

Exercise 15.2.1

What is the molarity of a solution made when 66.2 g of $C_6H_{12}O_6$ are dissolved to make 235 mL of solution?

Answer

1.57 M

The definition of molarity can be used to determine the amount of solute or the volume of solution, if the other information is given. Example 4 illustrates this situation.

Example 15.2.1:

How many moles of solute are present in 0.108 L of a 0.887 M NaCl solution?

Solution

We know the volume and the molarity; we can use the definition of molarity to mathematically solve for the amount in moles. Substituting the quantities into the definition of molarity:

$$0.887\,M = \frac{mol\ NaCl}{0.108\,L} \tag{15.2.9}$$

We multiply the 0.108 L over to the other side of the equation and multiply the units together; "molarity × liters" equals moles, according to the definition of molarity. So

mol NaCl = (0.887 M)(0.108 L) = 0.0958 mol

Exercise 15.2.1

How many moles of solute are present in 225 mL of a 1.44 M $CaCl_2$ solution?

Answer

0.324 mol

If you need to determine volume, remember the rule that the unknown quantity must be by itself and in the numerator to determine the correct answer. Thus rearrangement of the definition of molarity is required.

Example 15.2.1:

What volume of a 2.33 M $NaNO_3$ solution is needed to obtain 0.222 mol of solute?

Solution

Using the definition of molarity, we have

$$2.33\,M = \frac{0.222\,mol}{L} \tag{15.2.10}$$

To solve for the number of liters, we bring the 2.33 M over to the right into the denominator, and the number of liters over to the left in the numerator. We now have

$$L = \frac{0.222\,mol}{2.33\,M} \tag{15.2.11}$$

Dividing, **the volume is 0.0953 L = 95.3 mL.**

Exercise 15.2.1

What volume of a 0.570 M K_2SO_4 solution is needed to obtain 0.872 mol of solute?

Answer

1.53 L

A similar unit of concentration is **molality** (*m*), which is defined as the number of moles of solute per kilogram of solvent, not per liter of solution:

$$molality = \frac{moles\ solute}{kilograms\ solvent} \tag{15.2.12}$$

Mathematical manipulation of molality is the same as with molarity.

Another way to specify an amount is **percentage composition by mass** (or *mass percentage*, % m/m). It is defined as follows:

$$\%m/m = \frac{mass\ of\ solute}{mass\ of\ entire\ sample} \times 100\% \tag{15.2.13}$$

It is not uncommon to see this unit used on commercial products (Fig. 11.3.1 - Concentration in Commercial Applications)



Fig. 11.3.1 Concentration in Commercial Applications © Thinkstock

The percentage of urea in this package is 5% m/m, meaning that there are 5 g of urea per 100 g of product.

Example 15.2.1:

What is the mass percentage of Fe in a piece of metal with 87.9 g of Fe in a 113 g sample?

Solution

Using the definition of mass percentage, we have

$$\%m/m = \frac{87.9\,g\,Fe}{113\,g\,sample} \times 100\% = 77.8\%\,Fe \tag{15.2.14}$$

Exercise 15.2.1

What is the mass percentage of H_2O_2 in a solution with 1.67 g of H_2O_2 in a 55.5 g sample?

Answer

3.01%

Related concentration units are **parts per thousand (ppth), parts per million (ppm)** and **parts per billion (ppb).** Parts per thousand is defined as follows:

$$ppth = \frac{mass\ of\ solute}{mass\ of\ sample} \times 1000 \tag{15.2.15}$$

There are similar definitions for parts per million and parts per billion:

$$ppm = \frac{mass\ of\ solute}{mass\ of\ sample} \times 1,000,000 \tag{15.2.16}$$

and

$$ppb = \frac{mass\ of\ solute}{mass\ of\ sample} \times 1,000,000,000 \tag{15.2.17}$$

Each unit is used for progressively lower and lower concentrations. The two masses must be expressed in the same unit of mass, so conversions may be necessary.

Example 15.2.1:

If there is 0.6 g of Pb present in 277 g of solution, what is the Pb concentration in parts per thousand?

Solution

Use the definition of parts per thousand to determine the concentration. Substituting

$$\frac{0.6g\ Pb}{277g\ solution} \times 1000 = 2.17\,ppth \tag{15.2.18}$$

Exercise 15.2.1

If there is 0.551 mg of As in 348 g of solution, what is the As concentration in ppm?

Answer

1.58 ppm

As with molarity and molality, algebraic rearrangements may be necessary to answer certain questions.

Example 15.2.1:

The concentration of Cl^- ion in a sample of H_2O is 15.0 ppm. What mass of Cl^- ion is present in 240.0 mL of H_2O, which has a density of 1.00 g/mL?

Solution

First, use the density of H_2O to determine the mass of the sample:

$$240.0\,\cancel{mL} \times \frac{1.00\,g}{\cancel{mL}} = 240.0\,g \tag{15.2.19}$$

Now we can use the definition of ppm:

$$15.0\,ppm = \frac{mass\ of\ solute}{240.0\ g\ solution} \times 1,000,000 \tag{15.2.20}$$

Rearranging to solve for the mass of solute,

$$mass\ solute = \frac{(15.0\,ppm)(240.0\ g\ solution)}{1,000,000} = 0.0036g = 3.6\,mg \tag{15.2.21}$$

Exercise 15.2.1

The concentration of Fe^{3+} ion in a sample of H_2O is 335.0 ppm. What mass of Fe^{3+} ion is present in 3,450 mL of H_2O, which has a density of 1.00 g/mL?

Answer

1.16 g

For ionic solutions, we need to differentiate between the concentration of the salt versus the concentration of each individual ion. Because the ions in ionic compounds go their own way when a compound is dissolved in a solution, the resulting concentration of the ion may be different from the concentration of the complete salt. For example, if 1 M NaCl were prepared, the solution could also be described as a solution of 1 M $Na^+(aq)$ and 1 M $Cl^-(aq)$ because there is one Na^+ ion and one Cl^- ion per formula unit of the salt. However, if the solution were 1 M $CaCl_2$, there are two $Cl^-(aq)$ ions for every formula unit dissolved, so the concentration of $Cl^-(aq)$ would be 2 M, not 1 M.

In addition, the total ion concentration is the sum of the individual ion concentrations. Thus for the 1 M NaCl, the total ion concentration is 2 M; for the 1 M $CaCl_2$, the total ion concentration is 3 M.

Key Takeaway

- Quantitative units of concentration include molarity, molality, mass percentage, parts per thousand, parts per million, and parts per billion.

Exercise 15.2.1

1. Differentiate between molarity and molality.
2. Differentiate between mass percentage and parts per thousand.
3. What is the molarity of a solution made by dissolving 13.4 g of $NaNO_3$ in 345 mL of solution?
4. What is the molarity of a solution made by dissolving 332 g of $C_6H_{12}O_6$ in 4.66 L of solution?
5. How many moles of $MgCl_2$ are present in 0.0331 L of a 2.55 M solution?
6. How many moles of NH_4Br are present in 88.9 mL of a 0.228 M solution?
7. What volume of 0.556 M NaCl is needed to obtain 0.882 mol of NaCl?
8. What volume of 3.99 M H_2SO_4 is needed to obtain 4.61 mol of H_2SO_4?
9. What volume of 0.333 M $Al(NO_3)_3$ is needed to obtain 26.7 g of $Al(NO_3)_3$?
10. What volume of 1.772 M $BaCl_2$ is needed to obtain 123 g of $BaCl_2$?
11. What are the individual ion concentrations and the total ion concentration in 0.66 M $Mg(NO_3)_2$?
12. What are the individual ion concentrations and the total ion concentration in 1.04 M $Al_2(SO_4)_3$?
13. If the $C_2H_3O_2^-$ ion concentration in a solution is 0.554 M, what is the concentration of $Ca(C_2H_3O_2)_2$?
14. If the Cl^- ion concentration in a solution is 2.61 M, what is the concentration of $FeCl_3$?

Answers

1. Molarity is moles per liter, whereas molality is moles per kilogram of solvent.
2.
3. 0.457 M
4.
5. 0.0844 mol
6.
7. 1.59 L
8.
9. 0.376 L
10.

11. Mg^{2+} = 0.66 M; NO_3^- = 1.32 M; total: 1.98 M

12.

13. 0.277 M

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15.3: Solution Concentration - Molality, Mass Percent, ppm and ppb

A similar unit of concentration is **molality** (*m*), which is defined as the number of moles of solute per kilogram of solvent, not per liter of solution:

$$molality = \frac{moles\ solute}{kilograms\ solvent} \tag{15.3.1}$$

Mathematical manipulation of molality is the same as with molarity.

Another way to specify an amount is **percentage composition by mass** (or *mass percentage*, % m/m). It is defined as follows:

$$\%m/m = \frac{mass\ of\ solute}{mass\ of\ entire\ sample} \times 100\% \tag{15.3.2}$$

It is not uncommon to see this unit used on commercial products (Fig. 11.3.1 - Concentration in Commercial Applications)



Fig. 11.3.1 Concentration in Commercial Applications © Thinkstock

The percentage of urea in this package is 5% m/m, meaning that there are 5 g of urea per 100 g of product.

Example 15.3.1:

What is the mass percentage of Fe in a piece of metal with 87.9 g of Fe in a 113 g sample?

Solution

Using the definition of mass percentage, we have

$$\%m/m = \frac{87.9\,g\,Fe}{113\,g\,sample} \times 100\% = 77.8\%\,Fe \tag{15.3.3}$$

Exercise 15.3.1

What is the mass percentage of H_2O_2 in a solution with 1.67 g of H_2O_2 in a 55.5 g sample?

Answer

3.01%

Related concentration units are **parts per thousand (ppth), parts per million (ppm)** and **parts per billion (ppb).** Parts per thousand is defined as follows:

$$ppth = \frac{mass\ of\ solute}{mass\ of\ sample} \times 1000 \tag{15.3.4}$$

There are similar definitions for parts per million and parts per billion:

$$ppm = \frac{mass\ of\ solute}{mass\ of\ sample} \times 1,000,000 \tag{15.3.5}$$

and

$$ppb = \frac{mass\ of\ solute}{mass\ of\ sample} \times 1,000,000,000 \tag{15.3.6}$$

Each unit is used for progressively lower and lower concentrations. The two masses must be expressed in the same unit of mass, so conversions may be necessary.

Example 15.3.1:

If there is 0.6 g of Pb present in 277 g of solution, what is the Pb concentration in parts per thousand?

Solution

Use the definition of parts per thousand to determine the concentration. Substituting

$$\frac{0.6g\ Pb}{277g\ solution} \times 1000 = 2.17\ ppth \tag{15.3.7}$$

Exercise 15.3.1

If there is 0.551 mg of As in 348 g of solution, what is the As concentration in ppm?

Answer

1.58 ppm

As with molarity and molality, algebraic rearrangements may be necessary to answer certain questions.

Example 15.3.1:

The concentration of Cl^- ion in a sample of H_2O is 15.0 ppm. What mass of Cl^- ion is present in 240.0 mL of H_2O, which has a density of 1.00 g/mL?

Solution

First, use the density of H_2O to determine the mass of the sample:

$$240.0\ \cancel{mL} \times \frac{1.00\ g}{\cancel{mL}} = 240.0\ g \tag{15.3.8}$$

Now we can use the definition of ppm:

$$15.0\ ppm = \frac{mass\ of\ solute}{240.0\ g\ solution} \times 1,000,000 \tag{15.3.9}$$

Rearranging to solve for the mass of solute,

$$mass\ solute = \frac{(15.0\ ppm)(240.0\ g\ solution)}{1,000,000} = 0.0036g = 3.6\ mg \tag{15.3.10}$$

Exercise 15.3.1

The concentration of Fe^{3+} ion in a sample of H_2O is 335.0 ppm. What mass of Fe^{3+} ion is present in 3,450 mL of H_2O, which has a density of 1.00 g/mL?

Answer

1.16 g

For ionic solutions, we need to differentiate between the concentration of the salt versus the concentration of each individual ion. Because the ions in ionic compounds go their own way when a compound is dissolved in a solution, the resulting concentration of the ion may be different from the concentration of the complete salt. For example, if 1 M NaCl were prepared, the solution could also be described as a solution of 1 M $Na^+(aq)$ and 1 M $Cl^-(aq)$ because there is one Na^+ ion and one Cl^- ion per formula unit of the salt. However, if the solution were 1 M $CaCl_2$, there are two $Cl^-(aq)$ ions for every formula unit dissolved, so the concentration of $Cl^-(aq)$ would be 2 M, not 1 M.

In addition, the total ion concentration is the sum of the individual ion concentrations. Thus for the 1 M NaCl, the total ion concentration is 2 M; for the 1 M $CaCl_2$, the total ion concentration is 3 M.

Key Takeaway

- Quantitative units of concentration include molarity, molality, mass percentage, parts per thousand, parts per million, and parts per billion.

Exercise 15.3.1

1. Differentiate between molarity and molality.
2. Differentiate between mass percentage and parts per thousand.
3. What is the molarity of a solution made by dissolving 13.4 g of $NaNO_3$ in 345 mL of solution?
4. What is the molarity of a solution made by dissolving 332 g of $C_6H_{12}O_6$ in 4.66 L of solution?
5. How many moles of $MgCl_2$ are present in 0.0331 L of a 2.55 M solution?
6. How many moles of NH_4Br are present in 88.9 mL of a 0.228 M solution?
7. What volume of 0.556 M NaCl is needed to obtain 0.882 mol of NaCl?
8. What volume of 3.99 M H_2SO_4 is needed to obtain 4.61 mol of H_2SO_4?
9. What volume of 0.333 M $Al(NO_3)_3$ is needed to obtain 26.7 g of $Al(NO_3)_3$?
10. What volume of 1.772 M $BaCl_2$ is needed to obtain 123 g of $BaCl_2$?
11. What are the individual ion concentrations and the total ion concentration in 0.66 M $Mg(NO_3)_2$?
12. What are the individual ion concentrations and the total ion concentration in 1.04 M $Al_2(SO_4)_3$?
13. If the $C_2H_3O_2^-$ ion concentration in a solution is 0.554 M, what is the concentration of $Ca(C_2H_3O_2)_2$?
14. If the Cl^- ion concentration in a solution is 2.61 M, what is the concentration of $FeCl_3$?

Answers

1. Molarity is moles per liter, whereas molality is moles per kilogram of solvent.
2.
3. 0.457 M
4.
5. 0.0844 mol
6.
7. 1.59 L
8.

9. 0.376 L

10.

11. Mg^{2+} = 0.66 M; NO_3^- = 1.32 M; total: 1.98 M

12.

13. 0.277 M

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15.3: Solution Concentration - Molarity

Learning Objective

- Learn to determine specific concentrations with several common units.

Rather than qualitative terms (Section 11.2 - Definitions) we need quantitative ways to express the amount of solute in a solution; that is, we need specific units of concentration. In this section, we will introduce several common and useful units of concentration.

Molarity (M) is defined as the number of moles of solute divided by the number of liters of solution:

$$molarity = \frac{moles\ of\ solute}{liters\ of\ solution} \tag{15.3.1}$$

which can be simplified as

$$M = \frac{mol}{L},\ or\ mol/L \tag{15.3.2}$$

As with any mathematical equation, if you know any two quantities, you can calculate the third, unknown, quantity.

For example, suppose you have 0.500 L of solution that has 0.24 mol of NaOH dissolved in it. The concentration of the solution can be calculated as follows:

$$molarity = \frac{0.24\ mol\ NaOH}{0.500\ L} = 0.48\ M\ NaOH \tag{15.3.3}$$

The concentration of the solution is 0.48 M, which is spoken as “zero point forty-eight molarity” or “zero point forty-eight molar.” If the quantity of the solute is given in mass units, you must convert mass units to mole units before using the definition of molarity to calculate concentration. For example, what is the molar concentration of a solution of 22.4 g of HCl dissolved in 1.56 L? First, convert the mass of solute to moles using the molar mass of HCl (36.5 g/mol):

$$22.4\ \cancel{g\ HCl} \times \frac{1\ mol\ HCl}{36.5\ \cancel{g\ HCl}} = 0.614\ M\ HCl \tag{15.3.4}$$

Now we can use the definition of molarity to determine a concentration:

$$M = \frac{0.614\ mol\ HCl}{1.56\ L} = 0.394\ M \tag{15.3.5}$$

Example 15.3.1:

What is the molarity of a solution made when 32.7 g of NaOH are dissolved to make 445 mL of solution?

Solution

To use the definition of molarity, both quantities must be converted to the proper units. First, convert the volume units from milliliters to liters:

$$445\ \cancel{mL} \times \frac{1\ L}{1000\ \cancel{mL}} = 0.445\ L \tag{15.3.6}$$

Now we convert the amount of solute to moles, using the molar mass of NaOH, which is 40.0 g/mol:

$$32.7\ \cancel{g\ NaOH} \times \frac{1\ mol\ NaOH}{40.0\ \cancel{g\ NaOH}} = 0.818\ mol\ NaOH \tag{15.3.7}$$

Now we can use the definition of molarity to determine the molar concentration:

$$M = \frac{0.818\ mol\ NaOH}{0.445\ L} = 1.84\ M\ NaOH \tag{15.3.8}$$

Exercise 15.3.1

What is the molarity of a solution made when 66.2 g of $C_6H_{12}O_6$ are dissolved to make 235 mL of solution?

Answer

1.57 M

The definition of molarity can be used to determine the amount of solute or the volume of solution, if the other information is given. Example 4 illustrates this situation.

Example 15.3.1:

How many moles of solute are present in 0.108 L of a 0.887 M NaCl solution?

Solution

We know the volume and the molarity; we can use the definition of molarity to mathematically solve for the amount in moles. Substituting the quantities into the definition of molarity:

$$0.887\,M = \frac{mol\ NaCl}{0.108\,L} \tag{15.3.9}$$

We multiply the 0.108 L over to the other side of the equation and multiply the units together; "molarity × liters" equals moles, according to the definition of molarity. So

mol NaCl = (0.887 M)(0.108 L) = 0.0958 mol

Exercise 15.3.1

How many moles of solute are present in 225 mL of a 1.44 M $CaCl_2$ solution?

Answer

0.324 mol

If you need to determine volume, remember the rule that the unknown quantity must be by itself and in the numerator to determine the correct answer. Thus rearrangement of the definition of molarity is required.

Example 15.3.1:

What volume of a 2.33 M $NaNO_3$ solution is needed to obtain 0.222 mol of solute?

Solution

Using the definition of molarity, we have

$$2.33\,M = \frac{0.222\,mol}{L} \tag{15.3.10}$$

To solve for the number of liters, we bring the 2.33 M over to the right into the denominator, and the number of liters over to the left in the numerator. We now have

$$L = \frac{0.222\,mol}{2.33\,M} \tag{15.3.11}$$

Dividing, **the volume is 0.0953 L = 95.3 mL.**

Exercise 15.3.1

What volume of a 0.570 M K_2SO_4 solution is needed to obtain 0.872 mol of solute?

Answer

1.53 L

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15.4: Solution Concentration - Molality, Mass Percent, ppm and ppb

A similar unit of concentration is **molality** (*m*), which is defined as the number of moles of solute per kilogram of solvent, not per liter of solution:

$$molality = \frac{moles\ solute}{kilograms\ solvent} \tag{15.4.1}$$

Mathematical manipulation of molality is the same as with molarity.

Another way to specify an amount is **percentage composition by mass** (or *mass percentage*, % m/m). It is defined as follows:

$$\%m/m = \frac{mass\ of\ solute}{mass\ of\ entire\ sample} \times 100\% \tag{15.4.2}$$

It is not uncommon to see this unit used on commercial products (Fig. 11.3.1 - Concentration in Commercial Applications)



Fig. 11.3.1 Concentration in Commercial Applications © Thinkstock

The percentage of urea in this package is 5% m/m, meaning that there are 5 g of urea per 100 g of product.

Example 15.4.1:

What is the mass percentage of Fe in a piece of metal with 87.9 g of Fe in a 113 g sample?

Solution

Using the definition of mass percentage, we have

$$\%m/m = \frac{87.9\,g\,Fe}{113\,g\,sample} \times 100\% = 77.8\%\,Fe \tag{15.4.3}$$

Exercise 15.4.1

What is the mass percentage of H_2O_2 in a solution with 1.67 g of H_2O_2 in a 55.5 g sample?

Answer

3.01%

Related concentration units are **parts per thousand (ppth), parts per million (ppm)** and **parts per billion (ppb).** Parts per thousand is defined as follows:

$$ppth = \frac{mass\ of\ solute}{mass\ of\ sample} \times 1000 \tag{15.4.4}$$

There are similar definitions for parts per million and parts per billion:

$$ppm = \frac{mass\ of\ solute}{mass\ of\ sample} \times 1,000,000 \tag{15.4.5}$$

and

$$ppb = \frac{mass\ of\ solute}{mass\ of\ sample} \times 1,000,000,000 \tag{15.4.6}$$

Each unit is used for progressively lower and lower concentrations. The two masses must be expressed in the same unit of mass, so conversions may be necessary.

Example 15.4.1:

If there is 0.6 g of Pb present in 277 g of solution, what is the Pb concentration in parts per thousand?

Solution

Use the definition of parts per thousand to determine the concentration. Substituting

$$\frac{0.6g\ Pb}{277g\ solution} \times 1000 = 2.17\ ppth \tag{15.4.7}$$

Exercise 15.4.1

If there is 0.551 mg of As in 348 g of solution, what is the As concentration in ppm?

Answer

1.58 ppm

As with molarity and molality, algebraic rearrangements may be necessary to answer certain questions.

Example 15.4.1:

The concentration of Cl^- ion in a sample of H_2O is 15.0 ppm. What mass of Cl^- ion is present in 240.0 mL of H_2O, which has a density of 1.00 g/mL?

Solution

First, use the density of H_2O to determine the mass of the sample:

$$240.0\ \cancel{mL} \times \frac{1.00\ g}{\cancel{mL}} = 240.0\ g \tag{15.4.8}$$

Now we can use the definition of ppm:

$$15.0\ ppm = \frac{mass\ of\ solute}{240.0\ g\ solution} \times 1,000,000 \tag{15.4.9}$$

Rearranging to solve for the mass of solute,

$$mass\ solute = \frac{(15.0\ ppm)(240.0\ g\ solution)}{1,000,000} = 0.0036g = 3.6\ mg \tag{15.4.10}$$

Exercise 15.4.1

The concentration of Fe^{3+} ion in a sample of H_2O is 335.0 ppm. What mass of Fe^{3+} ion is present in 3,450 mL of H_2O, which has a density of 1.00 g/mL?

Answer

1.16 g

For ionic solutions, we need to differentiate between the concentration of the salt versus the concentration of each individual ion. Because the ions in ionic compounds go their own way when a compound is dissolved in a solution, the resulting concentration of the ion may be different from the concentration of the complete salt. For example, if 1 M NaCl were prepared, the solution could also be described as a solution of 1 M $Na^+(aq)$ and 1 M $Cl^-(aq)$ because there is one Na^+ ion and one Cl^- ion per formula unit of the salt. However, if the solution were 1 M $CaCl_2$, there are two $Cl^-(aq)$ ions for every formula unit dissolved, so the concentration of $Cl^-(aq)$ would be 2 M, not 1 M.

In addition, the total ion concentration is the sum of the individual ion concentrations. Thus for the 1 M NaCl, the total ion concentration is 2 M; for the 1 M $CaCl_2$, the total ion concentration is 3 M.

Key Takeaway

- Quantitative units of concentration include molarity, molality, mass percentage, parts per thousand, parts per million, and parts per billion.

Exercise 15.4.1

1. Differentiate between molarity and molality.
2. Differentiate between mass percentage and parts per thousand.
3. What is the molarity of a solution made by dissolving 13.4 g of $NaNO_3$ in 345 mL of solution?
4. What is the molarity of a solution made by dissolving 332 g of $C_6H_{12}O_6$ in 4.66 L of solution?
5. How many moles of $MgCl_2$ are present in 0.0331 L of a 2.55 M solution?
6. How many moles of NH_4Br are present in 88.9 mL of a 0.228 M solution?
7. What volume of 0.556 M NaCl is needed to obtain 0.882 mol of NaCl?
8. What volume of 3.99 M H_2SO_4 is needed to obtain 4.61 mol of H_2SO_4?
9. What volume of 0.333 M $Al(NO_3)_3$ is needed to obtain 26.7 g of $Al(NO_3)_3$?
10. What volume of 1.772 M $BaCl_2$ is needed to obtain 123 g of $BaCl_2$?
11. What are the individual ion concentrations and the total ion concentration in 0.66 M $Mg(NO_3)_2$?
12. What are the individual ion concentrations and the total ion concentration in 1.04 M $Al_2(SO_4)_3$?
13. If the $C_2H_3O_2^-$ ion concentration in a solution is 0.554 M, what is the concentration of $Ca(C_2H_3O_2)_2$?
14. If the Cl^- ion concentration in a solution is 2.61 M, what is the concentration of $FeCl_3$?

Answers

1. Molarity is moles per liter, whereas molality is moles per kilogram of solvent.
2.
3. 0.457 M
4.
5. 0.0844 mol
6.
7. 1.59 L
8.

9. 0.376 L

10.

11. Mg^{2+} = 0.66 M; NO_3^- = 1.32 M; total: 1.98 M

12.

13. 0.277 M

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15.5: Dilutions and Concentrations

Learning Objective

- Learn how to dilute and concentrate solutions.

Often, a worker will need to change the concentration of a solution by changing the amount of solvent. **Dilution** is the addition of solvent, which decreases the concentration of the solute in the solution. **Concentration** is the removal of solvent, which increases the concentration of the solute in the solution. (Do not confuse the two uses of the word *concentration* here!)

In both dilution and concentration, the amount of solute stays the same. This gives us a way to calculate what the new solution volume must be for the desired concentration of solute. From the definition of molarity,

$$\text{molarity} = \frac{\text{moles of solute}}{\text{liters of solution}} \tag{15.5.1}$$

we can solve for the number of moles of solute:

moles of solute = (molarity)(liters of solution)

A simpler way of writing this is to use M to represent molarity and V to represent volume. So the equation becomes

moles of solute = MV

Because this quantity does not change before and after the change in concentration, the product MV must be the same before and after the concentration change. Using numbers to represent the initial and final conditions, we have

$$M_1V_1 = M_2V_2$$

as the **dilution equation**. The volumes must be expressed in the same units. Note that this equation gives only the initial and final conditions, not the amount of the change. The amount of change is determined by subtraction.

Example 15.5.1

If 25.0 mL of a 2.19 M solution are diluted to 72.8 mL, what is the final concentration?

Solution

It does not matter which set of conditions is labeled 1 or 2, as long as the conditions are paired together properly. Using the dilution equation, we have

$$(2.19\ M)(25.0\ mL) = M_2(72.8\ mL)$$

$$M_2 = \frac{(2.19\ M)(25.0\ \cancel{mL})}{(72.8\ \cancel{mL})} \tag{15.5.2}$$

Solving for the second concentration (noting that the milliliter units cancel),

$$M_2 = 0.752\ M$$

The concentration of the solution has decreased. In going from 25.0 mL to 72.8 mL, 72.8 − 25.0 = 47.8 mL of solvent must be added.

Exercise 15.5.1

A 0.885 M solution of KBr whose initial volume is 76.5 mL has more water added until its concentration is 0.500 M. What is the new volume of the solution?

Answer

135.4 mL

Concentrating solutions involves removing solvent. Usually this is done by evaporating or boiling, assuming that the heat of boiling does not affect the solute. The dilution equation is used in these circumstances as well.

Chemistry Is Everywhere: Preparing IV Solutions

In a hospital emergency room, a physician orders an intravenous (IV) delivery of 100 mL of 0.5% KCl for a patient suffering from hypokalemia (low potassium levels). Does an aide run to a supply cabinet and take out an IV bag containing this concentration of KCl?

Not likely. It is more probable that the aide must make the proper solution from an IV bag of sterile solution and a more concentrated, sterile solution, called a *stock solution*, of KCl. The aide is expected to use a syringe to draw up some stock solution and inject it into the waiting IV bag and dilute it to the proper concentration. Thus the aide must perform a dilution calculation.

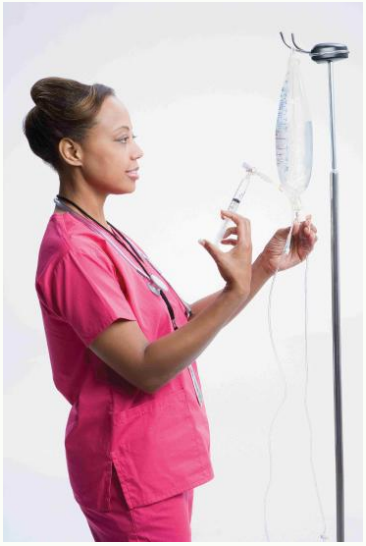


Fig. 11.4.1 Preparing IV Solution © Thinkstock. Medical personnel commonly must perform dilutions for IV solutions.

If the stock solution is 10.0% KCl and the final volume and concentration need to be 100 mL and 0.50%, respectively, then it is an easy calculation to determine how much stock solution to use:

$$(10\%)V_1 = (0.50\%)(100\text{ mL})V_1 = 5\text{ mL}$$

Of course, the addition of the stock solution affects the total volume of the diluted solution, but the final concentration is likely close enough even for medical purposes.

Medical and pharmaceutical personnel are constantly dealing with dosages that require concentration measurements and dilutions. It is an important responsibility: calculating the *wrong* dose can be useless, harmful, or even fatal!

Summary

- Calculate the new concentration or volume for a dilution or concentration of a solution.

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15.6: Concentrations as Conversion Factors

Learning Objective

- Apply concentration units as conversion factors.

Concentration can be a conversion factor between the amount of solute and the amount of solution or solvent (depending on the definition of the concentration unit). As such, concentrations can be useful in a variety of stoichiometry problems. In many cases, it is best to use the original definition of the concentration unit; it is that definition that provides the conversion factor.

A simple example of using a concentration unit as a conversion factor is one in which we use the definition of the concentration unit and rearrange; we can do the calculation again as a unit conversion, rather than as a definition. For example, suppose we ask how many moles of solute are present in 0.108 L of a 0.887 M NaCl solution. Because 0.887 M means 0.887 mol/L, we can use this second expression for the concentration as a conversion factor:

$$0.108 \cancel{L\,NaCl} \times \frac{0.887\,mol\,NaCl}{\cancel{L\,NaCl}} = 0.0958\,mol\,NaCl \tag{15.6.1}$$

(There is an understood 1 in the denominator of the conversion factor.) If we used the definition approach, we get the same answer, but now we are using conversion factor skills. Like any other conversion factor that relates two different types of units, the reciprocal of the concentration can be also used as a conversion factor.

Example 15.6.1

Using concentration as a conversion factor, how many liters of 2.35 M $CuSO_4$ are needed to obtain 4.88 mol of $CuSO_4$?

Solution

This is a one-step conversion, but the concentration must be written as the reciprocal for the units to work out:

$$4.88\,\cancel{mol\,CuSO_4} \times \frac{1\,L}{2.35\,\cancel{mol}} = 2.08\,L\,of\,solution \tag{15.6.2}$$

Exercise 15.6.1

Using concentration as a conversion factor, how many liters of 0.0444 M CH_2O are needed to obtain 0.0773 mol of CH_2O?

Answer:

1.74 L

Of course, once quantities in moles are available, another conversion can give the mass of the substance, using molar mass as a conversion factor.

Example 15.6.2

What mass of solute is present in 0.765 L of 1.93 M NaOH?

Solution

This is a two-step conversion, first using concentration as a conversion factor to determine the number of moles and then the molar mass of NaOH (40.0 g/mol) to convert to mass:

$$0.765 \cancel{L} \times \frac{1.93\,\cancel{mol\,NaOH}}{\cancel{L\,solution}} \times \frac{40.0g\,NaOH}{1\,\cancel{mol\,NaOH}} = 59.1\,g\,NaOH \tag{15.6.3}$$

Exercise 15.6.2

What mass of solute is present in 1.08 L of 0.0578 M H_2SO_4?

Answer

6.12 g

More complex stoichiometry problems using balanced chemical reactions can also use concentrations as conversion factors. For example, suppose the following equation represents a chemical reaction:

$$2\,AgNO_3\,(aq) + CaCl_2\,(aq) \longrightarrow 2\,AgCl\,(s) + Ca(NO_3)_2\,(aq) \tag{15.6.4}$$

If we wanted to know what volume of 0.555 M $CaCl_2$ would react with 1.25 mol of $AgNO_3$, we first use the balanced chemical equation to determine the number of moles of $CaCl_2$ that would react and then use concentration to convert to liters of solution:

$$1.25\ \cancel{mol\ AgNO_3} \times \frac{1\ \cancel{mol\ CaCl_2}}{2\ \cancel{mol\ AgNO_3}} \times \frac{1\ L\ solution}{0.555\ \cancel{mol\ CaCl_2}} = 1.13\ L\ CaCl_2 \tag{15.6.5}$$

This can be extended by starting with the mass of one reactant, instead of moles of a reactant.

Example 15.6.3

What volume of 0.0995 M $Al(NO_3)_3$ will react with 3.66 g of Ag according to the following chemical equation?

$$3\,Ag\,(s) + Al(NO_3)_3\,(aq) \longrightarrow 3\,AgNO_3 + Al\,(s) \tag{15.6.6}$$

Solution

Here, we first must convert the mass of Ag to moles before using the balanced chemical equation and then the definition of molarity as a conversion factor:

$$3.66\ \cancel{g\ Ag} \times \frac{1\ \cancel{mol\ Ag}}{107.97\ \cancel{g\ Ag}} \times \frac{1\ \cancel{mol\ Al(NO_3)_3}}{3\ \cancel{mol\ Ag}} \times \frac{1\ L\ solution}{0.0995\ \cancel{mol\ Al(NO_3)_3}} = 0.114\ L \tag{15.6.7}$$

The strikeouts show how the units cancel.

Exercise 15.6.3

What volume of 0.512 M NaOH will react with 17.9 g of $H_2C_2O_4$(s) according to the following chemical equation?

$$H_2C_2O_4\,(s) + 2\,NaOH\,(aq) \longrightarrow Na_2C_2O_4\,(aq) + 2\,H_2O(\ell) \tag{15.6.8}$$

Answer:

0.777 L

We can extend our skills even further by recognizing that we can relate quantities of one solution to quantities of another solution. Knowing the volume and concentration of a solution containing one reactant, we can determine how much of another solution of another reactant will be needed using the balanced chemical equation.

Example 15.6.4

A student takes a precisely measured sample, called an *aliquot*, of 10.00 mL of a solution of $FeCl_3$. The student carefully adds 0.1074 M $Na_2C_2O_4$ until all the Fe^{3+}(aq) has precipitated as $Fe_2(C_2O_4)_3$(s). Using a precisely measured tube called a burette, the student finds that 9.04 mL of the $Na_2C_2O_4$ solution was added to completely precipitate the Fe^{3+}(aq). What was the concentration of the $FeCl_3$ in the original solution? (A precisely measured experiment like this, which is meant to determine the amount of a substance in a sample, is called a *titration*.) The balanced chemical equation is as follows:

$$2\,FeCl_3\,(aq) + 3\,Na_2C_2O_4\,(aq) \longrightarrow Fe_2(C_2O_4)_3\,(s) + 6\,NaCl\,(aq) \tag{15.6.9}$$

Solution

First we need to determine the number of moles of $Na_2C_2O_4$ that reacted. We will convert the volume to liters and then use the concentration of the solution as a conversion factor:

$$9.04\ \cancel{mL} \times \frac{1\ \cancel{L}}{1000\ \cancel{mL}} \times \frac{0.1074 mol\ Na_2C_2O_4}{\cancel{L}} = 0.000971\ mol\ Na_2C_2O_4 \tag{15.6.10}$$

Now we will use the balanced chemical equation to determine the number of moles of Fe^{3+}(aq) that were present in the initial aliquot:

$$0.000971\ \cancel{mol\ Na_2C_2O_4} \times \frac{2\ mol\ FeCl_3}{3\ \cancel{mol\ Na_2C_2O_4}} = 0.000647\ mol\ FeCl_3 \tag{15.6.11}$$

Then we determine the concentration of $FeCl_3$ in the original solution. Converting 10.00 mL into liters (0.01000 L), we use the definition of molarity directly:

$$M = \frac{mol}{L} = \frac{0.000647\ mol\ FeCl_3}{0.01000 L} = 0.0647\ M\ FeCl_3 \tag{15.6.12}$$

Exercise 15.6.4

A student titrates 25.00 mL of H_3PO_4 with 0.0987 M KOH. She uses 54.06 mL to complete the chemical reaction. What is the concentration of H_3PO_4?

$$\mathrm{H_3PO_4\,(aq) + 3\,KOH\,(aq) \longrightarrow K_3PO_4\,(aq) + 3\,H_2O} \tag{15.6.13}$$

Answer:

0.0711 M



Fig. 11.5.1 Titration © Thinkstock When a student performs a titration, a measured amount of one solution is added to another reactant.

We have used molarity exclusively as the concentration of interest, but that will not always be the case. The next example shows a different concentration unit being used.

Example 15.6.5:

H_2O_2 is used to determine the amount of Mn according to this balanced chemical equation:

$$\mathrm{2\,MnO_4^-\,(aq) + 5\,H_2O_2\,(aq) + 6\,H^+\,(aq) \longrightarrow 2\,Mn_2^+\,(aq) + 5\,O_2\,(g) + 8\,H_2O(\ell)} \tag{15.6.14}$$

What mass of 3.00% m/m H_2O_2 solution is needed to react with 0.355 mol of MnO_4^-(aq)?

Solution

Because we are given an initial amount in moles, all we need to do is use the balanced chemical equation to determine the number of moles of H_2O_2 and then convert to find the mass of H_2O_2. Knowing that the H_2O_2 solution is 3.00% by mass, we can determine the mass of solution needed:

$$3.55\ \cancel{mol\ MnO_4^-} \times \frac{5\ \cancel{mol\ H_2O_2}}{2\ \cancel{mol\ MnO_4^-}} \times \frac{34.02\ g\ \cancel{H_2O_2}}{\cancel{mol\ H_2O_2}} \times \frac{100\ g\ solution}{3\ g\ \cancel{H_2O_2}} = 1006\ g\ sol \tag{15.6.15}$$

The first conversion factor comes from the balanced chemical equation, the second conversion factor is the molar mass of H_2O_2, and the third conversion factor comes from the definition of percentage concentration by mass.

Exercise 15.6.5

Use the balanced chemical reaction for MnO_4^- and H_2O_2 to determine what mass of O_2 is produced if 258 g of 3.00% m/m H_2O_2 is reacted with MnO_4^-.

Answer

7.28 g

Summary

Know how to apply concentration units as conversion factors.

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15.7: 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:

$$\text{\# mol HCl} = (0.02566\ \text{L})(0.1078\ \text{M}) = 0.002766\ \text{mol HCl}$$

We also have the balanced chemical reaction between HCl and NaOH:

$$\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$$

So we can construct a conversion factor to convert to number of moles of NaOH reacted:

$$0.002766\ \cancel{mol\ HCl} \times \frac{1\ mol\ NaOH}{1\ \cancel{mol\ HCl}} = 0.002766\ mol\ NaOH \tag{15.7.1}$$

Then we convert this amount to mass, using the molar mass of NaOH (40.00 g/mol):

$$0.002766\ \cancel{mol\ HCl} \times \frac{40.00\ g\ NaOH}{1\ \cancel{mol\ HCl}} = 0.1106\ g\ NaOH \tag{15.7.2}$$

This is type of calculation is performed as part of a titration.

Example 15.7.1:

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 HNO_3? 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 HNO_3 = (0.04402 L)(0.0885 M) = 0.00390 mol HNO_3

Using the balanced chemical equation, we can determine the number of moles of $Ca(OH)_2$ present in the analyte:

$$0.00390 \ \cancel{mol\ HNO_3} \times \frac{1\ mol\ Ca(OH)_2}{2\ \cancel{mol\ HNO_3}} = 0.00195\ mol\ Ca(OH)_2 \tag{15.7.3}$$

Then we convert this to a mass using the molar mass of $Ca(OH)_2$:

$$0.00195\ \cancel{mol\ Ca(OH)_2} \times \frac{74.1\ g\ Ca(OH)_2}{\cancel{mol\ Ca(OH)_2}} = 0.144\ g\ Ca(OH)_2 \tag{15.7.4}$$

Exercise 15.7.1

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:

$H_2C_2O_4 + 2NaOH \rightarrow Na_2C_2O_4 + 2H_2O$

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.

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15.8: Normality

Normality expresses concentration in terms of the equivalents of one chemical species reacting stoichiometrically with another chemical species. Note that this definition makes an equivalent, and thus normality, a function of the chemical reaction. Although a solution of H_2SO_4 has a single molarity, its normality depends on its reaction.

We define the number of equivalents, *n*, using a reaction unit, which is the part of a chemical species participating in the chemical reaction. In a precipitation reaction, for example, the reaction unit is the charge of the cation or anion participating in the reaction; thus, for the reaction

$$\mathrm{Pb^{2+}}(aq) + 2\,\mathrm{I^-}(aq) \rightleftharpoons \mathrm{PbI_2}(s) \tag{15.8.1}$$

n = 2 for $Pb^{2+}(aq)$ and *n* = 1 for 2 $I^-(aq)$. In an acid-base reaction, the reaction unit is the number of H^+ ions that an acid donates or that a base accepts. For the reaction between sulfuric acid and ammonia

$$\mathrm{H_2SO_4}(aq) + 2\,\mathrm{NH_3}(aq) \rightleftharpoons 2\,\mathrm{NH_4^+}(aq) + \mathrm{SO_4^{2-}}(aq) \tag{15.8.2}$$

n = 2 for $H_2SO_4(aq)$ because sulfuric acid donates two protons, and *n* = 1 for $NH_3(aq)$ because each ammonia accepts one proton. For a complexation reaction, the reaction unit is the number of electron pairs that the metal accepts or that the ligand donates. In the reaction between Ag^+ and NH_3

$$\mathrm{Ag^+}(aq) + 2\,\mathrm{NH_3}(aq) \rightleftharpoons \mathrm{Ag(NH_3)_2^+}(aq) \tag{15.8.3}$$

n = 2 for $Ag^+(aq)$ because the silver ion accepts two pairs of electrons, and *n* = 1 for NH_3 because each ammonia has one pair of electrons to donate. Finally, in an oxidation-reduction reaction the reaction unit is the number of electrons released by the reducing agent or accepted by the oxidizing agent; thus, for the reaction

$$2\,\mathrm{Fe^{3+}}(aq) + \mathrm{Sn^{2+}}(aq) \rightleftharpoons \mathrm{Sn^{4+}}(aq) + 2\,\mathrm{Fe^{2+}}(aq) \tag{15.8.4}$$

$n = 1$ for $\mathrm{Fe^{3+}}(aq)$ and $n = 2$ for $\mathrm{Sn^{2+}}(aq)$. Clearly, determining the number of equivalents for a chemical species requires an understanding of how it reacts.

Normality is the number of equivalent weights, ***EW***, per unit volume. An equivalent weight is the ratio of a chemical species' formula weight, *FW*, to the number of its equivalents, n.

$$EW = \frac{FW}{n} \tag{15.8.5}$$

The following simple relationship exists between normality, *N*, and molarity, *M*.

$$N = n \times M \tag{15.8.6}$$

Contributors and Attributions

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CHAPTER OVERVIEW

16: 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.

16.1: Arrhenius Acids and Bases

16.2: Brønsted-Lowry Acids and Bases

16.3: Strong and Weak Electrolytes

16.4: Strong and Weak Acids and Bases and their Salts

16.5 Autoionization of Water

16.6 The pH Scale

16.7: Buffers

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16.1: 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 an 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** (H_3O^+) as the actual chemical species that represents an H^+ ion. H^+ ions and H_3O^+ ions are often considered interchangeable when writing chemical equations (although a properly balanced chemical equation should also include the additional H_2O). Classic Arrhenius acids can be considered ionic compounds in which H^+ is the cation. Table **16.1.1** lists some Arrhenius acids and their names.

Table **16.1.1** Some Arrhenius Acids

Formula	Name
$HC_2H_3O_2$ (also written CH_3COOH)	acetic acid
$HClO_3$	chloric acid
HCl	hydrochloric acid
HBr	hydrobromic acid
HI	hydriodic acid
HF	hydrofluoric acid
HNO_3	nitric acid
$H_2C_2O_4$	oxalic acid
$HClO_4$	perchloric acid
H_3PO_4	phosphoric acid
H_2SO_4	sulfuric acid
H_2SO_3	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 16.1.1

Identify each compound as an Arrhenius acid, an Arrhenius base, or neither.

a. HNO_3
b. CH_3OH
c. $Mg(OH)_2$

Solution

a. This compound is an ionic compound between H^+ ions and NO_3^- 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 16.1.1

Identify each compound as an Arrhenius acid, an Arrhenius base, or neither.

1. KOH
2. H_2SO_4
3. C_2H_6

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 H_2 gas. They react with carbonate and hydrogen carbonate salts to give off CO_2 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:

$$\text{acid} + \text{base} \rightarrow H_2O + \text{salt}$$

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 16.1.2

Write the balanced chemical equation for the neutralization reaction between H_2SO_4 and KOH. What is the name of the salt that is formed?

Solution

The general reaction is as follows:

$$H_2SO_4 + KOH \rightarrow H_2O + \text{salt}$$

Because the acid has two H^+ ions in its formula, we need two OH^- ions to react with it, making two H_2O molecules as product. The remaining ions, K^+ and SO_4^{2-}, make the salt potassium sulfate (K_2SO_4). The balanced chemical reaction is as follows:

$$H_2SO_4 + 2KOH \rightarrow 2H_2O + K_2SO_4$$

? Exercise 16.1.2

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.

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16.2: 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 general definition more applicable to other chemical reactions and, importantly, independent of H_2O.

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:

$$\underset{\text{acid}}{H^+(aq)} + \underset{\text{base}}{OH^-(aq)} \rightarrow H_2O\,(l)$$

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):

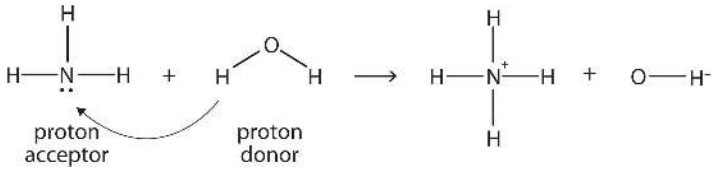
$$\underset{\text{PD}}{H^+(aq)} + \underset{\text{PA}}{OH^-(aq)} \rightarrow H_2O\,(l)$$

The proton donor is a Brønsted-Lowry acid, and the proton acceptor is the Brønsted-Lowry base:

$$\underset{\text{BL acid}}{H^+(aq)} + \underset{\text{BL base}}{OH^-(aq)} \rightarrow H_2O\,(l)$$

Thus H^+ is an acid by both definitions, and OH^- is a base by both definitions.

Ammonia (NH_3) 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 H_2O molecules; NH_3 acts like a Brønsted-Lowry base, and H_2O acts like a Brønsted-Lowry acid:



A reaction with water is called **hydrolysis**; we say that NH_3 hydrolyzes to make NH_4^+ 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:

$$HCl\,(g) + H_2O(\ell) \longrightarrow H_3O^+\,(aq) + Cl^-\,(aq)$$

HCl(g) is the proton donor and therefore a Brønsted-Lowry acid, while H_2O is the proton acceptor and a Brønsted-Lowry base. These two examples show that H_2O 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 16.2.1

Identify the Brønsted-Lowry acid and the Brønsted-Lowry base in this chemical equation.

$$\mathbf{C_6H_5OH + NH_2^- \longrightarrow C_6H_5O^- + NH_3}$$

Solution

The C_6H_5OH molecule is losing an H^+; it is the proton donor and the Brønsted-Lowry acid. The NH_2^- ion (called the amide ion) is accepting the H^+ ion to become NH_3, so it is the Brønsted-Lowry base.

Exercise 16.2.1: Aluminum Ions in Solution

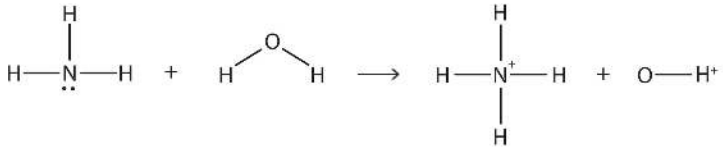
Identify the Brønsted-Lowry acid and the Brønsted-Lowry base in this chemical equation.

$$\mathbf{Al(H_2O)_6^{3+} + H_2O \longrightarrow Al(H_2O)_5(OH)^{2+} + H_3O^+}$$

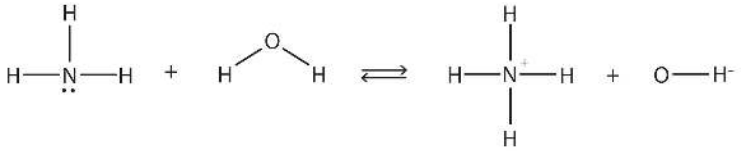
Answer

Brønsted-Lowry acid: $Al(H_2O)_6^{3+}$; Brønsted-Lowry base: H_2O

In the reaction between NH_3 and H_2O,



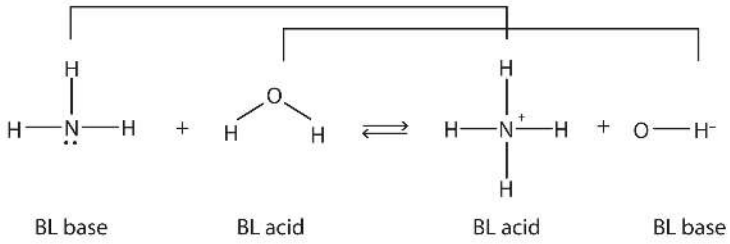
the chemical reaction does not go to completion; rather, the reverse process occurs as well, and eventually the two processes cancel out any additional change. At this point, we say the chemical reaction is at *equilibrium*. Both processes still occur, but any net change by one process is countered by the same net change of 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:



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 the OH^- ion, the proton acceptor, is acting as a Brønsted-Lowry base. The reverse reaction is also a Brønsted-Lowry acid base reaction:

BL bases. NH4+ and H2O are the BL acids. lt-chem-64081" style="width: 750px; height: 173px;" width="750px" height="173px" src="/@api/deki/files/92035/3765cabac9591a0fb3dd5878f56075e2.jpg" data-quail-id="174">

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—NH_3/NH_4^+ and H_2O/OH^-—are called **conjugate acid-base pairs**. We say that NH_4^+ is the conjugate acid of NH_3, OH^- is the conjugate base of H_2O, and so forth. Every Brønsted-Lowry acid-base reaction can be labeled with two conjugate acid-base pairs.

Example 16.2.2

Identify the conjugate acid-base pairs in this equilibrium.

$$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$$

Solution

One pair is H_2O and OH^-, where H_2O 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 $(CH_3)_3N$ and $(CH_3)_3NH^+$, where $(CH_3)_3NH^+$ is the conjugate acid (it has an additional proton) and $(CH_3)_3N$ is the conjugate base.

Exercise 16.2.2

Identify the conjugate acid-base pairs in this equilibrium.

$$NH_2^- + H_2O \rightleftharpoons NH_3 + OH^-$$

Answer

H_2O (acid) and OH^- (base); NH_2^- (base) and NH_3 (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 [$HC_2H_3O_2$(aq)]. In a medicine chest, one may find a bottle of vitamin C tablets; the chemical name of vitamin C is ascorbic acid ($HC_6H_7O_6$).

One of the more familiar household bases is NH_3, which is found in numerous cleaning products. NH_3 is a base because it increases the OH^- ion concentration by reacting with H_2O:

$NH_3(aq) + H_2O(\ell) \rightarrow NH_4^+(aq) + OH^-(aq)$

Many soaps are also slightly basic because they contain compounds that act as Brønsted-Lowry bases, accepting protons from H_2O 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, non-lye drain cleaners (like the one in the accompanying figure) use peroxide compounds to react on the materials in the clog and clear the drain.



Figure **16.2.1** 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.

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16.3: Strong and Weak Electrolytes

Car batteries are used around the world to provide the power to start car engines. One essential component of car batteries is the strong electrolyte sulfuric acid. In the battery, this material ionizes into hydrogen ions and sulfate ions. As the battery is used, the concentrations of these ions decreases. Older batteries had openings in the top where new sulfuric acid could be added to replenish the supply. Today, batteries are sealed to prevent leakage of hazardous sulfuric acid.

Strong and Weak Electrolytes

Some polar molecular compounds are nonelectrolytes when they are in their pure state, but become electrolytes when they are dissolved in water. Hydrogen chloride (HCl) is a gas in its pure molecular state and is a nonelectrolyte. However, when HCl is dissolved in water, it conducts a current well because the HCl molecule ionizes into hydrogen and chloride ions.

$$\mathrm{HCl}\,(g) \rightarrow \mathrm{H^+}\,(aq) + \mathrm{Cl^-}\,(aq)$$

HCl dissolved into water is called hydrochloric acid. A **strong electrolyte** is a solution in which a large fraction of the dissolved solute exists as ions. Ionic compounds, and some polar compounds, are completely broken apart into ions and thus conduct a current very well—this makes them strong electrolytes.

Some other polar molecular compounds become electrolytes upon being dissolved into water, but do not ionize to very great extent. Gaseous nitrous acid ionizes in solution to hydrogen ions and nitrite ions, but does so very weakly. Aqueous nitrous acid is composed of only about 5% ions and 95% intact nitrous acid molecules. A **weak electrolyte** is a solution in which only a small fraction of the dissolved solute exists as ions. The equation showing the ionization of a weak electrolyte utilizes a double arrow indicating an equilibrium between the reactants and products.

$$\mathrm{HNO_2}\,(g) \rightleftharpoons \mathrm{H^+}\,(aq) + \mathrm{NO_2^-}\,(aq)$$

Summary

- A strong electrolyte exists mainly as ions in solution.
- A weak electrolyte has only a small amount of ionization in solution.

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16.4: 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 H_2O, it completely dissociates into H^+(aq) and Cl^-(aq) ions; all the HCl molecules become ions:

$$HCl \xrightarrow{100\%} H^+(aq) + Cl^-(aq)$$

Any acid that dissociates 100% into ions is called a **strong acid**. If it does not dissociate 100%, it is a **weak acid**. $HC_2H_3O_2$ is an example of a weak acid:

$$HC_2H_3O_2 \xrightarrow{\sim 5\%} H^+(aq) + C_2H_3O_2^-(aq)$$

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 **16.4.1**. 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.

***Table* 16.4.1**: *Strong Acids and Bases*

Acids	Bases
HCl	LiOH
HBr	NaOH
HI	KOH
HNO_3	RbOH
H_2SO_4	CsOH
$HClO_3$	$Mg(OH)_2$
$HClO_4$	$Ca(OH)_2$
-	$Sr(OH)_2$
-	$Ba(OH)_2$

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 **16.4.1**); 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 16.4.1

Identify each acid or base as strong or weak.

a. HCl
b. $Mg(OH)_2$
c. C_5H_5N

Solution

a. Because HI is listed in Table 16.4.1, it is a strong acid.
b. Because $Mg(OH)_2$ is listed in Table 16.4.1, it is a strong base.
c. The nitrogen in C_5H_5N 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 16.4.1

Identify each acid or base as strong or weak.

a. RbOH
b. HNO_2

Answer a

strong base

Answer b

weak acid

Example 16.4.2

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:

$$Ca(OH)_2\,(aq) \rightarrow Ca^{2+}\,(aq) + 2\,OH^-\,(aq)$$

Because $Ca(OH)_2$ is listed in Table **16.4.1**, this reaction proceeds 100% to products.

Exercise 16.4.2

Write the balanced chemical equation for the dissociation of hydrazoic acid (HN_3) and indicate whether it proceeds 100% to products or not.

Answer

The reaction is as follows:

$$\mathbf{HN_3 \longrightarrow H^+\,(aq) + N_3^-\,(aq)}$$

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 NH_3 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:

$$\mathbf{NaCl \longrightarrow Na^+\,(aq) + Cl^-\,(aq)}$$

Will the $Na^+(aq)$ ion hydrolyze? If it does, it will interact with the OH^- ion to make NaOH:

$$\mathbf{Na^+\,(aq) + H_2O \longrightarrow NaOH + H^+\,(aq)}$$

However, NaOH is a strong base, which means that it is 100% ionized in solution:

$$\mathbf{NaOH \longrightarrow Na^+\,(aq) + OH^-\,(aq)}$$

The free $OH^-(aq)$ ion reacts with the $H^+(aq)$ ion to remake a water molecule:

$$\mathbf{H^+\,(aq) + OH^-\,(aq) \longrightarrow H_2O}$$

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:

$$Cl^-(aq) + H_2O \longrightarrow HCl + OH^-$$

However, HCl is a strong acid, which means that it is 100% ionized in solution:

$$HCl \longrightarrow H^+(aq) + Cl^-(aq)$$

The free $H^+(aq)$ ion reacts with the $OH^-(aq)$ ion to remake a water molecule:

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O$$

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 $NaC_2H_3O_2$. 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:

$$C_2H_3O_2^-(aq) + H_2O \rightleftharpoons HC_2H_3O_2 + OH^-(aq)$$

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 $NaC_2H_3O_2$ solutions are slightly basic, so such a salt is called a **basic salt**.

There are also salts whose aqueous solutions are slightly acidic. NH_4Cl is an example. When NH_4Cl is dissolved in H_2O, it separates into NH_4^+ ions and Cl^- ions. We have already seen that the Cl^- ion does not hydrolyze. However, the NH_4^+ ion will:

$$NH_4^+(aq) + H_2O \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

Recall from Section 11.2, that H_3O^+ 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 NH_3 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.

Example 16.4.3

Identify each salt as acidic, basic, or neutral.

a. KCl
b. KNO_2
c. NH_4Br

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 NO_2^- ion derives from a weak acid (HNO_2). Therefore the solution will be basic, and KNO_2 is a basic salt.
c. Although the Br^- ions derive from a strong acid (HBr), the NH_4^+ ion derives from a weak base (NH_3), so the solution will be acidic, and NH_4Br is an acidic salt.

Exercise 16.4.3

Identify each salt as acidic, basic, or neutral.

A. $(C_5H_5NH)Cl$

B. Na_2SO_3

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.

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16.5 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 H_2O can act as an acid or a base:

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \text{ } (H_2O \text{ acts as an acid})$$

$$HCl + H_2O \rightarrow H_3O^+ + Cl^- \text{ } (H_2O \text{ acts as a base})$$

It may not be surprising to learn, then, that within any given sample of water, some H_2O molecules are acting as acids, and other H_2O 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 H_2O 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 H_2O 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

$$[H^+] = [OH^-] = 1.0 \times 10^{-7} \text{ M}$$

for *any* sample of pure water because H_2O can act as both an acid and a base. The product of these two concentrations is 1.0×10^{-14}:

$$[H^+] \times [OH^-] = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$$

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:

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

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 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,

$$K_W = [H^+][OH^-] = 1.0 \times 10^{-14} = (1.0 \times 10^{-4})[OH^-]$$

We solve by dividing both sides of the equation by 1.0×10^{-4}:

$$[OH^-] = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-4}} = 1.0 \times 10^{-10} M$$

It is assumed that the concentration unit is molarity, so $[OH^-]$ is 1.0×10^{-10} M.

Exercise 1

What is $[H^+]$ of an aqueous solution if $[OH^-]$ is 1.0×10^{-9} M?

Answer

1.0×10^{-5} 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 2

What is $[H^+]$ in a 0.0044 M solution of $Ca(OH)_2$?

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:

$$[H^+][OH^-] = 1.0 \times 10^{-14} = [H^+](0.0088 \text{ M})$$

Divide both sides by 0.0088:

$$[H^+] = \frac{1.0 \times 10^{-14}}{(0.0088)} = 1.1 \times 10^{-12} M$$

$[H^+]$ has decreased significantly in this basic solution.

Exercise 2

What is $[OH^-]$ in a 0.00032 M solution of H_2SO_4? (Hint: assume both H^+ ions ionize.)

Answer

1.6×10^{-11} 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 3

A 0.0788 M solution of $HC_2H_3O_2$ is 3.0% ionized into H^+ ions and $C_2H_3O_2^-$ 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:

$[H^+] = 0.030 \times 0.0788 = 0.00236$ M

With this $[H^+]$, then $[OH^-]$ can be calculated as follows:

$$[OH^-] = \frac{1.0 \times 10^{-14}}{0.00236} = 4.2 \times 10^{-12} M$$

This is about 30 times higher than would be expected for a strong acid of the same concentration.

Exercise 3

A 0.0222 M solution of pyridine (C_5H_5N) is 0.44% ionized into pyridinium ions ($C_5H_5NH^+$) and OH^- ions. What are $[OH^-]$ and $[H^+]$ for this solution?

Answer

$[OH^-] = 9.77 \times 10^{-5}$ M; $[H^+] = 1.02 \times 10^{-10}$ M

Summary

In any aqueous solution, the product of [H+] and [OH−] equals $\mathbf{1.0 \times 10^{-14}}$ (at room temperature).

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16.6 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 commonly defined as a logarithmic function of $[H^+]$:

$$\mathbf{pH} = -\log[\mathbf{H^+}] \tag{1}$$

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 scale and is the range of values from 0 to 14 that describes the acidity or basicity of a solution. You can use pH to quickly determine whether a given aqueous solution is acidic, basic, or neutral.

Example 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 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 **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 **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 depending 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 (Equation 1), 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:

$$[H^+] = 10^{-pH}$$

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.

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16.7: 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.

This 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 $HC_2H_3O_2/NaC_2H_3O_2$ 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 $HC_2H_3O_2$ in an acid-base reaction:

$$HC_2H_3O_2(aq) + OH^-(aq) \rightarrow H_2O(\ell) + C_2H_3O_2^-(aq) \tag{16.7.1}$$

Rather than changing the pH dramatically by making the solution basic, the added OH^- ions react to make H_2O, 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 $HC_2H_3O_2$ is a weak acid, it is not ionized much. This means that if lots of H^+ ions and $C_2H_3O_2^-$ ions are present in the same solution, they will come together to make $HC_2H_3O_2$:

$$H^+(aq) + C_2H_3O_2^-(aq) \rightarrow HC_2H_3O_2(aq) \tag{16.7.2}$$

Rather than changing the pH dramatically and making the solution acidic, the added H^+ ions react to make molecules of a weak acid. Figure **16.7.1** illustrates both actions of a buffer.

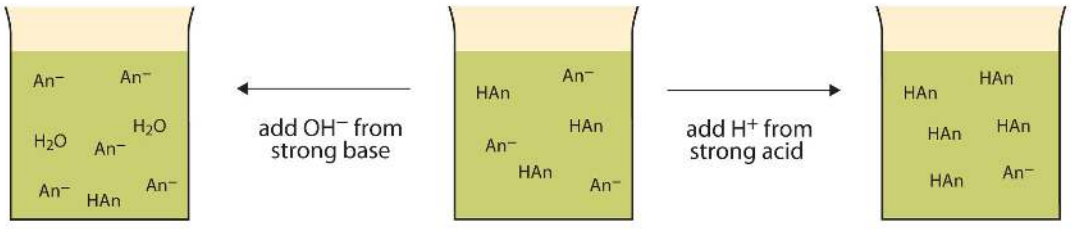


Figure **16.7.1** The Actions of Buffers. Buffers can react with both strong acids (top) and strong bases (side) to minimize large changes in pH.

Buffers made from weak bases and salts of weak bases act similarly. For example, in a buffer containing NH_3 and NH_4Cl, NH_3 molecules can react with any excess H^+ ions introduced by strong acids:

$$NH_3(aq) + H^+(aq) \rightarrow NH_4^+(aq) \tag{16.7.3}$$

while the **ammonium ion** ($NH_4^+(aq)$) can react with any hydroxide ions introduced by strong bases:

$$NH_4^+(aq) + OH^-(aq) \rightarrow NH_3(aq) + H_2O(\ell) \tag{16.7.4}$$

Example 16.7.1

Which combinations of compounds can make a buffer solution?

1. $HCHO_2$ and $NaCHO_2$
2. HCl and NaCl
3. CH_3NH_2 and CH_3NH_3Cl
4. NH_3 and NaOH

Solution

1. $HCHO_2$ is formic acid, a weak acid, while $NaCHO_2$ is the salt made from the anion of the weak acid (the formate ion [CHO_2^-]). 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. CH_3NH_2 is methylamine, which is like NH_3 with one of its H atoms substituted with a CH_3 group. Because it is not listed in Table **16.7.1**, we can assume that it is a weak base. The compound CH_3NH_3Cl is a salt made from that weak base, so the combination of these two solutes would make a buffer solution.
4. NH_3 is a weak base, but NaOH is a strong base. The combination of these two solutes would not make a buffer solution.

Exercise 16.7.1

Which combinations of compounds can make a buffer solution?

1. $NaHCO_3$ and NaCl
2. H_3PO_4 and NaH_2PO_4
3. NH_3 and $(NH_4)_3PO_4$
4. NaOH and NaCl

Answer a

Yes.

Answer b

No. Need a weak acid or base and a salt of its conjugate base or acid.

Answer c

Yes.

Answer d

No. Need a weak base or acid.

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 initial solute dissolved within them 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 Application: 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 **16.7.1**, 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.

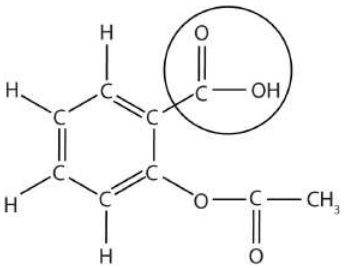


Figure **16.7.2**: The Molecular Structure of Aspirin. The circled atoms are the acid part of the molecule.

The molecule of aspartame is shown. The CO2H is circled to indicate that it is the acidic 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 will remain on the market.

Summary

A buffer is a solution that resists sudden changes in pH.

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CHAPTER OVERVIEW

18: Oxidation and Reduction

One important type of chemical reaction is the oxidation-reduction reaction, also known as the redox reaction. Although we introduced redox reactions in Section 4.7, it is worth reviewing some basic concepts.

18.1: Oxidation-Reduction Reactions
18.2: Balancing Redox Reactions By Inspection
18.3: Balancing Oxidation-Reduction Reactions Using the Half Reaction Method
18.4: Balancing Redox Reactions in Solution
18.5: Electrochemical Reaction
18.6: Batteries
18.7: Corrosion
18.8: Voltaic Cells
18.9: Electrolysis

Thumbnail: Copper from a wire is displaced by silver in a silver nitrate solution it is dipped into, and solid silver precipitates out. Image used with permission (CC SA-BY 3.0 au; Toby Hudson).

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18.1: Oxidation-Reduction Reactions

Learning Objectives

- Define *oxidation* and *reduction*.
- Assign oxidation numbers to atoms in simple compounds.
- Recognize a reaction as an oxidation-reduction reaction.

Consider this chemical reaction:

$$\mathrm{Mg\,(s) + Cl_2\,(g) \longrightarrow MgCl_2} \tag{18.1.1}$$

The reactants are two electrically neutral elements; they have the same number of electrons as protons. The product, however, is ionic; it is composed of Mg^{2+} and Cl^- ions. Somehow, the individual Mg atoms lose two electrons to make the Mg^{2+} ion, while the Cl atoms gain an electron to become Cl^- ions. This reaction involves the *transfer of electrons* between atoms.

The process of losing and gaining electrons occurs simultaneously. However, mentally we can separate the two processes. **Oxidation** is defined as the loss of one or more electrons by an atom. **Reduction** is defined as the gain of one or more electrons by an atom. O.I.L. R.I.G. is a useful mnemonic, standing for **O**xidation **I**s **L**oss, **R**eduction **I**s **G**ain. So oxidation and reduction always occur together; it is only mentally that we can separate them. Chemical reactions that involve the transfer of electrons are called **oxidation-reduction (or redox) reactions**.

Redox reactions require that we keep track of the electrons assigned to each atom in a chemical reaction. How do we do that? We use **oxidation numbers** to keep track of electrons in atoms. Oxidation numbers are assigned to atoms based on four rules. Oxidation numbers are not necessarily equal to the charge on the atom (although sometimes they can be); we must keep the concepts of charge and oxidation numbers separate.

Assigning Oxidation Numbers

The rules for assigning oxidation numbers to atoms are not arbitrarily assigned, they are based on the relative electronegativity of the elements. The oxidation number tells us how many electrons the atom has gained or lost, relative to the neutral atom, as a result of chemically bonding to the other elements in the molecule.

Our rules for assigning oxidation numbers are as follows:

1. **Atoms in their elemental state are assigned an oxidation number of 0.**
    - If an atom is in it's elemental state it is either by itself or bonded to another atom of the same element, for example H_2, O_2, F_2, or S_8. In all of these cases the electronegativities of all of the atoms is the same and no one atom is going to be electronegative enough to steal an electron from another.
2. **Atoms in monatomic (i.e., one-atom) ions are assigned an oxidation number equal to their charge. Oxidation numbers are usually written with the sign first, then the magnitude, to differentiate them from charges.**
    - As the oxidation number tells us how many electrons the atom has gained or lost relative to the neutral atom and the charge on an ion tells us the same thing the charge is equal to the oxidation number for monatomic ions.
    - Examples: Cu^{2+} has an oxidation number of +2, Cl^- has an oxidation number of -1, O^{2-} has an oxidation number of -2.
3. **In compounds, fluorine is assigned a −1 oxidation number; oxygen is usually assigned a −2 oxidation number [except in peroxide compounds (where it is −1) and in binary compounds with fluorine (where it is positive)]; and hydrogen is usually assigned a +1 oxidation number [except when it exists as the hydride ion (H^-), in which case rule 2 prevails].**
    - Fluorine is the most electronegative element on the periodic table and wants one more electron to look like the nearest noble gas. With the highest electronegativity once fluorine is bonded to any other element its electronegativity allows it to take the extra electron it wants and fluorine will always have a -1 oxidation number if bonded to any other element.
    - Oxygen is the second most electronegative element on the periodic table and wants two more electrons to look like the nearest noble gas. When bonding to anyone but fluorine (who is more electronegative) oxygen will take as many electrons as it can until it has 2 additional electrons and has an oxidation number of -2.
        - In H_2O oxygen will take one electron from each hydrogen, as each hydrogen only has one to offer, and have an oxidation number of -2, each hydrogen will have an oxidation number of +1.

- In H_2O_2 or H-O-O-H each hydrogen only has 1 electron available for the oxygens to take. Each oxygen gets a -1 oxidation number and each hydrogen gets a +1 oxidation number.
  - In LiH, lithium is less electronegative than hydrogen. Hydrogen can either gain an electron to look like helium or it can give one up. As the hydrogen is less more electronegative than lithium the hydrogen has a -1 oxidation state and lithium has a +1 oxidation state in LiH.

4. **In compounds, all other atoms are assigned an oxidation number so that the sum of the oxidation numbers on all the atoms in the species equals the charge on the species (which is zero if the species is neutral).**
   - From drawing Lewis structures we know that the total number of electrons for any compound is the sum of the valence electrons plus or minus any charge on the molecule. The oxidation numbers tell us where in the molecule the electrons are living, but if we add up all the oxidation numbers they have to total to the charge on the molecule.

Here are some examples for practice. In H_2, both H atoms have an oxidation number of 0 by rule 1. In $MgCl_2$, magnesium has an oxidation number of +2, while chlorine has an oxidation number of −1 by rule 2. In H_2O, the H atoms each have an oxidation number of +1, while the O atom has an oxidation number of −2, even though hydrogen and oxygen do not exist as ions in this compound (rule 3). By contrast, by rule 3, each H atom in hydrogen peroxide (H_2O_2) has an oxidation number of +1, while each O atom has an oxidation number of −1. We can use rule 4 to determine oxidation numbers for the atoms in SO_2. Each O atom has an oxidation number of −2; for the sum of the oxidation numbers to equal the charge on the species (which is zero), the S atom is assigned an oxidation number of +4. Does this mean that the sulfur atom has a 4+ charge on it? No, it means only that the S atom is assigned a +4 oxidation number by our rules of apportioning electrons among the atoms in a compound.

Example 18.1.1

Assign oxidation numbers to the atoms in each substance.

1. Cl_2
2. GeO_2
3. $Ca(NO_3)_2$

Solution

1. Cl_2 is the elemental form of chlorine. Rule 1 states each atom has an oxidation number of 0.
2. By rule 3, oxygen is normally assigned an oxidation number of −2. For the sum of the oxidation numbers to equal the charge on the species (zero), the Ge atom is assigned an oxidation number of +4.
3. $Ca(NO_3)_2$ can be separated into two parts: the Ca^{2+} ion and the NO_3^- ion. Considering these separately, the Ca^{2+} ion has an oxidation number of +2 by rule 2. Now consider the NO_3^- ion. Oxygen is assigned an oxidation number of −2, and there are three of them. According to rule 4, the sum of the oxidation numbers on all atoms must equal the charge on the species, so we have the simple algebraic equation

   $x + 3(-2) = -1$

   where x is the oxidation number of the N atom and the −1 represents the charge on the species. Evaluating for x,

   $x + (-6) = -1x = +5$

   Thus the oxidation number on the N atom in the NO_3^- ion is +5.

Exercise 18.1.1: Phosphoric Acid

Assign oxidation numbers to the atoms in H_3PO_4.

Answer

H: +1; O: −2; P: +5

All redox reactions occur with a simultaneous change in the oxidation numbers of some atoms. At least two elements must change their oxidation numbers. When an oxidation number of an atom is increased in the course of a redox reaction, that atom is being

oxidized. When an oxidation number of an atom is decreased in the course of a redox reaction, that atom is being *reduced*. Thus oxidation and reduction can also be defined in terms of increasing or decreasing oxidation numbers, respectively.

Example 18.1.2:

Identify what is being oxidized and reduced in this redox reaction.

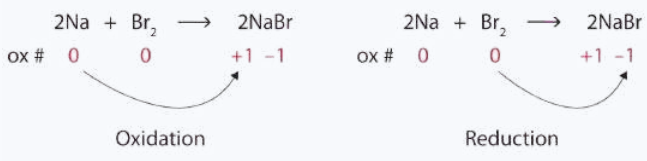
$$2\,Na + Br_2 \longrightarrow 2\,NaBr$$

Solution

Both reactants are the elemental forms of their atoms, so the Na and Br atoms have oxidation numbers of 0. In the ionic product, the Na^+ ions have an oxidation number of +1, while the Br^- ions have an oxidation number of −1.

$$\underset{0}{2Na} + \underset{0}{Br_2} \rightarrow \underset{+1-1}{2NaBr}$$

Sodium is increasing its oxidation number from 0 to +1, so it is being oxidized; bromine is decreasing its oxidation number from 0 to −1, so it is being reduced:



Because oxidation numbers are changing, this is a redox reaction. The total number of electrons being lost by sodium (two, one lost from each Na atom) is gained by bromine (two, one gained for each Br atom).

Exercise 18.1.2

Identify what is being oxidized and reduced in this redox reaction.

$$C + O_2 \longrightarrow CO_2$$

Answer

C is being oxidized from 0 to +4; O is being reduced from 0 to −2.

Oxidation reactions can become quite complex, as attested by the following redox reaction:

$$6H^+(aq) + 2\underset{+7}{MnO_4^-}(aq) + 5\underset{-1}{H_2O_2}(l) \rightarrow 2\underset{+2}{Mn^{2+}}(aq) + 5\underset{0}{O_2}(g) + 8H_2O(l) \tag{18.1.2}$$

To demonstrate that this is a redox reaction, the oxidation numbers of the species being oxidized and reduced are listed; can you determine what is being oxidized and what is being reduced? This is also an example of a net ionic reaction; spectator ions that do not change oxidation numbers are not displayed in the equation. Eventually, we will need to learn techniques for writing correct (i.e., balanced) redox reactions.

Food and Drink Application: Fortifying Food with Iron

Iron is an essential mineral in our diet; iron-containing compounds like the heme protein in hemoglobin could not function without it. Most biological iron has the form of the Fe^{2+} ion; iron with other oxidation numbers is almost inconsequential in human biology (although the body does contain an enzyme to reduce Fe^{3+} to Fe^{2+}, so Fe^{3+} must have some biological significance, albeit minor). To ensure that we ingest enough iron, many foods are enriched with iron. Although Fe^{2+} compounds are the most logical substances to use, some foods—bread and breakfast cereals are the most well-known examples—use "reduced iron" as an ingredient. Reduced iron is simply iron metal; iron is added as a fine metallic powder. The metallic iron is oxidized to Fe^{2+} in the digestive system and then absorbed by the body, but the question remains: Why are we ingesting metallic iron? Why not just use Fe^{2+} salts as an additive?



Fig. 14.2.1 Ingredients Many prepared foods list reduced iron in their ingredients list.

Although it is difficult to establish conclusive reasons, a search of scientific and medical literature suggests a few reasons. One reason is that fine iron filings do not affect the taste of the product. The size of the iron powder (several dozen micrometers) is not noticeable when chewing iron-supplemented foods, and the tongue does not detect any changes in flavor that can be detected when using Fe^{2+} salts. Fe^{2+} compounds can affect other properties of foodstuffs during preparation and cooking, like dough pliability, yeast growth, and color. Finally, of the common iron substances that might be used, metallic iron is the least expensive. These factors appear to be among the reasons why metallic iron is the supplement of choice in some foods.

Key Takeaways

- Oxidation-reduction (redox) reactions involve the transfer of electrons from one atom to another.
- Oxidation numbers are used to keep track of electrons in atoms.
- There are rules for assigning oxidation numbers to atoms.
- Oxidation is an increase in oxidation number (loss of electrons); reduction is a decrease in oxidation number (gain of electrons).

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18.2: Balancing Redox Reactions By Inspection

Learning Objectives

- Learn to balanced simple redox reactions by inspection.
- Learn to balance complex redox reactions by the half reaction method.
- Use the solvent, or parts of it, as a reactant or a product in balancing a redox reaction.

Balancing simple redox reactions can be a straightforward matter of going back and forth between products and reactants. For example, in the redox reaction of Na and Cl_2:

$$\mathrm{Na + Cl_2 \longrightarrow NaCl} \tag{18.2.1}$$

it should be immediately clear that the Cl atoms are not balanced. We can fix this by putting the coefficient 2 in front of the product:

$$\mathrm{Na + Cl_2 \longrightarrow 2\,NaCl} \tag{18.2.2}$$

However, now the sodium is unbalanced. This can be fixed by including the coefficient 2 in front of the Na reactant:

$$\mathrm{2\,Na + Cl_2 \longrightarrow 2\,NaCl} \tag{18.2.3}$$

This reaction is now balanced. That was fairly straightforward; we say that we are able to balance the reaction *by inspection*. Many simple redox reactions can be balanced by inspection.

Example 18.2.1:

Balance this redox reaction by inspection.

$SO_2 + O_2 \rightarrow SO_3$

Solution

There is one S atom on both sides of the equation, so the sulfur is balanced. However, the reactant side has four O atoms while the product side has three. Clearly we need more O atoms on the product side, so let us start by including the coefficient 2 on the SO_3:

$SO_2 + O_2 \rightarrow 2SO_3$

This now gives us six O atoms on the product side, and it also imbalances the S atoms. We can balance both the elements by adding coefficient 2 on the SO_2 on the reactant side:

$2SO_2 + O_2 \rightarrow 2SO_3$

This gives us two S atoms on both sides and a total of six O atoms on both sides of the chemical equation. This redox reaction is now balanced.

Exercise 18.2.1

Balance this redox reaction by inspection.

$Al + O_2 \rightarrow Al_2O_3$

Answer

$4Al + 3O_2 \rightarrow 2Al_2O_3$

The first thing you should do when encountering an unbalanced redox reaction is to try to balance it by inspection.

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18.3: Balancing Oxidation-Reduction Reactions Using the Half Reaction Method

Some redox reactions are not easily balanced by inspection. Consider this redox reaction:

$$Al + Ag^{+} \rightarrow Al^{3+} + Ag$$

At first glance, this equation seems balanced: there is one Ag atom on both sides and one Al atom on both sides. However, if you look at the total charge on each side, there is a charge imbalance: the reactant side has a total charge of 1+, while the product side has a total charge of 3+. Something is amiss with this chemical equation; despite the equal number of atoms on each side, it is not balanced.

A fundamental point about redox reactions that has not arisen previously is that *the total number of electrons being lost must equal the total number of electrons being gained* for a redox reaction to be balanced. This is not the case for the aluminum and silver reaction: the Al atom loses three electrons to become the Al^{3+} ion, while the Ag^{+} ion gains only one electron to become elemental silver.

To balance this, we will write each oxidation and reduction reaction separately, listing the number of electrons explicitly in each. Individually, the oxidation and reduction reactions are called **half reactions**. We will then take multiples of each reaction until the number of electrons on each side cancels completely and combine the half reactions into an overall reaction, which should then be balanced. This method of balancing redox reactions is called the **half reaction method**.

The oxidation half reaction involves aluminum, which is being oxidized:

$$Al \rightarrow Al^{3+}$$

This half reaction is not completely balanced because the overall charges on each side are not equal. When an Al atom is oxidized to Al^{3+}, it loses three electrons. We can write these electrons explicitly as products:

$$Al \rightarrow Al^{3+} + 3e^{-}$$

Now this half reaction is balanced—in terms of both atoms and charges.

The reduction half reaction involves silver:

$$Ag^{+} \rightarrow Ag$$

The overall charge is not balanced on both sides. But we can fix this by adding one electron to the reactant side because the Ag^{+} ion must accept one electron to become the neutral Ag atom:

$$Ag^{+} + e^{-} \rightarrow Ag$$

This half reaction is now also balanced.

When combining the two half reactions into a balanced chemical equation, the key is that *the total number of electrons must cancel*, so the number of electrons lost by atoms are equal to the number of electrons gained by other atoms. This may require we multiply one or both half reaction(s) by an integer to make the number of electrons on each side equal. With three electrons as products and one as reactant, the least common multiple of these two numbers is three: we can use a single aluminum reaction but must take three times the silver reaction:

$$Al \rightarrow Al^{3+} + 3e^{-} 3 \times [Ag^{+} + e^{-} \rightarrow Ag]$$

The 3 on the second reaction is distributed to all species in the reaction:

$$Al \rightarrow Al^{3+} + 3e^{-} 3Ag^{+} + 3e^{-} \rightarrow 3Ag$$

Now the two half reactions can be combined just like two algebraic equations, with the arrow serving as the equals sign. The same species on opposite sides of the arrow can be canceled:

$$\boldsymbol{Al + 3Ag^{+} + 3e^{-} \rightarrow Al^{3+} + 3Ag + 3e^{-}} \tag{18.3.1}$$

The net balanced redox reaction is as follows:

$$Al + 3Ag^{+} \rightarrow Al^{3+} + 3Ag$$

There is still only one Al atom on each side of the chemical equation, but there are now three Ag atoms, and the total charge on each side of the equation is the same (3+ for both sides). This redox reaction is balanced. It took more effort to use the half reaction method than by inspection, but the correct balanced redox reaction was obtained.

Example 18.3.1:

Balance this redox reaction by using the half reaction method.

$Fe^{2+} + Cr \rightarrow Fe + Cr^{3+}$

Solution

We start by writing the two half reactions. Chromium is being oxidized, and iron is being reduced:

$Cr \rightarrow Cr^{3+}$ oxidation$Fe^{2+} \rightarrow Fe$ reduction

Then we include the appropriate number of electrons on the proper side to balance the charges for each reaction:

$Cr \rightarrow Cr^{3+} + 3e^{-}Fe^{2+} + 2e^{-} \rightarrow Fe$

The first reaction involves three electrons, while the second reaction involves two electrons. The least common multiple of these two numbers is six, so to get six electrons in each reaction we need to double the first reaction and triple the second one:

$2 \times [Cr \rightarrow Cr^{3+} + 3e^{-}] = 2Cr \rightarrow 2Cr^{3+} + 6e^{-}3 \times [Fe^{2+} + 2e^{-} \rightarrow Fe] = 3Fe^{2+} + 6e^{-} \rightarrow 3Fe$

We can combine the two final reactions, noting that the electrons cancel:

$$2Cr + 3Fe^{2+} + 6e^{-} \rightarrow 2Cr^{3+} + 3Fe + 6e^{-} \tag{18.3.2}$$

The overall, balanced redox reaction is

$2Cr + 3Fe^{2+} \rightarrow 2Cr^{3+} + 3Fe$

Exercise 18.3.1

Balance this redox reaction by using the half reaction method.

$O^{2-} + F_2 \rightarrow O_2 + F^{-}$

Answer

$2O^{2-} + 2F_2 \rightarrow O_2 + 4F^{-}$

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18.4: Balancing Redox Reactions in Solution

Many redox reactions occur in aqueous solution—in water. Because of this, in many cases H_2O or a fragment of an H_2O molecule (H^+ or OH^-, in particular) can participate in the redox reaction. As such, we need to learn how to incorporate the solvent into a balanced redox equation.

Consider the following oxidation half reaction in aqueous solution, which has one Cr atom on each side:

$$Cr^{3+} \rightarrow CrO_4^-$$

Here, the Cr atom is going from the +3 to the +7 oxidation state. To do this, the Cr atom must lose four electrons. Let us start by listing the four electrons as products:

$$Cr^{3+} \rightarrow CrO_4^- + 4e^-$$

But where do the O atoms come from? They come from water molecules or a common fragment of a water molecule that contains an O atom: the OH^- ion. When we balance this half reaction, we should feel free to include either of these species in the reaction to balance the elements. Let us use H_2O to balance the O atoms; we need to include four water molecules to balance the four O atoms in the products:

$$4H_2O + Cr^{3+} \rightarrow CrO_4^- + 4e^-$$

This balances the O atoms, but now introduces hydrogen to the reaction. We can balance the H atoms by adding an H^+ ion, which is another fragment of the water molecule. We need to add eight H^+ ions to the product side:

$$4H_2O + Cr^{3+} \rightarrow CrO_4^- + 4e^- + 8H^+$$

The Cr atoms are balanced, the O atoms are balanced, and the H atoms are balanced; if we check the total charge on both sides of the chemical equation, they are the same (3+, in this case). This half reaction is now balanced, using water molecules and parts of water molecules as reactants and products.

Reduction reactions can be balanced in a similar fashion. When oxidation and reduction half reactions are individually balanced, they can be combined in the same fashion as before: by taking multiples of each half reaction as necessary to cancel all electrons. Other species, such as H^+, OH^-, and H_2O, may also have to be canceled in the final balanced reaction.

Unless otherwise noted, it does not matter if you add H_2O or OH^- as a source of O atoms, although a reaction may specify *acidic solution* or *basic solution* as a hint of what species to use or what species to avoid. OH^- ions are not very common in acidic solutions, so they should be avoided in those circumstances.

Example 18.4.1:

Balance this redox reaction. Assume a basic solution.

$$MnO_2 + CrO_3^- \rightarrow Mn + CrO_4^-$$

Solution

We start by separating the oxidation and reduction processes so we can balance each half reaction separately. The oxidation reaction is as follows:

$$CrO_3^- \rightarrow CrO_4^-$$

The Cr atom is going from a +5 to a +7 oxidation state and loses two electrons in the process. We add those two electrons to the product side:

$$CrO_3^- \rightarrow CrO_4^- + 2e^-$$

Now we must balance the O atoms. Because the solution is basic, we should use OH^- rather than H_2O:

$$OH^- + CrO_3^- \rightarrow CrO_4^- + 2e^-$$

We have introduced H atoms as part of the reactants; we can balance them by adding H^+ as products:

$$OH^- + CrO_3^- \rightarrow CrO_4^- + 2e^- + H^+$$

If we check the atoms and the overall charge on both sides, we see that this reaction is balanced. However, if the reaction is occurring in a basic solution, it is unlikely that H^+ ions will be present in quantity. The way to address this is to add an additional OH^- ion to each side of the equation:

$$OH^- + CrO_3^- + OH^- \rightarrow CrO_4^- + 2e^- + H^+ + OH^-$$

The two OH^- ions on the left side can be grouped together as $2OH^-$. On the right side, the H^+ and OH^- ions can be grouped into an H_2O molecule:

$$2OH^- + CrO_3^- \rightarrow CrO_4^- + 2e^- + H_2O$$

This is a more appropriate form for a basic solution.

Now we balance the reduction reaction:

$$MnO_2 \rightarrow Mn$$

The Mn atom is going from +4 to 0 in oxidation number, which requires a gain of four electrons:

$$4e^- + MnO_2 \rightarrow Mn$$

Then we balance the O atoms and then the H atoms:

$$4e^- + MnO_2 \rightarrow Mn + 2OH^-2H^+ + 4e^- + MnO_2 \rightarrow Mn + 2OH^-$$

We add two OH^- ions to each side to eliminate the H^+ ion in the reactants; the reactant species combine to make two water molecules, and the number of OH^- ions in the product increases to four:

$$2H_2O + 4e^- + MnO_2 \rightarrow Mn + 4OH^-$$

This reaction is balanced for a basic solution.

Now we combine the two balanced half reactions. The oxidation reaction has two electrons, while the reduction reaction has four. The least common multiple of these two numbers is four, so we multiply the oxidation reaction by 2 so that the electrons are balanced:

$$2 \times [2OH^- + CrO_3^- \rightarrow CrO_4^- + 2e^- + H_2O]2H_2O + 4e^- + MnO_2 \rightarrow Mn + 4OH^-$$

Combining these two equations results in the following equation:

$$4OH^- + 2CrO_3^- + 2H_2O + 4e^- + MnO_2 \rightarrow 2CrO_4^- + 4e^- + 2H_2O + Mn + 4OH^-$$

The four electrons cancel. So do the two H_2O molecules and the four OH^- ions. What remains is

$$2CrO_3^- + MnO_2 \rightarrow 2CrO_4^- + Mn$$

which is our final balanced redox reaction.

Exercise 18.4.1

Balance this redox reaction. Assume a basic solution.

$$Cl^- + MnO_4^- \rightarrow MnO_2 + ClO_3^-$$

Answer

$$H_2O + Cl^- + 2MnO_4^- \rightarrow 2MnO_2 + ClO_3^- + 2OH^-$$

Key Takeaways

- Redox reactions can be balanced by inspection or by the half reaction method.
- A solvent may participate in redox reactions; in aqueous solutions, H_2O, H^+, and OH^- may be reactants or products.

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18.5: Electrochemical Reaction

Metal sculptures exposed to the outside elements will usually corrode if not protected. The corrosion process is a series of redox reactions involving the metal of the sculpture. In some situations, the metals are deliberately left unprotected so that the surface will undergo changes that may enhance the esthetic value of the work.

Electrochemical Reactions

Chemical reactions either absorb or release energy, which can be in the form of electricity. **Electrochemistry** is a branch of chemistry that deals with the interconversion of chemical energy and electrical energy. Electrochemistry has many common applications in everyday life. All sorts of batteries, from those used to power a flashlight to an automobile, rely on chemical reactions to generate electricity. Electricity is used to plate objects with decorative metals like gold or chromium. Electrochemistry is important in the transmission of nerve impulses in biological systems. Redox chemistry, the transfer of electrons, is behind all electrochemical processes.

The reaction of zinc metal with copper (II) ions is called a direct redox process or reaction. The electrons that are transferred in the reaction go directly from the $\mathbf{Zn}$ atoms on the surface of the strip to the $\mathbf{Cu^{2+}}$ ions in the area of the solution right next to the zinc strip. Electricity, on the other hand, requires the passage of electrons through a conducting medium, such as a wire, in order to do work. This work could be lighting a light bulb or powering a refrigerator or heating a house. When the redox reaction is direct, those electrons cannot be made to do work. Instead, we must separate the oxidation process from the reduction process and force the electrons to move from one place to another in between. That is the key to the structure of the electrochemical cell. An **electrochemical cell** is any device that converts chemical energy into electrical energy, or electrical energy into chemical energy.

There are three components that make up an electrochemical reaction. There must be a solution where redox reactions can occur. These reactions generally take place in water to facilitate electron and ion movement. A conductor must exist for electrons to be transferred. This conductor is usually some kind of wire so that electrons can move from one site to another. Ions also must be able to move through some form of salt bridge that facilitates ion migration.

Summary

- Electrochemistry is a branch of chemistry that deals with the interconversion of chemical energy and electrical energy.
- An electrochemical cell is any device that converts chemical energy into electrical energy, or electrical energy into chemical energy.
- An electrochemical reaction requires:
  - A solution where redox reactions can occur.
  - A conductor for electron transfer.
  - A salt bridge for ions to move through.

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18.6: Batteries

Alessandro Volta developed the first "voltaic cell" in 1800. This battery consisted of alternating disks of zinc and silver, with pieces of cardboard soaked in brine that separated the disks. There were no voltmeters at the time (and no insight that the electric current was due to electron flow). So, Volta had to rely on another measure of battery strength: the amount of shock produced (it's never a good idea to test things on yourself). He found that the intensity of the shock increased with the number of metal plates in the system. Devices with twenty plates produced a shock that was quite painful. It's lucky that we have voltmeters today to measure electric current, instead of having to test the voltage out for ourselves! Two variations on the basic voltaic cell are the dry cell and the lead storage battery.

Batteries: Dry Cells

Many common batteries, such as those used in a flashlight or remote control, are voltaic dry cells. These batteries are called dry cells because the electrolyte is a paste. They are relatively inexpensive, but do not last a long time and are not rechargeable.

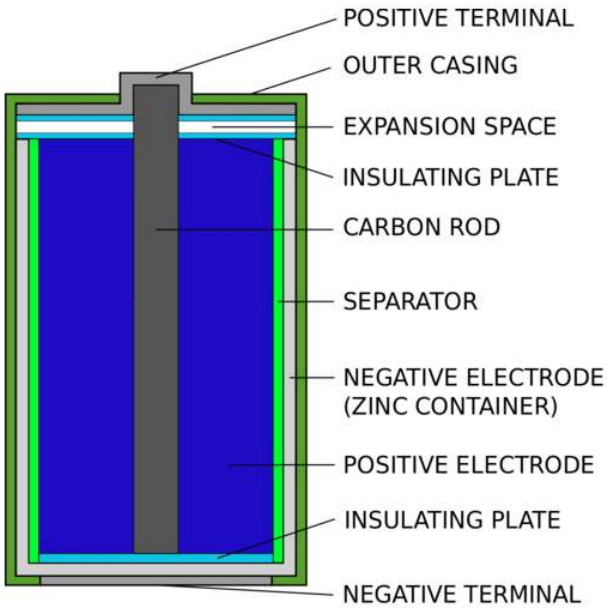


Figure 18.6.1: A zinc-carbon dry cell.

In the zinc-carbon dry cell, the anode is a zinc container, while the cathode is a carbon rod through the center of the cell. The paste is made of manganese (IV) oxide ($\mathbf{MnO_2}$), ammonium chloride ($\mathbf{NH_4Cl}$), and zinc chloride ($\mathbf{ZnCl_2}$) in water. The half-reactions for this dry cell are:

Anode (oxidation):

$$\mathrm{Zn}\,(s) \rightarrow \mathrm{Zn^{2+}}\,(aq) + 2\mathrm{e^-}$$

Cathode (reduction):

$$2\mathrm{MnO_2}\,(s) + 2\mathrm{NH_4^+}\,(aq) + 2\mathrm{e^-} \rightarrow \mathrm{Mn_2O_3}\,(s) + 2\mathrm{NH_3}\,(aq) + \mathrm{H_2O}\,(l)$$

The paste prevents the contents of the dry cell from freely mixing, so a salt bridge is not needed. The carbon rod is a conductor only and does not undergo reduction. The voltage produced by a fresh dry cell is $\mathbf{1.5\ V}$, but decreases during use.

An alkaline battery is a variation on the zinc-carbon dry cell. The alkaline battery has no carbon rod and uses a paste of zinc metal and potassium hydroxide, instead of a solid metal anode. The cathode half-reaction is the same, but the anode half-reaction is different.

Anode (oxidation):

$$\mathrm{Zn}\,(s) + 2\mathrm{OH^-}\,(aq) \rightarrow \mathrm{Zn(OH)_2}\,(s) + 2\mathrm{e^-}$$

Advantages of the alkaline battery are that it has a longer shelf life, and the voltage does not decrease during use.

Lead Storage Batteries

A **battery** is a group of electrochemical cells combined together as a source of direct electric current at a constant voltage. Dry cells are not true batteries since they are only one cell. The lead storage battery is commonly used as the power source in cars and other vehicles. It consists of six identical cells joined together, each of which has a lead anode and a cathode made of lead (IV) oxide ($\mathbf{PbO_2}$) packed on a metal plate.

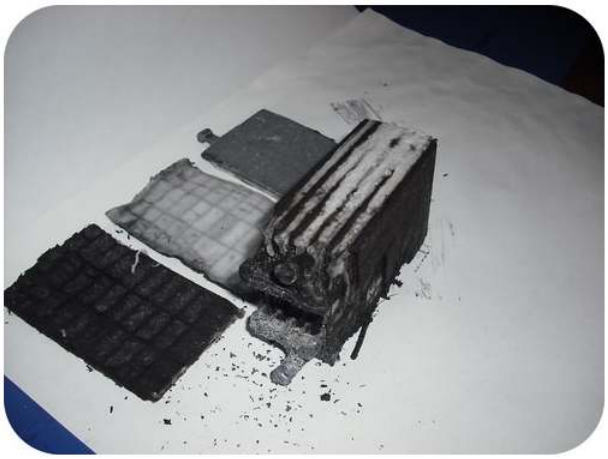


Figure **18.6.2**: A lead storage battery, such as those used in cars, consists of six identical electrochemical cells and is rechargeable.

The cathode and anode are both immersed in an aqueous solution of sulfuric acid, which acts as the electrolyte. The cell reactions are:

Anode (oxidation):

$$\mathbf{Pb\,(\mathit{s})} + \mathbf{{SO_4}^{2-}\,(\mathit{aq})} \rightarrow \mathbf{PbSO_4\,(\mathit{s})} + \mathbf{2e^-}$$

Cathode (reduction):

$$\mathbf{PbO_2\,(\mathit{s})} + \mathbf{4H^+\,(\mathit{aq})} + \mathbf{{SO_4}^{2-}\,(\mathit{aq})} + \mathbf{2e^-} \rightarrow \mathbf{PbSO_4\,(\mathit{s})} + \mathbf{2H_2O\,(\mathit{l})}$$

Overall:

$$\mathbf{Pb\,(\mathit{s})} + \mathbf{PbO_2\,(\mathit{s})} + \mathbf{4H^+\,(\mathit{aq})} + \mathbf{2{SO_4}^{2-}\,(\mathit{aq})} \rightarrow \mathbf{2PbSO_4\,(\mathit{s})} + \mathbf{2H_2O\,(\mathit{l})}$$

Each cell in a lead storage battery produces $\mathbf{2\ V}$, so a total of $\mathbf{12\ V}$ is generated by the entire battery. This is used to start a car or power other electrical systems.

Unlike a dry cell, the lead storage battery is rechargeable. Note that the forward redox reaction generates solid lead (II) sulfate which slowly builds up on the plates. Additionally, the concentration of sulfuric acid decreases. When the car is running normally, its generator recharges the battery by forcing the above reactions to run in the opposite, or nonspontaneous, direction.

$$\mathbf{2PbSO_4\,(\mathit{s})} + \mathbf{2H_2O\,(\mathit{l})} \rightarrow \mathbf{Pb\,(\mathit{s})} + \mathbf{PbO_2\,(\mathit{s})} + \mathbf{4H^+\,(\mathit{aq})} + \mathbf{2{SO_4}^{2-}\,(\mathit{aq})}$$

This reaction regenerates the lead, lead (IV) oxide, and sulfuric acid needed for the battery to function properly. Theoretically, a lead storage battery should last forever. In practice, the recharge is not $\mathbf{100\%}$ efficient, because some of the lead (II) sulfate falls from the electrodes and collects on the bottom of the cells.

Summary

- Construction of a dry cell and a battery are given.
- Chemical reactions for both types are described.

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18.7: Corrosion

Learning Objectives

- Define corrosion
- List some of the methods used to prevent or slow corrosion

Corrosion is usually defined as the degradation of metals due to an electrochemical process. The formation of rust on iron, tarnish on silver, and the blue-green patina that develops on copper are all examples of corrosion. The total cost of corrosion in the United States is significant, with estimates in excess of half a trillion dollars a year.

Changing Colors

The Statue of Liberty is a landmark every American recognizes. The Statue of Liberty is easily identified by its height, stance, and unique blue-green color. When this statue was first delivered from France, its appearance was not green. It was brown, the color of its copper "skin." So how did the Statue of Liberty change colors? The change in appearance was a direct result of corrosion. The copper that is the primary component of the statue slowly underwent oxidation from the air. The oxidation-reduction reactions of copper metal in the environment occur in several steps. Copper metal is oxidized to copper(I) oxide ($\mathbf{Cu_2O}$), which is red, and then to copper(II) oxide, which is black.

$$2\,\mathrm{Cu\,(s)} + \tfrac{1}{2}\,\mathrm{O_2\,(g)} \rightarrow \underset{\text{red}}{\mathrm{Cu_2O\,(s)}}$$

$$\mathrm{Cu_2O\,(s)} + \tfrac{1}{2}\,\mathrm{O_2\,(g)} \rightarrow 2\,\underset{\text{black}}{\mathrm{CuO\,(s)}}$$

Coal, which was often high in sulfur, was burned extensively in the early part of the last century. As a result, sulfur trioxide, carbon dioxide, and water all reacted with the $\mathbf{CuO}$.

$$2\,\mathrm{CuO\,(s)} + \mathrm{CO_2\,(g)} + \mathrm{H_2O\,(l)} \rightarrow \underset{\text{green}}{\mathrm{Cu_2CO_3(OH)_2\,(s)}}$$

$$3\,\mathrm{CuO\,(s)} + 2\,\mathrm{CO_2\,(g)} + \mathrm{H_2O\,(l)} \rightarrow \underset{\text{blue}}{\mathrm{Cu_2(CO_3)_2(OH)_2\,(s)}}$$

$$4\,\mathrm{CuO\,(s)} + \mathrm{SO_3\,(g)} + 3\,\mathrm{H_2O\,(l)} \rightarrow \underset{\text{green}}{\mathrm{Cu_4SO_4(OH)_6\,(s)}}$$

These three compounds are responsible for the characteristic blue-green patina seen today. Fortunately, formation of the patina created a protective layer on the surface, preventing further corrosion of the copper skin. The formation of the protective layer is a form of passivation, which is discussed further in a later chapter.

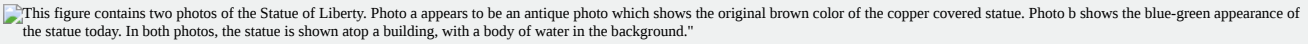

This figure contains two photos of the Statue of Liberty. Photo a appears to be an antique photo which shows the original brown color of the copper covered statue. Photo b shows the blue-green appearance of the statue today. In both photos, the statue is shown atop a building, with a body of water in the background."

Figure **18.7.1**: (a) The Statue of Liberty is covered with a copper skin, and was originally brown, as shown in this painting. (b) Exposure to the elements has resulted in the formation of the blue-green patina seen today.

Perhaps the most familiar example of corrosion is the formation of rust on iron. Iron will rust when it is exposed to oxygen and water. The main steps in the rusting of iron appear to involve the following. Once exposed to the atmosphere, iron rapidly oxidizes.

$$\text{anode: } \mathrm{Fe_{(s)}} \rightarrow \mathrm{Fe^{2+}{}_{(aq)}} + 2\,\mathrm{e^-} \quad E^\circ_{\mathrm{Fe^{2+}/Fe}} = -0.44\ \mathrm{V}$$

The electrons reduce oxygen in the air in acidic solutions.

$$\text{cathode: } \mathrm{O_{2(g)}} + 4\,\mathrm{H^+{}_{(aq)}} + 4\,\mathrm{e^-} \rightarrow 2\,\mathrm{H_2O_{(l)}} \quad E^\circ_{\mathrm{O_2/O_2}} = +1.23\ \mathrm{V}$$

$$\text{overall: } 2\,\mathrm{Fe_{(s)}} + \mathrm{O_{2(g)}} + 4\,\mathrm{H^+{}_{(aq)}} \rightarrow 2\,\mathrm{Fe^{2+}{}_{(aq)}} + 2\,\mathrm{H_2O_{(l)}} \quad E^\circ_{\text{cell}} = +1.67\ \mathrm{V}$$

What we call rust is hydrated iron(III) oxide, which forms when iron(II) ions react further with oxygen.

$$4\,\mathrm{Fe^{2+}{}_{(aq)}} + \mathrm{O_{2(g)}} + (4+2x)\mathrm{H_2O_{(l)}} \rightarrow 2\,\mathrm{Fe_2O_3 \cdot}\,x\mathrm{H_2O_{(s)}} + 8\,\mathrm{H^+{}_{(aq)}}$$

The number of water molecules is variable, so it is represented by *x*. Unlike the patina on copper, the formation of rust does not create a protective layer and so corrosion of the iron continues as the rust flakes off and exposes fresh iron to the atmosphere.

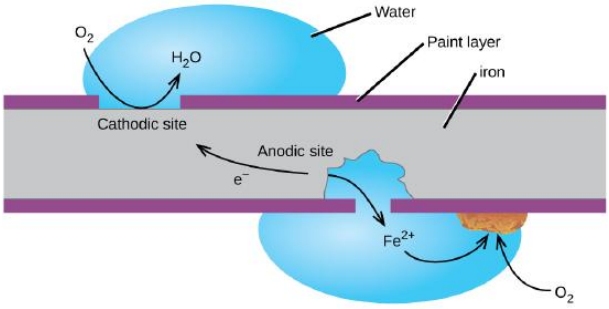


Figure **18.7.2**: Once the paint is scratched on a painted iron surface, corrosion occurs and rust begins to form. The speed of the spontaneous reaction is increased in the presence of electrolytes, such as the sodium chloride used on roads to melt ice and snow or in salt water.

A grey rectangle, labeled “iron,” is shown with thin purple layers, labeled “Paint layer,” at its upper and lower surfaces. A gap in the upper purple layer at the upper left of the diagram is labeled “Cathodic site.” A blue droplet labeled “water” is positioned on top of the gap. A curved arrow extends from a space above the droplet to the surface of the grey region and into the water droplet. The base of the arrow is labeled “O subscript 2” and the tip of the arrow is labeled “H subscript 2 O.” A gap to the right and on the bottom side of the grey region shows that some of the grey region is gone from the region beneath the purple layer. A water droplet covers this gap and extends into the open space in the grey rectangle. The label “F e superscript 2 positive” is at the center of the droplet. A curved arrow points from the edge of the grey area below to the label. A second curved arrow extends from the F e superscript 2 positive arrow to a rust brown chunk on the lower surface of the purple layer at the edge of the water droplet. A curved arrow extends from O subscript 2 outside the droplet into the droplet to the rust brown chunk. The grey region at the lower right portion of the diagram is labeled “Anodic site.” An arrow extends from the anodic site toward the cathodic site, which is labeled “e superscript negative.”

One way to keep iron from corroding is to keep it painted. The layer of paint prevents the water and oxygen necessary for rust formation from coming into contact with the iron. As long as the paint remains intact, the iron is protected from corrosion.

Other strategies include alloying the iron with other metals. For example, stainless steel is mostly iron with a bit of chromium. The chromium tends to collect near the surface, where it forms an oxide layer that protects the iron.

Zinc-plated or galvanized iron uses a different strategy. Zinc is more easily oxidized than iron because zinc has a lower reduction potential. Since zinc has a lower reduction potential, it is a more active metal. Thus, even if the zinc coating is scratched, the zinc will still oxidize before the iron. This suggests that this approach should work with other active metals.



Figure **18.7.3**: One way to protect an underground iron storage tank is through cathodic protection. Using an active metal like zinc or magnesium for the anode effectively makes the storage tank the cathode, preventing it from corroding (oxidizing).

A diagram is shown of an underground storage tank system. Underground, to the left end of the diagram is a horizontal grey tank which is labeled “Object to be protected.” A black line extends upward from the center of the tank above ground. An arrow points upward at the left side of the line segment. A horizontal black line segment continues right above ground, which is labeled “No power source is needed.” A line segment extends up and to the right, which is labeled “ Lead wire.” A line segment with a downward pointing arrow to its right extends downward below the ground to a second metal tank-like structure, labeled “Sacrificial anode” which is vertically oriented. Five black arrows point left underground toward the first tank. These arrows are collectively labeled “Protective current.”

Another important way to protect metal is to make it the cathode in a galvanic cell. This is cathodic protection and can be used for metals other than just iron. For example, the rusting of underground iron storage tanks and pipes can be prevented or greatly reduced by connecting them to a more active metal such as zinc or magnesium. This is also used to protect the metal parts in water heaters. The more active metals (lower reduction potential) are called sacrificial anodes because as they get used up as they corrode (oxidize) at the anode. The metal being protected serves as the cathode, and so does not oxidize (corrode). When the anodes are properly monitored and periodically replaced, the useful lifetime of the iron storage tank can be greatly extended.

Summary

Corrosion is the degradation of a metal caused by an electrochemical process. Large sums of money are spent each year repairing the effects of, or preventing, corrosion. Some metals, such as aluminum and copper, produce a protective layer when they corrode

in air. The thin layer that forms on the surface of the metal prevents oxygen from coming into contact with more of the metal atoms and thus “protects” the remaining metal from further corrosion. Iron corrodes (forms rust) when exposed to water and oxygen. The rust that forms on iron metal flakes off, exposing fresh metal, which also corrodes. One way to prevent, or slow, corrosion is by coating the metal. Coating prevents water and oxygen from contacting the metal. Paint or other coatings will slow corrosion, but they are not effective once scratched. Zinc-plated or galvanized iron exploits the fact that zinc is more likely to oxidize than iron. As long as the coating remains, even if scratched, the zinc will oxidize before the iron. Another method for protecting metals is cathodic protection. In this method, an easily oxidized and inexpensive metal, often zinc or magnesium (the sacrificial anode), is electrically connected to the metal that must be protected. The more active metal is the sacrificial anode, and is the anode in a galvanic cell. The “protected” metal is the cathode, and remains unoxidized. One advantage of cathodic protection is that the sacrificial anode can be monitored and replaced if needed.

Glossary

cathodic protection
: method of protecting metal by using a sacrificial anode and effectively making the metal that needs protecting the cathode, thus preventing its oxidation

corrosion
: degradation of metal through an electrochemical process

galvanized iron
: method for protecting iron by covering it with zinc, which will oxidize before the iron; zinc-plated iron

sacrificial anode
: more active, inexpensive metal used as the anode in cathodic protection; frequently made from magnesium or zinc

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18.8: Voltaic Cells

Luigi Galvani (1737-1798) was an Italian physician and scientist who did research on nerve conduction in animals. His accidental observation of the twitching of frog legs when they were in contact with an iron scalpel, while the legs hung on copper hooks, led to studies on electrical conductivity in muscles and nerves. He believed that animal tissues contained an "animal electricity" similar to the natural electricity that caused lightning to form.

Voltaic Cells

A **voltaic cell** is an electrochemical cell that uses a spontaneous redox reaction to produce electrical energy.

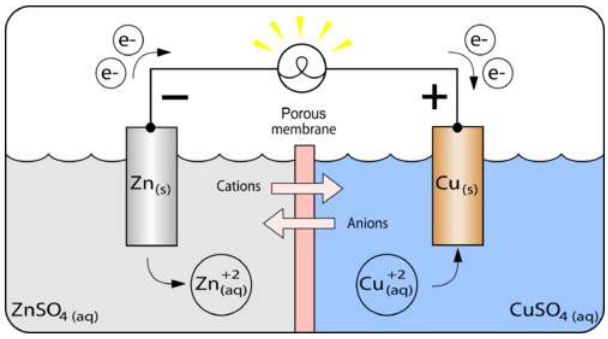


Figure 18.8.1: Voltaic cell.

The voltaic cell (see figure above) consists of two separate compartments. A **half-cell** is one part of a voltaic cell in which either the oxidation or reduction half-reaction takes place. The left half-cell is a strip of zinc metal in a solution of zinc sulfate. The right half-cell is a strip of copper metal in a solution of copper (II) sulfate. The strips of metal are called electrodes. An **electrode** is a conductor in a circuit that is used to carry electrons to a nonmetallic part of the circuit. The nonmetallic part of the circuit is the electrolyte solution in which the electrodes are placed. A metal wire connects the two electrodes. A switch opens or closes the circuit. A porous membrane is placed between the two half-cells to complete the circuit.

The various electrochemical processes that occur in a voltaic cell occur simultaneously. It is easiest to describe them in the following steps, using the above zinc-copper cell as an example.

1. Zinc atoms from the zinc electrode are oxidized to zinc ions. This happens because zinc is higher than copper on the activity series, and so is more easily oxidized.

$$\mathrm{Zn}\,(s) \rightarrow \mathrm{Zn}^{2+}\,(aq) + 2\mathrm{e}^{-}$$

The electrode at which oxidation occurs is called the **anode**. The zinc anode gradually diminishes as the cell operates, due to the loss of zinc metal. The zinc ion concentration in the half-cell increases. Because of the production of electrons at the anode, it is labeled as the negative electrode.

2. The electrons that are generated at the zinc anode travel through the external wire and register a reading on the voltmeter. They continue to the copper electrode.

3. Electrons enter the copper electrode where they combine with the copper (II) ions in the solution, reducing them to copper metal.

$$\mathrm{Cu}^{2+}\,(aq) + 2\mathrm{e}^{-} \rightarrow \mathrm{Cu}\,(s)$$

The electrode at which reduction occurs is called the **cathode**. The cathode gradually increases in mass because of the production of copper metal. The concentration of copper (II) ions in the half-cell solution decreases. The cathode is the positive electrode.

4. Ions move through the membrane to maintain electrical neutrality in the cell. In the cell illustrated above, sulfate ions will move from the copper side to the zinc side to compensate for the decrease in Cu^{2+} and the increase in Zn^{2+}.

The two half-reactions can again be summed to provide the overall redox reaction occurring in the voltaic cell:

$$\mathrm{Zn}\,(s) + \mathrm{Cu}^{2+}\,(aq) \rightarrow \mathrm{Zn}^{2+}\,(aq) + \mathrm{Cu}\,(s)$$

Summary

- A **voltaic cell** is an electrochemical cell that uses a spontaneous redox reaction to produce electrical energy.
- The structure of a voltaic cell includes two half-cells; each being one part of a voltaic cell in which either the oxidation or reduction half-reaction takes place, and each containing an electrode.
  - The electrode at which oxidation occurs is called the anode.
  - The electrode at which reduction occurs is called the cathode.
- The reactions producing electron flow are given.

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18.9: Electrolysis

Learning Objectives

- Describe electrolysis from a perspective of redox reactions.
- Give examples of electrolysis applications.

Up to this point, we have considered redox reactions for processes that are spontaneous. When set up as a voltaic cell or battery, such reactions can be used as a source of electricity. However, it is possible to go in the other direction. By forcing electricity into a cell, we can make a redox reaction occur that normally would not be spontaneous. Under these circumstances, the cell is called an **electrolytic cell**, and the process that occurs in the cell is called **electrolysis** (Figure 18.9.1).

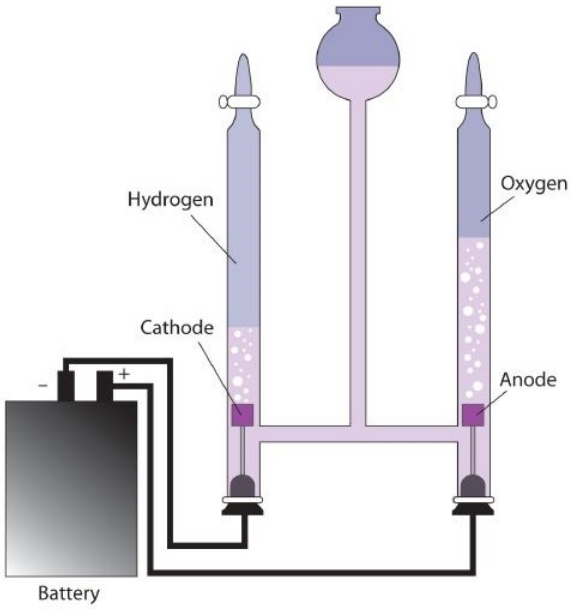


Figure 18.9.1: Electrolysis. In an electrolytic cell, electricity is forced through the cell to induce a non-spontaneous redox reaction. Here, the redox reaction $2H_2O \rightarrow 2H_2 + O_2$ is being caused by the introduction of electricity, which is supplied by the battery.

Electrolysis has many applications. For example, if NaCl is melted at about 800°C in an electrolytic cell and an electric current is passed through it, elemental sodium will appear at the cathode and elemental chlorine will appear at the anode as the following two reactions occur:

$$Na^+ + e^- \rightarrow Na$$

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

Normally we expect elemental sodium and chlorine to react spontaneously to make NaCl. However, by using an input of electricity, we can force the opposite reaction to occur and generate the elements. Lithium, potassium, and magnesium can also be isolated from compounds by electrolysis.

Another element that is isolated by electrolysis is aluminum. Aluminum formerly was a difficult metal to isolate in its elemental form; in fact, the top of the Washington Monument has a 2.8 kg cap of aluminum metal, which at the time (1884) was the largest piece of elemental aluminum ever isolated. However, in 1886, the American Charles Hall and the Frenchman Paul Héroult almost simultaneously worked out an electrolytic process for isolating aluminum from bauxite—an ore of aluminum whose chemical formula is $AlO_x(OH)_{3-2x}$. The basic reactions are as follows:

$$Al^{3+} + 3e^- \rightarrow Al_2O^{2-} \rightarrow O_2 + 4e^-$$

With the development of the Hall-Héroult process, the price of aluminum dropped by a factor of over 200, and aluminum metal became common. So much elemental aluminum is produced in the United States each year that it has been estimated that the

electrolysis of aluminum uses 5% of all the electricity in the country. (Recycling aluminum requires about 1/70th the energy of refining aluminum from ore, which illustrates the tremendous energy savings that recycling provides.)

Another application of electrolysis is electroplating, which is the deposition of a thin layer of metal on an object for protective or decorative purposes (Figure **18.9.2**). Essentially, a metal object is connected to the cathode of an electrolytic cell and immersed in a solution of a particular metal cation. When the electrolytic cell is operated, a thin coating of the metal cation is reduced to the elemental metal on the surface of the object; the thickness of the coating can be as little as a few micrometers (10^{-6} m). Jewelry, eating utensils, electrical contacts, and car parts like bumpers are common items that are electroplated. Gold, silver, nickel, copper, and chromium are common metals used in electroplating.

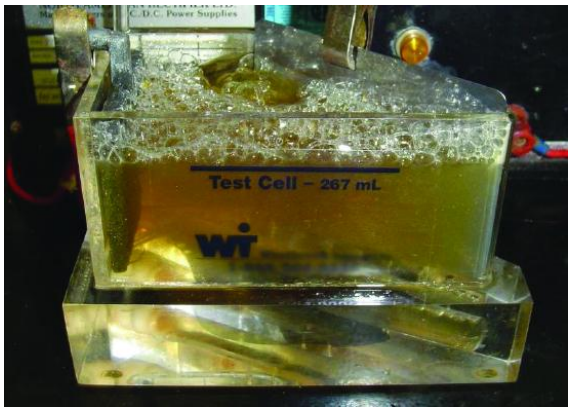


Figure **18.9.2**: Electroplating Source. Photo courtesy of Fstep, http://commons.wikimedia.org/wiki/File:Hullcell.jpg(opens in new window).

Key Takeaways

- Electrolysis is a forced non-spontaneous redox occurence by the introduction of electricity into a cell from an outside source.
- Electrolysis is used to isolate elements and electroplate objects.

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CHAPTER OVERVIEW

19: Nuclear Chemistry

Most chemists pay little attention to the nucleus of an atom except to consider the number of protons it contains because that determines an element's identity. However, 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. Many people are aware of nuclear power plants and nuclear bombs, but nuclear chemistry also has applications ranging from smoke detectors to medicine, from the sterilization of food to the analysis of ancient artifacts. 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.

19.01: Radioactivity
19.02: The History and Basics of Fission
19.03: Instruments for Radiation Detection
19.04: Half-Life
19.5: Uses of Radioactive Isotopes
19.06: Nuclear Energy
19.07: Fission and Fusion
19.08: Nuclear Reactors
19.09: Breeder Reactors
19.10: Nuclear Fusion
19.11: Biological Effects of Radiation

Thumbnail: Part of carbon–nitrogen–oxygen (CNO) reaction chain diagram, made just to be illustrative for nuclear reactions in general. Image used with permission (CC BY-SA 3.0; Michalsmid).

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19.01: Radioactivity

Learning Objective

- Define and give examples of the major types of radioactivity.

We saw in 3: Atoms, Molecules, and Ions, that 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 an atom, while electrons circle the nucleus in shells and subshells and account for an atom's size.

We also introduced in 3: Atoms, Molecules, and Ions the notation for succinctly representing an isotope of a particular atom:

$$^{12}_{6}\mathrm{C} \tag{19.1.1}$$

The element in this example, represented by the symbol C, is carbon. Its atomic number, 6, is the subscript next to the symbol and is the number of protons in the atom. The mass number, the superscript next to 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 neurons). 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—$^{2}\mathrm{H}$ and $^{3}\mathrm{H}$—are given their own names and symbols: deuterium (D) and tritium (T), respectively.

Atomic theory in the nineteenth 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 being 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 is the same as a helium nucleus. We often use

$$^{4}_{2}\mathrm{He} \tag{19.1.2}$$

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:

$$^{235}_{92}\mathrm{U} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{231}_{90}\mathrm{Th} \tag{19.1.3}$$

Rather than calling this equation a chemical equation, we call it a **nuclear equation** to emphasize that the change occurs in an atomic nucleus. How do we know that a product of this reaction is $^{231}_{90}\mathrm{Th}$? 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 nuclear equation. If our uranium nucleus loses 2 protons, there are 90 protons remaining, identifying the element as thorium. Moreover, if we lose four nuclear particles of the original 235, there are 231 remaining. Thus we use subtraction to identify the isotope of the Th atom—in this case,

$$^{231}_{90}\mathrm{Th} \tag{19.1.4}$$

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,

$$^{235}_{92}\mathrm{U} \tag{19.1.5}$$

is the parent isotope, and

$$^{231}_{90}\mathrm{Th} \tag{19.1.6}$$

is the daughter isotope. When one element changes into another in this manner, it undergoes **radioactive decay**.

Example 19.1.1:

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

$$^{222}_{86}\text{Rn} \tag{19.1.7}$$

We represent the alpha particle as

$$^{4}_{2}\text{He} \tag{19.1.8}$$

Use subtraction (222 − 4 = 218 and 86 − 2 = 84) to identify the daughter isotope as polonium:

$$^{222}_{86}\text{Rn} \rightarrow {}^{4}_{2}\text{He} + {}^{218}_{84}\text{Th} \tag{19.1.9}$$

Exercise 19.1.1

Test Yourself

Write the nuclear equation that represents radioactive decay of polonium-208 by alpha particle emission and identify the daughter isotope.

Answer

$$^{208}_{80}\text{Po} \rightarrow {}^{4}_{2}\text{He} + {}^{204}_{82}\text{Pb} \tag{19.1.10}$$

Daughter isotope:

$$^{204}_{82}\text{Pb} \tag{19.1.11}$$

The second major type of radioactive emission is called a **beta particle**, symbolized by the Greek letter β. A beta particle is an electron ejected from the nucleus (not from the shells of electrons about the nucleus) and has a 1− charge. We can also represent a beta particle as $^{0}_{-1}\text{e}$. The net effect of beta particle emission on a nucleus is that a neutron is converted to a proton. The overall mass number stays the same, but because the number of protons increases by one, the atomic number goes up by one. Carbon-14 decays by emitting a beta particle:

$$^{14}_{6}\text{C} \rightarrow {}^{14}_{7}\text{N} + {}^{0}_{-1}\text{e} \tag{19.1.12}$$

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:

$$^{222}_{86}\text{Rn} \rightarrow {}^{218}_{84}\text{Po} + {}^{4}_{2}\text{He} + \gamma \tag{19.1.13}$$

This may not seem like much energy, but if 1 mol of Rn atoms were to decay, the gamma ray energy would be 4.9×10^{7} kJ!

Example 19.1.1:

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 \[_{2}^{4}\textrm{He}\]

while one of the products is

$$^{0}_{-1}e \tag{19.1.14}$$

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:

$$^{12}_{5}B \rightarrow {}^{12}_{6}C + {}^{0}_{-1}e + \gamma \tag{19.1.15}$$

The daughter isotope is carbon-12.

Exercise 19.1.1

Test Yourself

Write the nuclear equation that represents the radioactive decay of technetium-133 by beta particle emission and identify the daughter isotope. A gamma ray is emitted simultaneously with the beta particle.

Answer

$$^{133}_{43}Tc \rightarrow {}^{133}_{44}Ru + {}^{0}_{-1}e + \gamma \tag{19.1.16}$$

Daughter isotope: ruthenium-133

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 15.2.1 - The Three Main Forms of Radioactive Emissions, summarizes the properties of the three main types of radioactive emissions.

Table 15.2.1 The Three Main Forms of Radioactive Emissions

Characteristic	Alpha Particles	Beta Particles	Gamma Rays
symbols	α, $^{4}_{2}He$	β, $^{0}_{-1}e$	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

$$^{235}_{92}Tc \rightarrow {}^{139}_{56}Ba + {}^{94}_{36}Kr + 2\,{}^{1}_{0}n \tag{19.1.17}$$

where \(\ce{_0^1n}\) is a neutron. As with any nuclear process, the sums of the atomic numbers and 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 Takeaways

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

- Fission is a type of radioactivity in which large nuclei spontaneously break apart into smaller nuclei.

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19.02: The History and Basics of Fission

Learning Objectives

- When given a reaction, distinguish between decay/emission and artificial transmutation.
- Write and balance artificial transmutation reactions.
- Determine the origins of U-235 and Pu-239.
- Know the history of fission.
- Determine why only certain atoms can undergo fission or fusion.
- Explain the mechanism and applications of fission and fusion

Understanding the Neutron

In 1911, Ernest Rutherford applied a beam of alpha particle to a gold foil. This experiment helped him to determine the positive center of the atom, which he named the nucleus. Eight years later, this same scientist discovered the existence of proton by performing the following nuclear reaction:

$$^{14}_{7}\text{N} + ^{4}_{2}\text{He} \longrightarrow ^{17}_{8}\text{O} + ^{1}_{1}\text{H}$$

This reaction is an example of artificial transmutation. By taking a particle and hitting any existing nucleus, a new atom will be synthesized artificially. Note how this reaction differs from a decay/emission reaction. In the latter type of reaction, only one reactant will produce at least two products. Transmutations will illustrate a minimum of two reactants and various number of products.

Example 19.2.1: Artificial Transmutation or Decay Reactions?

Label each as being an artificial transmutation or a decay reaction.

a. $^{238}_{92}\text{U} \rightarrow ^{4}_{2}\text{He} + ^{234}_{90}\text{Th}$
b. $^{198}_{78}\text{Pt} + ^{1}_{0}\text{n} \rightarrow ^{199}_{78}\text{Pt} \rightarrow ^{199}_{79}\text{Au} + ^{0}_{-1}\beta$
c. $^{239}_{93}\text{Np} \rightarrow ^{239}_{94}\text{Pu} + ^{0}_{-1}\beta$
d. $^{11}_{6}\text{C} \rightarrow ^{11}_{5}\text{B} + ^{0}_{+1}\beta$
e. $^{27}_{13}\text{Al} + ^{4}_{2}\text{He} \longrightarrow ^{30}_{15}\text{P} + ^{1}_{0}\text{n}$

Answer

Only reactions b and e are artificial transmutations. The other reactions are examples of decays/emissions.

Throughout the 1930s, many scientists became focused on producing new radioactive elements. Before this time period, newly discovered elements were extracted from natural ores obtained from mining. Irene (daughter of Marie and Pierre Curie) and her husband Frederic Joliot-Curie bombarded existing elements with alpha particles. These experiments yielded new radioactive isotopes by an artificial process. For their efforts, Irene and Frederic were awarded the 1935 Noble Prize in chemistry. One of their key syntheses involve the bombardment of aluminum foil with alpha particles.

$$^{27}_{13}\text{Al} + ^{4}_{2}\text{He} \longrightarrow ^{30}_{15}\text{P} + ^{1}_{0}\text{n}$$

In their laboratory, the Joliet-Curies could not explain or identify the existence of the neutron. Their measurements showed that an additional, non-charged substance was produced in the aluminum foil reaction. They hypothesized that this unknown piece of the reaction must be a gamma-ray, which has a neutral charge.



Figure 19.2.1: Irene and Frederic Joliot-Curie working in their lab to synthesize new isotopes by artificial transmutation. Image is taken from upload.wikimedia.org/wikiped...Curie_1935.jpg

The Significance of Artificial Transmutation

Unfortunately, the Joliot-Curies were incorrect in their analysis. Around the same time, a British scientist named James Chadwick bombarded beryllium with alpha particles to produce the species below:

$$^{9}_{4}\mathrm{Be} + {}^{4}_{2}\mathrm{He} \longrightarrow {}^{12}_{6}\mathrm{C} + {}^{1}_{0}\mathrm{n}$$

Using this reaction, he was able to characterize and explain the existence of this new atomic subatomic particle. He noted this atomic piece was the same mass as a proton but had no charge. In 1935, James Chadwick was awarded the Nobel Prize in physics for the discovery of the neutron.

Example 19.2.2

Translate the following reactions to A/Z symbols. Balance these artificial transmutations by finding the missing pieces.

a. sodium-23 is hit with an alpha particle to produce a proton and another isotope
b. fluorine-19 is bombarded a neutron to produce an alpha particle and another isotope
c. uranium-238 is hit with a neutron to produce an isotope and a beta particle

Solution

a. missing isotope piece = Mg-26
b. missing isotope piece = N-16
c. missing isotope piece = Np-239

Artificial transmutation has been utilized to make new elements. All elements with atomic numbers greater than 92 are produced synthetically. These elements are called transuranium elements and have been prepared by bombarding suitable target nuclei with smaller particles. The first of the transuranium elements to be made was neptunium (Z = 93), which was synthesized in 1940 by bombarding a ^{238}U target with neutrons. As shown below, this reaction occurs in two steps. Initially, a neutron combines with a ^{238}U nucleus to form ^{239}U, which is unstable and undergoes beta decay to produce ^{239}Np:

$$^{238}_{92}\mathrm{U} + {}_{0}{}^{1}\,\mathrm{n} \rightarrow {}^{239}_{92}\mathrm{U}$$

$$^{239}_{92}\mathrm{U} \rightarrow {}^{239}_{93}\,\mathrm{Np} + {}^{0}_{-1}\beta \qquad (19.2.1)$$

Subsequent beta decay of ^{239}Np produces the second transuranium element, plutonium (Z = 94):

$$^{239}_{93}\mathrm{Np} \rightarrow {}^{239}_{94}\mathrm{Pu} + {}^{0}_{-1}\beta \qquad (19.2.2)$$

Bombarding the target with more massive nuclei creates elements that have atomic numbers significantly greater than that of the target nucleus (Table 19.2.1). Such techniques have resulted in the creation of the superheavy elements 114 and 116, both of which lie in or near the “island of stability." As of this writing, 22 transuranium elements have been produced and officially recognized by IUPAC; several other elements have formation claims that are waiting for approval.

Table 19.2.1: Preparation of Some of the Transuranium Elements

Name	Symbol	Atomic Number	Reaction
americium	Am	95	$^{239}_{94}\text{Pu} + {}^{1}_{0}\text{n} \longrightarrow {}^{240}_{95}\text{Am} + {}^{0}_{-1}\text{e}$
curium	Cm	96	$^{239}_{94}\text{Pu} + {}^{4}_{2}\text{He} \longrightarrow {}^{242}_{96}\text{Cm} + {}^{1}_{0}\text{n}$
californium	Cf	98	$^{242}_{96}\text{Cm} + {}^{4}_{2}\text{He} \longrightarrow {}^{243}_{97}\text{Bk} + 2{}^{1}_{0}\text{n}$
einsteinium	Es	99	$^{238}_{92}\text{U} + 15{}^{1}_{0}\text{n} \longrightarrow {}^{253}_{99}\text{Es} + 7{}^{0}_{-1}\text{e}$
mendelevium	Md	101	$^{253}_{99}\text{Es} + {}^{4}_{2}\text{He} \longrightarrow {}^{256}_{101}\text{Md} + {}^{1}_{0}\text{n}$
nobelium	No	102	$^{246}_{96}\text{Cm} + {}^{12}_{6}\text{C} \longrightarrow {}^{254}_{102}\text{No} + 4{}^{1}_{0}\text{n}$
rutherfordium	Rf	104	$^{249}_{98}\text{Cf} + {}^{12}_{6}\text{C} \longrightarrow {}^{257}_{104}\text{Rf} + 4{}^{1}_{0}\text{n}$
seaborgium	Sg	106	$^{206}_{82}\text{Pb} + {}^{54}_{24}\text{Cr} \longrightarrow {}^{257}_{106}\text{Sg} + 3{}^{1}_{0}\text{n}$ $^{249}_{98}\text{Cf} + {}^{18}_{8}\text{O} \longrightarrow {}^{263}_{106}\text{Sg} + 4{}^{1}_{0}\text{n}$
meitnerium	Mt	107	$^{209}_{83}\text{Bi} + {}^{58}_{26}\text{Fe} \longrightarrow {}^{266}_{109}\text{Mt} + {}^{1}_{0}\text{n}$

Particle Accelerators: Artificial Transmutators

To perform artificial transmutation reactions, there are two large machines that can be utilized. A device called a **particle accelerator** can accelerate positively charged particles to the speeds needed to overcome the electrostatic repulsions between them and then target nuclei by using electrical and magnetic fields. Operationally, the simplest particle accelerator is the linear accelerator (Figure **19.2.2**), in which a beam of particles is injected at one end of a long evacuated tube. A modern linear accelerator such as the Stanford Linear Accelerator (SLAC) at Stanford University is about 2 miles long.

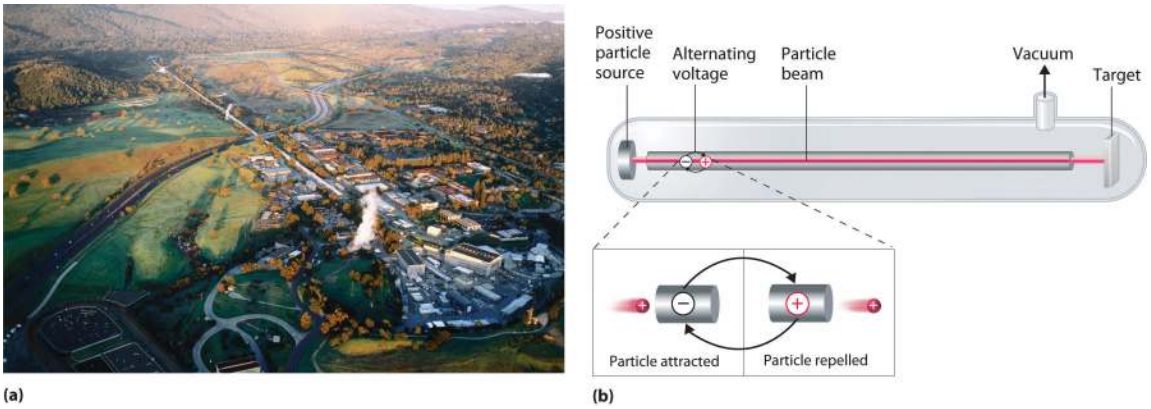


Figure **19.2.2**: A Linear Particle Accelerator. (a) An aerial view of the SLAC, the longest linear particle accelerator in the world; the overall length of the tunnel is 2 miles. (b) Rapidly reversing the polarity of the electrodes in the tube causes the charged particles to be alternately attracted as they enter one section of the tube and repelled as they leave that section. As a result, the particles are continuously accelerated along the length of the tube. (CC BY-SA-NC; anonymous)

To achieve the same outcome in less space, a particle accelerator called a **cyclotron** forces the charged particles to travel in a circular path rather than a linear one. The particles are injected into the center of a ring and accelerated by rapidly alternating the polarity of two large D-shaped electrodes above and below the ring, which accelerates the particles outward along a spiral path toward the target.

Fission and Fusion: Selecting the Isotopes

Fission is the splitting of an atomic nucleus. In nuclear weapons and reactors, neutrons hit unstable nuclei to form smaller atoms. Nuclei that are larger than Fe-56 may undergo fission. Of these elements, fission requires heavy, unstable nuclei. This means selected atoms would have low binding energies and would have large atomic masses. Figure four shows the relative binding energies for various isotopes. According to figure 4, uranium-238 and uranium-235 both have lower binding energies with heavy masses. These two isotopes would be suitable for splitting based on these requirements. Of these two isotopes, only uranium-235 is readily fissionable. This is due to the odd neutron count contributing to additional instability. Another fissionable isotope not shown

in figure 4, is plutonium-239. This is a synthetic isotope produced by transmutation and decay reactions. Like uranium-235, it has low binding energy, high mass, and an odd number of neutrons. U-235 and Pu-239 are used in atomic bombs (fission based) and nuclear reactors.

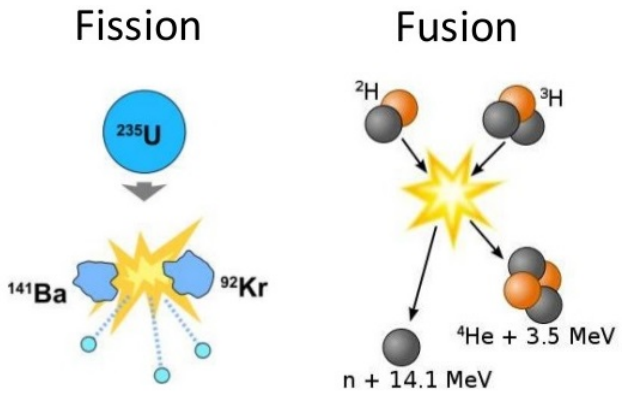


Figure **19.2.3**: (left) Nuclear fission occurs with one large nuclear is split into two or more smaller nuclei. (right) Nuclear fusion happens when two small nuclei combine to make a larger nucleus.

Fusion is the bringing together of two atomic nuclei to form a larger atom. Positively charged centers of atoms make this type of reaction extremely difficult. For this reason, smaller atoms are suitable for fusion reactions. In addition, these particular isotopes need to have low binding energies in order to undergo fusion. Atoms that possess these two qualities are H-2 and H-3. For fusion to occur, extreme temperatures are required to fuse the deuterium and tritium together.

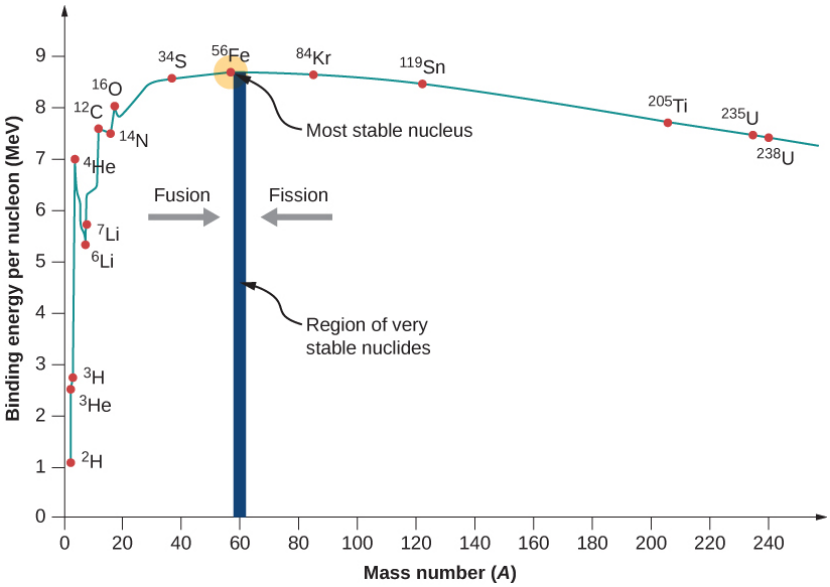


Figure **19.2.4**: In this graph of binding energy per nucleon for stable nuclei, the BEN is greatest for nuclei with a mass near ^{56}Fe. Therefore, fusion of nuclei with mass numbers much less than that of Fe, and fission of nuclei with mass numbers greater than that of Fe, are exothermic processes. (CC BY 4.0; OpenStax).

Fission and Chain Reactions

In both fission and fusion, large amounts of energy are given off in the form of heat, light, and gamma radiation. Italian physicist, Enrico Fermi, performed the first fission reaction in 1934. He was unaware that he had split a uranium atom into two smaller nuclei. Four years later, two German scientists, Otto Hahn and Fritz Strassman repeated Fermi's uranium reaction. While performing this experiment, two other scientists, Lise Meitner and Otto Frisch analyzed the data. Meitner, an Austrian physicist, noted that the uranium atom had split into two smaller pieces. She used the term "fission" to describe her observations.



Figure 19.2.5: Austrian physicist, Lise Meitner who coined the term "fission" to explain the neutron bombardment of U-238. I. (Public Domain; via Wikipedia)

The nuclear equation illustrating this fission reaction is shown below:

$$ {}^{1}_{0}\mathrm{n} + {}^{235}_{92}\mathrm{U} \rightarrow {}_{56}{}^{141}\mathrm{Ba} + {}^{92}_{36}\mathrm{Kr} + 3\,{}^{1}_{0}\mathrm{n} $$

The products shown are only one of many sets of products from the disintegration of a U-235 nucleus. Over 35 different elements have been observed in the fission products of U-235. Fission has been used in nuclear weapons and powers all nuclear reactors. Approximately fifty-five countries worldwide possess fission technology in the form of research or energy reactors. Less than ten of these countries have fission weapons.

On the other hand, fusion technology is not as accessible. Only five countries (five permanent members of the United Nations Security Council) have knowledge and scientific capability of constructing fusion weapons. Unlike fission reactors. there are no commercial fusion reactors. Fusing nuclei is quite difficult to perform in a safe and controlled environment. For more insight as to the differences between fission and fusion, click on the informational video below.



Energy of Reactions

Although Albert Einstein was not directly involved in the construction of nuclear weapons, he did devise a theory to explain the amount of energy released during a nuclear reaction (fission or fusion).

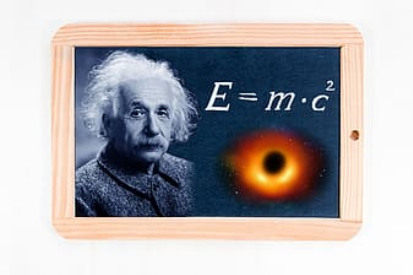


Figure 19.2.6: Albert Einstein and his famous equation. Image courtesy of Royalty free HD einstein formula photos | Pikrepo

This theory is known as special relativity as is shown below:

$$ E = mc^2 \tag{19.2.3} $$

Here, the mass can be converted to significant amounts of energy in nuclear reactions. Understanding the speed of light to be $3.0x10^8$ m/s can give you an appreciation for how much energy can be produced per unit of matter. Nuclear reactions require very small amounts of fissionable material to produce large amounts of energy (as in a nuclear reactor) or destruction (as in a bomb).

Sources

1. https://www.aps.org/publications/aps...icshistory.cfm

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19.03: Instruments for Radiation Detection

Because radiation is harmful to humans and other organisms, it is very important that we be able to detect it and measure how much is present. Such measurements are complicated by two factors. First, we cannot see, hear, smell, taste, or touch radiation, and so special instruments are required to measure it. Second, different types of radiation are more dangerous than others, and corrections must be made for the relative harm done by α particles as opposed to, say, γ rays.

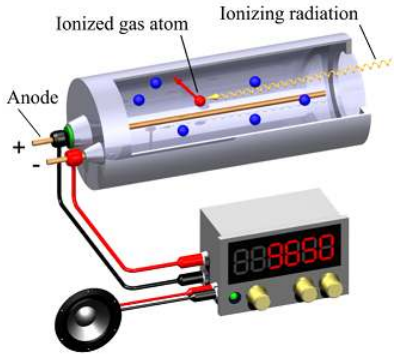


Figure **19.3.1**: Schematic of a Geiger-Müller counter using an "end window" tube for low penetration radiation. A loudspeaker is also used for indication. (CC-BY-SA-3.0 Svjo-2 vai Wikipedia).

Perhaps the most common instrument for measuring radiation levels is the **Geiger-Müller counter** (the same Geiger who worked with Rutherford to discover the atomic nucleus). A schematic diagram of a Geiger-Müller counter is shown in Figure **19.3.1**. A metal tube containing Ar gas is sealed at one end with a thin glass or plastic window and contains a central wire well insulated from it. A potential difference of about 1000 V is applied between the central wire and the tube. Any incoming α, β or γ ray will ionize some of the Ar atoms. These Ar^+ ions are quickly accelerated to a high velocity by the large potential difference, high enough for them in turn to start ionizing further Ar atoms. Thus, for every ray that enters the tube, a large number of ions is formed and a pulse of electrical current is produced. This pulse is amplified and allowed to drive a digital electronic counter which operates on a principle similar to that of a digital watch. The number of particles passing through the tube in a given time can thus be found. Alternatively, the tube can be made to operate a meter indicating the *rate* at which radiation is passing into the Geiger-Müller tube.

Another type of detector, much used for γ rays, is the **scintillation counter**. When a γ ray penetrates a special crystal or solution, it produces a momentary flash of light (called a scintillation) which is detected by a photoelectric cell. Again the output can be amplified and fed into a counter or a meter. A third kind of detector is used to monitor how much exposure laboratory workers have been subjected to in the course of their work. This is simply a strip of photographic film. The degree to which this film is darkened is a measure of the total quantity of radiation to which the worker has been subjected.

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19.04: 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 ^{3}H (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 ^{3}He by emitting a beta particle, so that only 50.0 g of the original ^{3}H remains. After another 12.3 y—making a total of 24.6 y—another half of the remaining ^{3}H will have decayed, leaving 25.0 g of ^{3}H. After another 12.3 y—now a total of 36.9 y—another half of the remaining ^{3}H will have decayed, leaving 12.5 g of ^{3}H. This sequence of events is illustrated in Figure **19.4.1**.

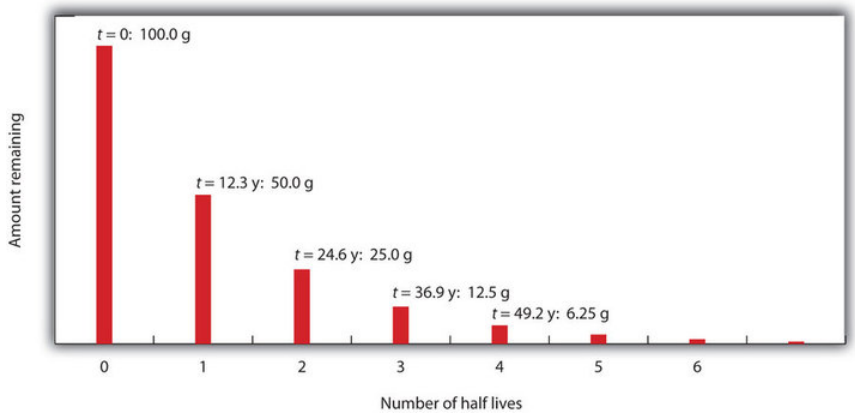


Figure **19.4.1**: Radioactive Decay. During each successive half-life, half of the initial amount will radioactively decay.

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

$$\text{amount remaining} = \text{initial amount} \times \left(\frac{1}{2}\right)^{n} \tag{19.4.1}$$

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

Example 19.4.1

The half-life of ^{20}F is 11.0 s. If a sample initially contains 5.00 g of ^{20}F, how much ^{20}F 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 19.4.1 with $n = 4$. Substituting and solving results in the following:

$$\begin{aligned}\text{amount remaining} &= 5.00\ g \times \left(\frac{1}{2}\right)^{4} \\ &= 5.00\ g \times \frac{1}{16} \\ &= 0.313\ g\end{aligned}$$

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

? Exercise 19.4.2

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

Answer

0.075 g.

Half-lives of isotopes range from fractions of a microsecond to billions of years. Table **19.4.1** lists the half-lives of some isotopes.

Table **19.4.1**: Half-Lives of Various Isotopes

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

✓ Example 19.4.2

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:

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

Then we simply count activity:

$$\begin{aligned}\textbf{initial activity } (t_0) &= \textbf{32,000 cpm}\\ \textbf{after one half-life} &= \textbf{16,000 cpm}\\ \textbf{after two half-lives} &= \textbf{8,000 cpm}\\ \textbf{after three half-lives} &= \textbf{4,000 cpm}\end{aligned}$$

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).

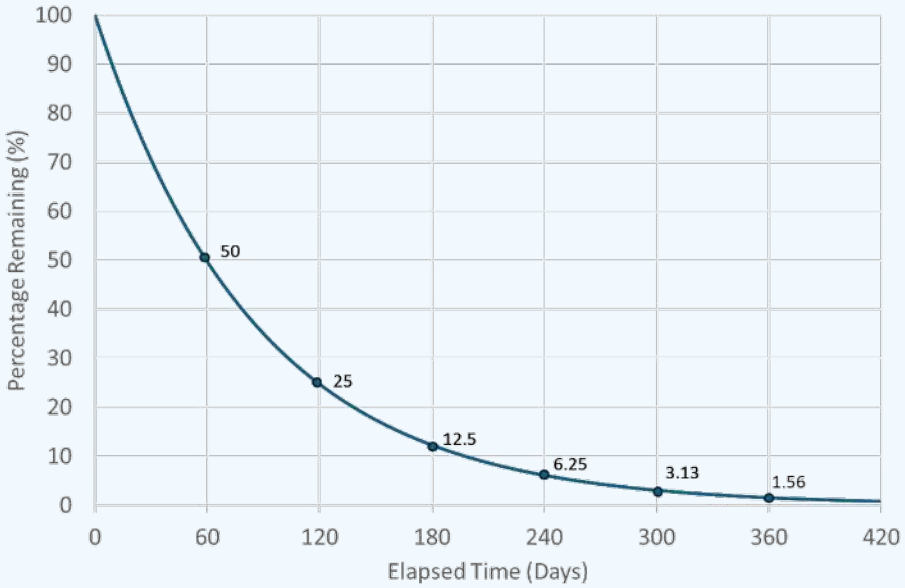
Equation 19.4.1 can be used to calculate the amount of radioactivity remaining after a given time:

$$N_t = N_0 \times (0.5)^{\text{number of half-lives}}$$

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

If we have an initial activity of $32,000$ cpm, what will the activity be after four half-lives?

$$\begin{aligned} N_t &= N_0\,(0.5)^4 \\ &= (32,000)\,(0.5)\,(0.5)\,(0.5)\,(0.5) \\ &= 2000 \text{ cpm} \end{aligned}$$



Typical radioactive decay curve. (CC BY-NC-SA 3.0; LibreTexts)

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

19.4.2 Exercise

A sample of Ac-225 originally contained 80 grams and after 50 days only 2.5 grams of the original Ac-225 remain. What is the half life of Ac-225?

Answer

5 days

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 longest-lived isotope of lawrencium, ^{262}Lr, has a half-life of 3.6 h, while the shortest-lived isotope of lawrencium, ^{252}Lr, 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.

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19.5: Uses of Radioactive Isotopes

Learning Objective

- Learn some applications of radioactivity.

Radioactive isotopes have a variety of applications. Generally, however, they are useful because either 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 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 carbon-14 to determine the steps involved in photosynthesis in plants. We know these steps because researchers followed the progress of carbon-14 throughout the process.

Radioactive Dating

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 $4.5 \times 10^9 y$. Many analyses like this, using a wide variety of isotopes, have indicated that age of the earth itself is over $4 \times 10^9 y$.

In another interesting example of radioactive dating, hydrogen-3 dating has been used to verify the stated vintages of some old fine wines.

One isotope, carbon-14, is particularly useful in determining the age of once-living artifacts. 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, albeit very low, level. Once a living thing dies, it no longer acquires carbon-14; as time passes the carbon-14 that was in the tissues decays. (The half-life of carbon-14 is 5,370 y.) If a once-living artifact is discovered and analyzed many years after its death and the remaining carbon-14 is 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 (Figure **19.5.1** purported by some to be the burial cloth of Jesus Christ and composed of flax fibers, a type of plant) 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.

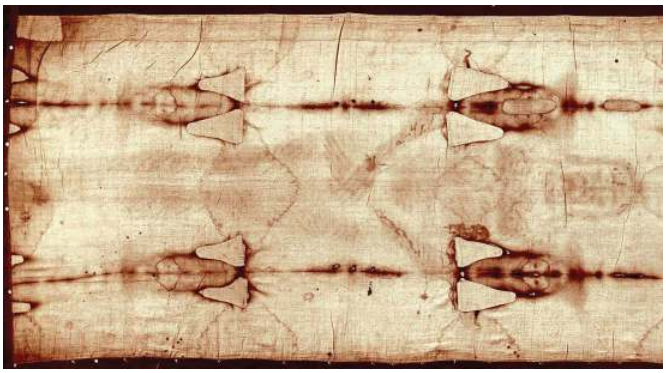


Figure **19.5.1**: Shroud of Turin. In 1989, several groups of scientists used carbon-14 dating to demonstrate that the Shroud of Turin was only 600–700 y. Many people still cling to a different notion, despite the scientific evidence.

Irradiation of Food

The radiation emitted by some radioactive substances can be used to kill microorganisms on a variety of foodstuffs, extending the shelf life of these products. Produce such as tomatoes, mushrooms, sprouts, and berries are irradiated with the emissions from coba . 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.

Medical Applications

Radioactive isotopes have numerous medical applications in diagnosing and treating illness and diseases. One example of a diagnostic application is using radioactive iodine-131 to test for thyroid activity (Figure **19.5.1**). 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 ^{131}I 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.

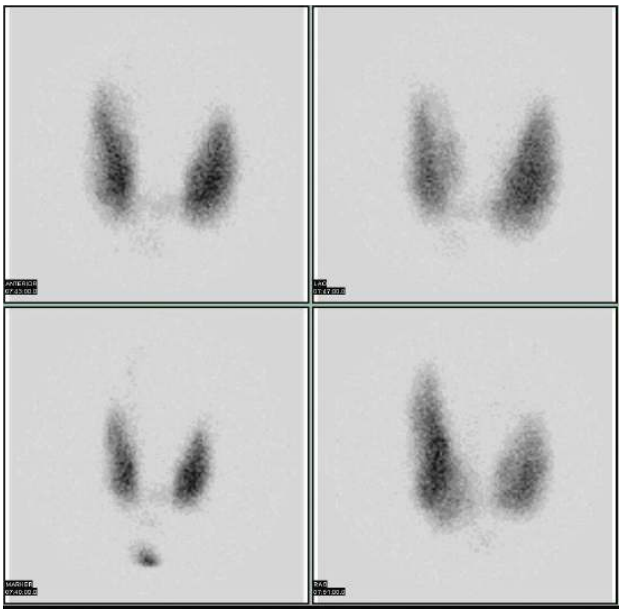


Figure **19.5.2**: Medical Diagnostics. Radioactive iodine can be used to image the thyroid gland for diagnostic purposes. Source: Scan courtesy of Myo Han, en.Wikipedia.org/wiki/File:Thyroid_scan.jpg.

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 were detected, a much larger infusion (thousands of rem, as opposed to a diagnostic dose of less than 40 rem) of iodine-131 could help destroy the tumor cells. Similarly, radioactive strontium is used to not only detect, but also to ease the pain of bone cancers. Table **19.5.1** lists several radioactive isotopes and their medical uses.

Table **19.5.1**: Some Radioactive Isotopes with 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

*The "m" means that it is a metastable form of this isotope of technetium.

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.

Food and Drink Application: Radioactivity in Wines

Wine lovers put some stock in *vintages*, or the years in which the wine grapes were grown before they were turned into wine. Wine can differ in quality depending on the vintage. Some wine lovers willingly pay much more for a bottle of wine with a certain vintage. But how does one verify that a bottle of wine was in fact part of a certain vintage? Is the label a fake? Is that stash of wine found in the basement of a French chateau really from the 1940s, or was it made in 2009?

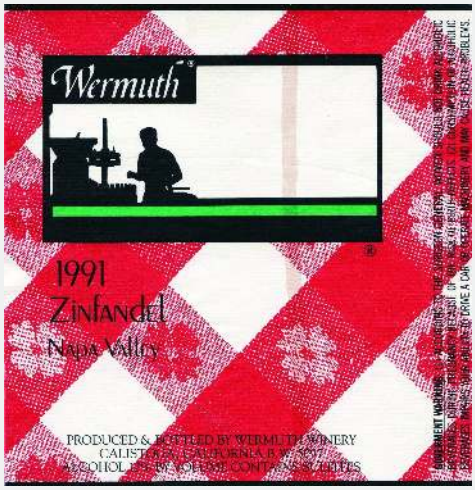


Figure **19.5.3**: A wine label. This wine label from a bottle of wine claims a vintage of 1991. Is the wine really from this vintage, or is it a fake? Radioactivity can help determine the answer. Source: Used by permission of Ralph E. Wermuth.

Cesium-137 is a radioactive isotope that has a half-life of 30.1 y. It was introduced into the atmosphere in the 1940s and 1950s by the atmospheric testing of nuclear weapons by several countries after World War II. A significant amount of cesium-137 was released during the Chernobyl nuclear disaster in 1986. As a result of this atmospheric contamination, scientists have precise measurements of the amount of cesium-137 available in the environment since 1950. Some of the isotope of cesium is taken up by living plants, including grape vines. Using known vintages, oenologists (wine scientists) can construct a detailed analysis of the cesium-137 of various wines through the years.

The verification of a wine's vintage requires the measurement of the activity of cesium-137 in the wine. By measuring the current activity of cesium-137 in a sample of wine (the gamma rays from the radioactive decay pass through glass wine bottles easily, so there's no need to open the bottle), comparing it to the known amount of cesium-137 from the vintage, and taking into account the passage of time, researchers can collect evidence for or against a claimed wine vintage.

> Before about 1950, the amount of cesium-137 in the environment was negligible, so if a wine dated before 1950 shows any measurable cesium-137 activity, it is almost surely a fake, so do not shell out lots of money for it! It may be a good wine, but it is almost definitely not over 60 years old.

Summary

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

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19.06: 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:

$$\underbrace{^{235}\text{U}}_{235.0439} \rightarrow \underbrace{^{139}\text{Ba}}_{138.9088} + \underbrace{^{94}\text{Kr}}_{93.9343} + \underbrace{2\,^{1}\text{n}}_{2\times1.0087}$$

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:

$$E = mc^2 \tag{19.6.1}$$

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:

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

Hence, 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:

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

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-in-law of Marie Curie.

Example 19.6.1

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:

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

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:

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

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

? Exercise 19.6.1

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.

Answer

$$^{1}_{0}\text{n} + {}^{238}_{92}\text{U} \rightarrow {}^{135}_{55}\text{Cs} + {}^{96}_{37}\text{Rb} + 8{}^{1}_{0}\text{n}$$

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

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 19.6.1 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.

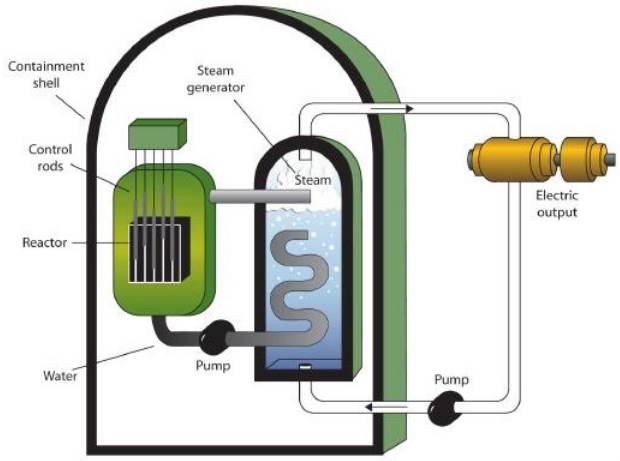


Figure 19.6.1: A Diagram of a Nuclear Power Plant for Generating Electricity. The two main components of the power plant are the nuclear reactor itself and the steam-driven turbine and electricity generator.

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:

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

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:

$$4\,{}^{1}\mathrm{H} \rightarrow {}^{4}\mathrm{He} + 2.58 \times 10^{12}\ J$$

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.

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19.07: Fission and Fusion

Learning Outcomes

- Define fission.
- Describe a nuclear chain reaction and how it is applied in both a fission bomb and in a nuclear power plant.
- Define fusion.

Nuclear Fission

The most stable nuclei are of intermediate mass. To become more stable, the heaviest nuclei are capable of splitting into smaller fragments. **Nuclear fission** *is a process in which a very heavy nucleus (mass > 200) splits into smaller nuclei of intermediate mass*. Because the smaller nuclei are more stable, the fission process releases tremendous amounts of energy. Nuclear fission may occur spontaneously or may occur as a result of bombardment. When uranium-235 is hit with a slow-moving neutron, it absorbs it and temporarily becomes the very unstable uranium-236. This nucleus splits into two medium-mass nuclei while also emitting more neutrons. The mass of the products is less than the mass of the reactants, with the lost mass being converted to energy.

Nuclear Chain Reactions

Because the fission process produces more neutrons, a chain reaction can result. A **chain reaction** *is a reaction in which the material that starts the reaction is also one of the products and can start another reaction*. Illustrated below is a nuclear chain reaction for the fission of uranium-235.

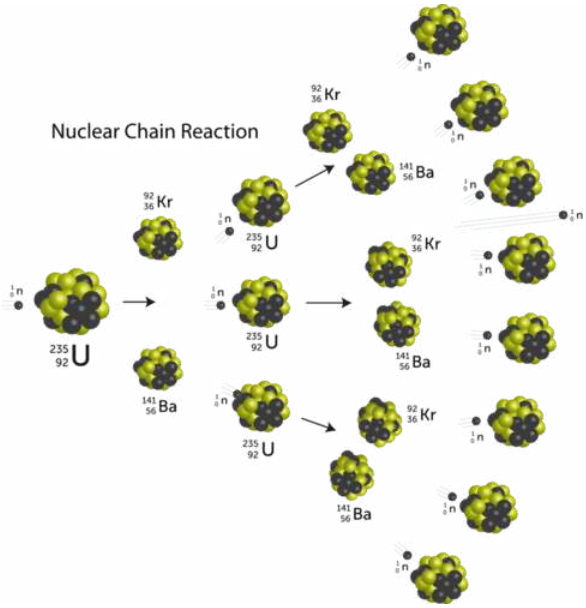


Figure 19.7.1: The nuclear chain reaction is a series of fission processes that sustains itself due to the continuous production of neutrons in each reaction.

The original uranium-235 nucleus absorbs a neutron, splits into a krypton-92 nucleus and a barium-141 nucleus, and releases three more neutrons upon splitting.

$$^{235}_{92}\mathrm{U} + ^{1}_{0}\mathrm{n} \rightarrow ^{92}_{36}\mathrm{Kr} + ^{141}_{56}\mathrm{Ba} + 3^{1}_{0}\mathrm{n} \tag{19.7.1}$$

Those three neutrons are then able to cause the fission of three more uranium-235 nuclei, each of which release more neutrons, and so on. The chain reaction continues until all of the uranium-235 nuclei have been split, or until the released neutrons escape the sample without striking any more nuclei. If the size of the original sample of uranium-235 is sufficiently small, too many neutrons escape without striking other nuclei, and the chain reaction quickly ceases. The **critical mass** *is the minimum amount of fissionable material needed to sustain a chain reaction*. Atomic bombs and nuclear reactors are two ways to harness the large energy released during nuclear fission.

Atomic Bombs - Uncontrolled Nuclear Reactions

In an atomic bomb, or fission bomb, the nuclear chain reaction is designed to be uncontrolled, releasing huge amounts of energy in a short amount of time. A critical mass of fissionable plutonium is contained within the bomb, but not at a sufficient density. Conventional explosives are used to compress the plutonium, causing it to go critical and trigger a nuclear explosion.

Nuclear Power Plants- Controlled Nuclear Reactions

A nuclear power plant (see figure below) uses a controlled fission reaction to produce large amounts of heat. The heat is then used to generate electrical energy.

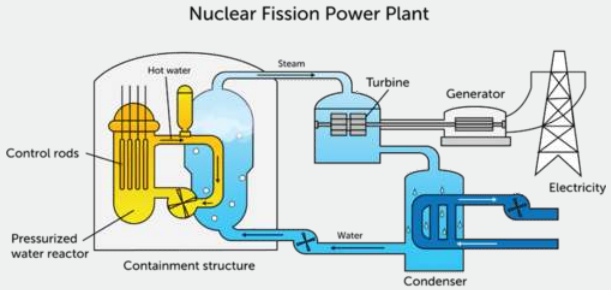


Figure **19.7.2**: A nuclear reactor harnesses the energy of nuclear fission to generate electricity.

Uranium-235, the usual fissionable material in a nuclear reactor, is first packaged into fuel rods. In order to keep the chain reaction from processing unchecked, moveable control rods are placed in between the fuel rods. **Control rods** *limit the amount of available neutrons by absorbing some of them and preventing the reaction from proceeding too rapidly*. Common control rod materials include alloys with various amounts of silver, indium, cadmium, or boron. A **moderator** *is a material that slows down high-speed neutrons*. This is beneficial because slow-moving neutrons are more efficient at splitting nuclei. Water is often used as a moderator. The heat released by the fission reaction is absorbed by constantly circulating coolant water. The coolant water releases its heat to a steam generator, which turns a turbine and generates electricity. The core of the reactor is surrounded by a containment structure that absorbs radiation.

Nuclear Fusion

The lightest nuclei are also not as stable as nuclei of intermediate mass. **Nuclear fusion** *is a process in which light-mass nuclei combine to form a heavier and more stable nucleus*. Fusion produces even more energy than fission. In the sun and other stars, four hydrogen nuclei combine at extremely high temperatures and pressures to produce a helium nucleus. The concurrent loss of mass is converted into extraordinary amounts of energy (see figure below).

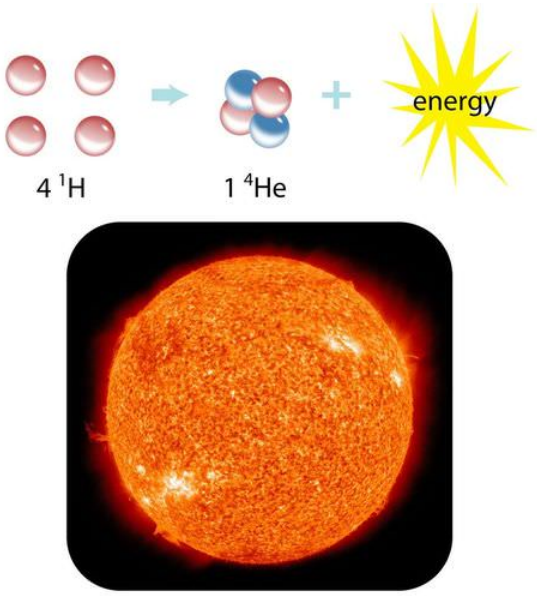


Figure 19.7.3: Nuclear fusion takes place when small nuclei combine to make larger ones. The enormous amounts of energy produced by fusion powers our sun and other stars.

Fusion is even more appealing than fission as an energy source because no radioactive waste is produced and the only reactant needed is hydrogen. However, fusion reactions only occur at very high temperatures - in excess of $40,000,000°C$. No known materials can withstand such temperatures, so there is currently no feasible way to harness nuclear fusion for energy production, although research is ongoing.

Uses of Radiation

As we saw earlier, different types of radiation vary in their abilities to penetrate through matter. Alpha particles have very low penetrating ability and are stopped by skin and clothing. Beta particles have a penetrating ability that is about 100 times that of alpha particles. Gamma rays have very high penetrating ability, and great care must be taken to avoid overexposure to gamma rays.

Exposure and Detection

Radiation emitted by radioisotopes is called ionizing radiation. **Ionizing radiation** *is radiation that has enough energy to knock electrons off the atoms of a bombarded substance and produce ions*. The **roentgen** *is a unit that measures nuclear radiation and is equal to the amount of radiation that produces* 2×10^{9} *ion pairs when it passes through* $1\ cm^{3}$ *of air.* The primary concern is that ionizing radiation can do damage to living tissues. Radiation damage is measured in rems, which stands for roentgen equivalent man . A **rem** *is the amount of ionizing radiation that does as much damage to human tissue as is done by 1 roentgen of high-voltage x-rays*. Tissue damage from ionizing radiation can cause genetic mutations due to interactions between the radiation and DNA, which can lead to cancer.

You are constantly being bombarded with background radiation from space and from geologic sources that vary depending on where you live. Average exposure is estimated to be about 0.1 rem per year. The maximum permissible does of radiation exposure for people in the general population is 0.5 rem per year. Some people are naturally at higher risk because of their occupations, so reliable instruments to detect radiation exposure have been developed. A **Geiger counter** *is a device that uses a gas-filled metal tube to detect radiation* (see figure below). When the gas is exposed to ionizing radiation, it conducts a current, and the Geiger counter registers this as audible clicks. The frequency of the clicks corresponds to the intensity of the radiation.



Figure **19.7.4**: A Geiger counter is used to detect radiation.

A **scintillation counter** *is a device that uses a phosphor-coated surface to detect radiation by the emission of bright bursts of light.* Workers who are at risk of exposure to radiation wear small portable film badges. A **film badge** *consists of several layers of photographic film that can measure the amount of radiation to which the wearer has been exposed*. Film badges are removed and analyzed at periodic intervals to ensure that the person does not become overexposed to radiation on a cumulative bases.

Medicine and Agriculture

Radioactive nuclides, such as cobalt-60, are frequently used in medicine to treat certain types of cancers. The faster growing cancer cells are exposed to the radiation and are more susceptible to damage than healthy cells. Thus, the cells in the cancerous area are killed by the exposure to high-energy radiation. Radiation treatment is risky because some healthy cells are also killed, and cells at the center of a cancerous tumor can become resistant to the radiation.

Radioactive tracers *are radioactive atoms that are incorporated into substances so that the movement of these substances can be tracked by a radiation detector*. Tracers are used in the diagnosis of cancer and other diseases. For example, iodine-131 is used to detect problems with a person's thyroid. A patient first ingests a small amount of iodine-131. About two hours later, the iodine uptake by the thyroid is determined by a radiation scan of the patient's throat. In a similar way, technetium-99 is used to detect brain tumors and liver disorders, and phosphorus-32 is used to detect skin cancer.

Radioactive tracers can be used in agriculture to test the effectiveness of various fertilizers. The fertilizer is enriched with a radioisotope, and the uptake of the fertilizer by the plant can be monitored by measuring the emitted radiation levels. Nuclear radiation is also used to prolong the shelf life of produce by killing bacteria and insects that would otherwise cause the food to spoil faster.

Contributors and Attributions

-
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19.08: Nuclear Reactors

A **nuclear reactor** is a device in which nuclear reactions are generated, and the chain reaction is controlled to release large amount of steady heat, thereby producing energy.

Introduction

Nuclear fission is the process in which the nucleus of an atom is split, forming nuclei of lighter atoms and neutrons. The mass of these products is less than the original mass. According to Einstein's equation $E = mc^2$, the small amount of missing mass is converted into a large amount of energy.

A chain reaction occurs when the neutrons released in fission collide with at least one other nuclei, causing the fission of another nuclei. The process then repeats. In today's nuclear reactors, Uranium-235 is commonly used. During each U235/92 fission, 2.5 neutrons are released on average. Note here; Uranium 235 is used because it has a fairly large nucleus which facilitates the process of fission. An explosion could only occur if the reaction becomes uncontrolled. When one mass of U-235 exceeds the mass of U-235 that is large enough to hold down a chain reaction, also known as **critical mass**, an explosion occurs. A great example of this phenomenon would be a nuclear bomb. In uncontrolled reactions, neutrons escape too quickly to maintain a chain reaction. This rapid release of nuclear energy causes an explosion. However, in a nuclear reactor, energy is being produced at a controlled, constant rate; a nuclear explosion is unlikely to occur.

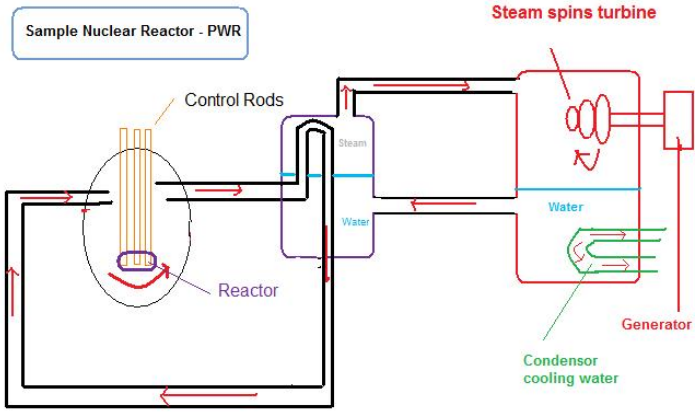


Figure 3

The opposite of a nuclear explosion, nuclear reactors are the controlled release of fission energy. They serve the purpose of converting “nuclear energy” to heat. To produce energy, a nuclear reactor contains several major components: fuel elements (or rods), control rods, and coolant/moderator, besides the vessel itself containing everything. The fuel elements contains the fissile material, typically uranium or plutonium, which is used as the fuel to undergo fission and provide the nuclear energy. The fissile material is encased in a solid cladding, made of Zircalloy (alloy of zirconium, having low capacity to absorb neutrons), to contain both the fuel and the resulting fission products and keep then from escaping into the moderator, coolant, or anywhere outside the cladding. The moderator and coolant flows between the fuel elements (or rods) moderating the neutrons and carrying away the heat. The region inside the nuclear reactor where the fuel elements undergo fission to generate heat is called the nuclear reactor core. The control rods, usually made of cadmium metal, absorb neutrons in order to control the rate of fission. By raising or lowering the control rods in the reactor, the concentration of neutrons, called the neutron flux, in the core increases or decreases respectively. The other component is the coolant. Since the process of fission produces large amounts of heat, the coolant is used to carry away the heat. The heat carried away causes incoming cooler water to turn into steam. This steam spins a turbine, which then powers an electric generator. Generally speaking, water is used, however; helium gas and liquid sodium can be used as substitutes. A pressurized water reactor (PWR) is a common design of a nuclear reactor. In a PWR, water functions as a coolant and as a moderator. A moderator slows down the neutrons, because slower moving neutrons are better at causing fission to occur. A moderator is usually water; however, graphite and heavy water can also be used. A boiling water reactor (BWR) is another common design of current nuclear reactor plants in commercial use. In a BWR, water also functions as both a coolant and moderator.

Another type of reactor used in civilian power plants in the former Soviet Union called an RBMK reactor used graphite (carbon) as a moderator, but is considered insufficiently safe.

Most of the power from nuclear fission reactors comes directly from the fission, which can be rapidly stopped by a shutdown of the reactor. However, about 7% comes from heat of decay of highly radioactive fission products, which cannot be stopped by shutting down the reactor, and must continue to be removed from the reactor to prevent overheating and damage to the reactor core. Therefore, coolant pumps must continue to be run for many hours after the reactor is shutdown to remove the decay heat, which over the course of hours eventually decreases. If the coolant pumps do not work, emergency cooling methods must be used to remove decay heat to prevent damage to the core, possible meltdown or release of highly radioactive fission products to where they should not be.

Nuclear Fusion

Nuclear Fusion is the process by which two elements collide to form a new element, releasing a tremendous amount of energy much greater than that of a fission reaction. Similar to nuclear fission, the mass of the resulting element does not exactly match the combined masses of the two smaller elements, but is converted to energy. Stars throughout the universe, including our Sun, release energy through the fusion of two hydrogen atoms into a single helium atom (Figure 3). While electrostatic forces of repulsion would normally drive the positively-charged regions of two hydrogen nuclei away from each other and prevent such a reaction, the extreme heat (15,000,000 °C in the Sun) and density of a star overcomes these forces and allows fusion to occur. With so much potential as a source of energy, the prospect of a fusion reactor on Earth has become a highly sought after technological advancement, even though the challenges of creating such a reactor are immense.

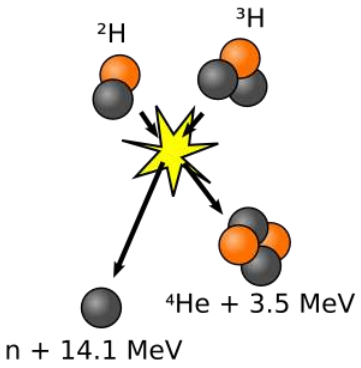


Figure 3: http://commons.wikimedia.org/wiki/File:D-t-fusion.png

The most promising reaction being attempted by scientists today to produce fusion power is the collision of two hydrogen isotopes, deuterium (^2H) and tritium (^3H), to produce a ^4He atom, a neutron, and a large quantity of energy. Just as in a star, however, the nuclei of the hydrogen isotopes repel each other and must be brought together for fusion at extremely high thermal energies reaching 150,000,000 °C (ten times greater than that required in the Sun). At temperatures this high, the reactant gases transform into a *plasma*- a hot, fully ionized gas consisting of atomic nuclei and electrons. A problem of central importance to the as of yet theoretical fusion reactor is containing that plasma so that it does not lose thermal energy by touching surrounding materials. A collaborative effort funded by multiple nations known as the International Thermonuclear Experimental Reactor (ITER) aims to solve this problem by confining the plasma in a magnetic field created by powerful superconducting magnets. Such a design is known as a tokamak reactor (See Figure 4).



Figure 4: http://commons.wikimedia.org/wiki/File:Tcv_int.jpg

While the feasibility of a controlled fusion reaction occurring on Earth has yet to be adequately verified, the potential benefits of fusion as opposed to fission may be immense. Deuterium may be extracted from water and lithium, the tritium source for the fusion reaction, is estimated to exist on earth in quantities that will last for one million years. Additionally, there is far less nuclear waste that decays much faster compared to that produced by fission.

Nuclear Safety

There have been three major accidents involving full-scale civilian nuclear power plants.

- The first occurred in 1979 at Three Mile Island Unit 2 in Pennsylvania. Due mechanical failure, the main water pumps stopped running, leading to a partial meltdown of the fuel rods. Excessive heat caused a fracture in one of the reactors, allowing a small amount of radioactive steam into the atmosphere. Fortunately, no one was killed or even injured. This incident also lead to heightened regulation and safety precautions of nuclear reactors in the United States.
- On April 26, 1986, the worst accident in nuclear history occurred in Chernobyl, Ukraine. During a routine test, an uncontrollable power surge burned the control rods, and massive amounts of radioactive smoke were released. 237 people suffered from acute radiation sickness, and 31 died within the first three months of the accident. Other effects of the radiation included an increase in down's syndrome, chromosomal aberrations, neural tube defects, and thyroid cancer. Perhaps the most important effect was psychological as the accident caused severe anxiety for the survivors and a general lack of trust in the government.



- Due to a severe earthquake and tsunami in Japan in March 11, 2011, several BWR (Boiling Water Reactor) nuclear reactors at the Fukushima power plant lost electrical power for cooling, underwent explosions, and suffered reactor core damage from post-shutdown decay heat coming from highly radioactive fission products. Workers eventually pumped seawater into the reactors to cool them down and limit any further damage.

Problems

1. What is the function of control rods in a nuclear reactor?
2. True or False? The accident at Three Mile Island led to the radiation poisoning of possibly hundreds of thousands of people.

3. How does nuclear fission lead to a chain reaction?
4. What two functions can water serve in a nuclear reactor?
5. What is critical mass? What will occur if the mass of a reaction surpasses its critical mass?

Answers

1. In a fission reactor, control rods absorb neutrons to control the rate of a reaction. Lowering the rods into the reactor decreases the rate of fission and removing them increases the rate.
2. False. The accident at Three Mile Island was only minor and no one was killed or injured.
3. When a neutron strikes a fissile material breaking it into smaller fragments, more neutrons are released (2.5 on average). These neutrons then collide with other fissile atoms producing even more neutrons, which continue the chain reaction either in a stable manner (reactor) or violently (atomic bomb).
4. In a fission reactor, water serves as a moderator (slows down highly energetic neutrons to the appropriate thermal energy for a reaction) and produces steam by coming into contact with the hot water near the reactor and transferring heat. This steam can then power turbines to generate electricity.
5. The critical mass of a fission reactor is the mass of fissile material required to maintain a chain reaction. If the mass of a reaction surpasses its critical mass, the result is an uncontrolled chain reaction that culminates in a large explosion (this is how an atomic bomb works).

External Links

For more information on the subject of nuclear reactor, the following links may be helpful:

- http://en.Wikipedia.org/wiki/Nuclear_Reactor_Technology
- http://www.howstuffworks.com/nuclear-power.htm
- http://www.youtube.com/watch?v=rvAJ_u3Q0Hw&feature=related
- people.moreheadstate.edu/students/alsimp01 /files/technology.html

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19.09: Breeder Reactors

Because $^{235}_{92}\mathrm{U}$ is only 0.7 percent of naturally occurring uranium, its supply is fairly limited and could well only last for about 50 years of full-scale use. The other 99 percent of the uranium can also be utilized if it is first converted into plutonium by neutron bombardment:

$$^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{239}_{94}\mathrm{Pu} + 2\,{}^{0}_{-1}\mathrm{e}$$

$^{239}_{94}\mathrm{Pu}$ is also fissionable, and so it could be used in a nuclear reactor as well as $^{235}_{92}\mathrm{U}$.

The production of plutonium can be carried out in a breeder reactor which not only produces energy like other reactors but is designed to allow some of the fast neutrons to bombard the $^{235}_{92}\mathrm{U}$, producing plutonium at the same time. More fuel is then produced than is consumed.

Breeder reactors present additional safety hazards to those already outlined. They operate at higher temperatures and use very reactive liquid metals such as sodium in their cooling systems, and so the possibility of a serious accident is higher. In addition the large quantities of plutonium which would be produced in a breeder economy would have to be carefully safeguarded. Plutonium is an α emitter and is very dangerous if taken internally. Its half-life is 24,000 years, and so it will remain in the environment for a long time if dispersed. Moreover, $^{239}_{94}\mathrm{Pu}$ can be separated chemically (not by the much more expensive gaseous diffusion used to concentrate $^{235}_{92}\mathrm{U}$ from fission products and used to make bombs. Such a material will obviously be attractive to terrorist groups, as well as to countries which are not currently capable of producing their own atomic weapons.

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19.10: Nuclear Fusion

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19.11: Biological Effects of Radiation

Skills to Develop

- Describe the biological impact of ionizing radiation
- Define units for measuring radiation exposure
- Explain the operation of common tools for detecting radioactivity
- List common sources of radiation exposure in the US

The increased use of radioisotopes has led to increased concerns over the effects of these materials on biological systems (such as humans). All radioactive nuclides emit high-energy particles or electromagnetic waves. When this radiation encounters living cells, it can cause heating, break chemical bonds, or ionize molecules. The most serious biological damage results when these radioactive emissions fragment or ionize molecules. For example, alpha and beta particles emitted from nuclear decay reactions possess much higher energies than ordinary chemical bond energies. When these particles strike and penetrate matter, they produce ions and molecular fragments that are extremely reactive. The damage this does to biomolecules in living organisms can cause serious malfunctions in normal cell processes, taxing the organism's repair mechanisms and possibly causing illness or even death (Figure **19.11.1**).

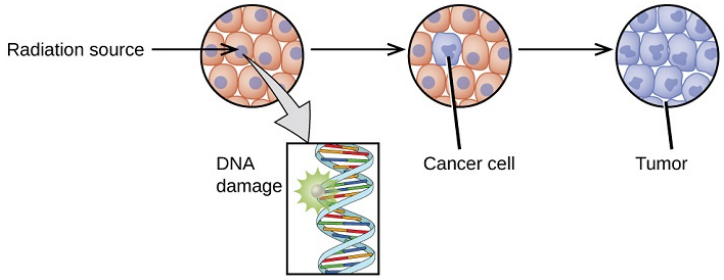


Figure* 19.11.1: Radiation can harm biological systems by damaging the DNA of cells. If this damage is not properly repaired, the cells may divide in an uncontrolled manner and cause cancer.*

Ionizing vs. Nonionizing Radiation

There is a large difference in the magnitude of the biological effects of nonionizing radiation (for example, light and microwaves) and ionizing radiation, emissions energetic enough to knock electrons out of molecules (for example, α and β particles, γ rays, X-rays, and high-energy ultraviolet radiation) (Figure **19.11.2**).

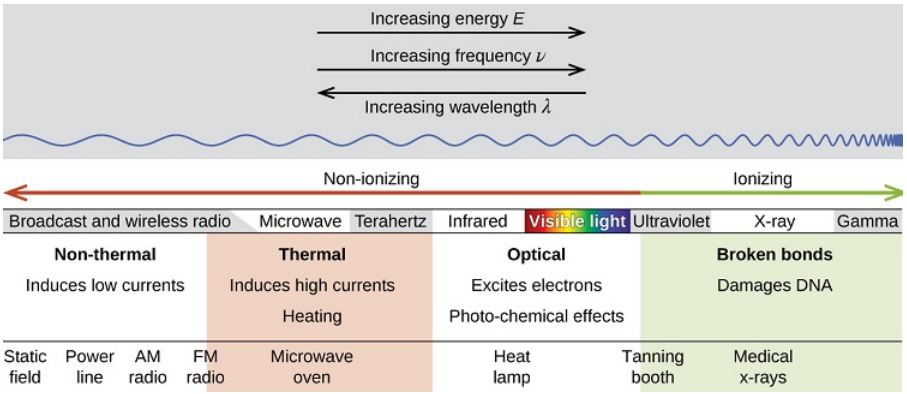


Figure* 19.11.2: Lower frequency, lower-energy electromagnetic radiation is nonionizing, and higher frequency, higher-energy electromagnetic radiation is ionizing.*

Energy absorbed from nonionizing radiation speeds up the movement of atoms and molecules, which is equivalent to heating the sample. Although biological systems are sensitive to heat (as we might know from touching a hot stove or spending a day at the beach in the sun), a large amount of nonionizing radiation is necessary before dangerous levels are reached. Ionizing radiation,

however, may cause much more severe damage by breaking bonds or removing electrons in biological molecules, disrupting their structure and function. The damage can also be done indirectly, by first ionizing H_2O (the most abundant molecule in living organisms), which forms a H_2O^+ ion that reacts with water, forming a hydronium ion and a hydroxyl radical:

$$H_2O + \text{radiation} \xrightarrow{e^-} H_2O^+ + H_2O \longrightarrow H_3O^+ + OH^\bullet$$

Because the hydroxyl radical has an unpaired electron, it is highly reactive. (This is true of any substance with unpaired electrons, known as a free radical.) This hydroxyl radical can react with all kinds of biological molecules (DNA, proteins, enzymes, and so on), causing damage to the molecules and disrupting physiological processes. Examples of direct and indirect damage are shown in Figure **19.11.3**.

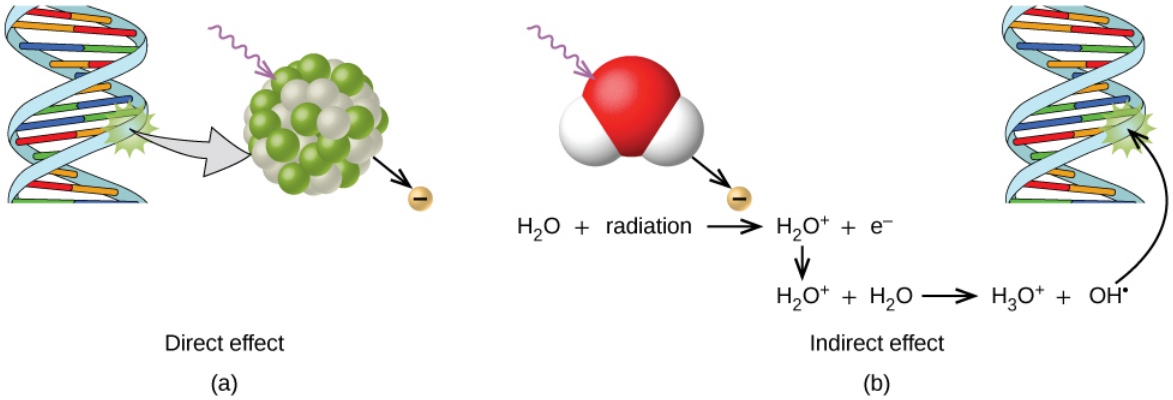


***Figure* 19.11.3**: *Ionizing radiation can (a) directly damage a biomolecule by ionizing it or breaking its bonds, or (b) create an H_2O^+ ion, which reacts with H_2O to form a hydroxyl radical, which in turn reacts with the biomolecule, causing damage indirectly.*

Biological Effects of Exposure to Radiation

Radiation can harm either the whole body (somatic damage) or eggs and sperm (genetic damage). Its effects are more pronounced in cells that reproduce rapidly, such as the stomach lining, hair follicles, bone marrow, and embryos. This is why patients undergoing radiation therapy often feel nauseous or sick to their stomach, lose hair, have bone aches, and so on, and why particular care must be taken when undergoing radiation therapy during pregnancy.

Different types of radiation have differing abilities to pass through material (Figure **19.11.4**). A very thin barrier, such as a sheet or two of paper, or the top layer of skin cells, usually stops alpha particles. Because of this, alpha particle sources are usually not dangerous if outside the body, but are quite hazardous if ingested or inhaled (see the Chemistry in Everyday Life feature on Radon Exposure). Beta particles will pass through a hand, or a thin layer of material like paper or wood, but are stopped by a thin layer of metal. Gamma radiation is very penetrating and can pass through a thick layer of most materials. Some high-energy gamma radiation is able to pass through a few feet of concrete. Certain dense, high atomic number elements (such as lead) can effectively attenuate gamma radiation with thinner material and are used for shielding. The ability of various kinds of emissions to cause ionization varies greatly, and some particles have almost no tendency to produce ionization. Alpha particles have about twice the ionizing power of fast-moving neutrons, about 10 times that of β particles, and about 20 times that of γ rays and X-rays.

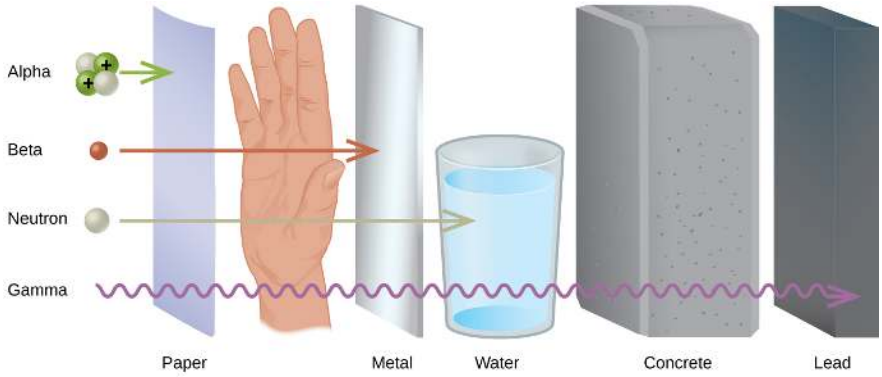


Figure* 19.11.4*: *The ability of different types of radiation to pass through material is shown. From least to most penetrating, they are alpha < beta < neutron < gamma.*

For many people, one of the largest sources of exposure to radiation is from radon gas (Rn-222). Radon-222 is an α emitter with a half–life of 3.82 days. It is one of the products of the radioactive decay series of U-238, which is found in trace amounts in soil and rocks. The radon gas that is produced slowly escapes from the ground and gradually seeps into homes and other structures above. Since it is about eight times more dense than air, radon gas accumulates in basements and lower floors, and slowly diffuses throughout buildings (Figure 19.11.5).

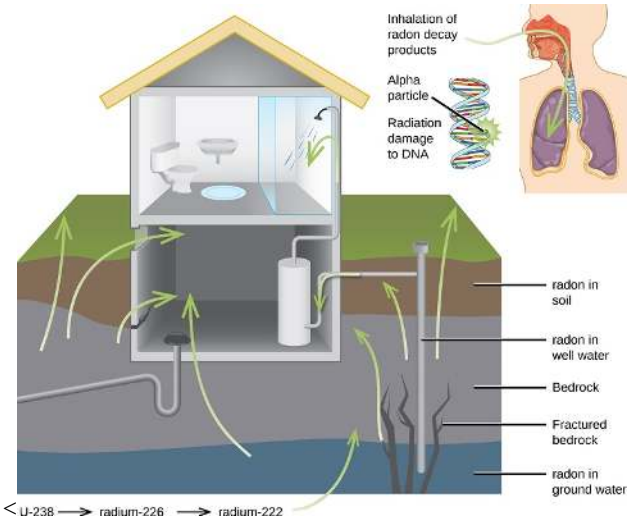


Figure* 19.11.5*: *Radon-222 seeps into houses and other buildings from rocks that contain uranium-238, a radon emitter. The radon enters through cracks in concrete foundations and basement floors, stone or porous cinderblock foundations, and openings for water and gas pipes.*

Radon is found in buildings across the country, with amounts depending on where you live. The average concentration of radon inside houses in the US (1.25 pCi/L) is about three times the levels found in outside air, and about one in six houses have radon levels high enough that remediation efforts to reduce the radon concentration are recommended. Exposure to radon increases one's risk of getting cancer (especially lung cancer), and high radon levels can be as bad for health as smoking a carton of cigarettes a day. Radon is the number one cause of lung cancer in nonsmokers and the second leading cause of lung cancer overall. Radon exposure is believed to cause over 20,000 deaths in the US per year.

Measuring Radiation Exposure

Several different devices are used to detect and measure radiation, including Geiger counters, scintillation counters (scintillators), and radiation dosimeters (Figure 19.11.6). Probably the best-known radiation instrument, the Geiger counter (also called the Geiger-Müller counter) detects and measures radiation. Radiation causes the ionization of the gas in a Geiger-Müller tube. The rate of ionization is proportional to the amount of radiation. A scintillation counter contains a scintillator—a material that emits light

(luminesces) when excited by ionizing radiation—and a sensor that converts the light into an electric signal. Radiation dosimeters also measure ionizing radiation and are often used to determine personal radiation exposure. Commonly used types are electronic, film badge, thermoluminescent, and quartz fiber dosimeters.



Figure **19.11.6*:*** *Devices such as (a) Geiger counters, (b) scintillators, and (c) dosimeters can be used to measure radiation. (credit c: modification of work by "osaMu"/Wikimedia commons).*

A variety of units are used to measure various aspects of radiation (Table **19.11.1**). The SI unit for rate of radioactive decay is the becquerel (Bq), with 1 Bq = 1 disintegration per second. The curie (Ci) and millicurie (mCi) are much larger units and are frequently used in medicine (1 curie = 1 Ci = $\mathbf{3.7 \times 10^{10}}$ disintegrations per second). The SI unit for measuring radiation dose is the gray (Gy), with 1 Gy = 1 J of energy absorbed per kilogram of tissue. In medical applications, the radiation absorbed dose (rad) is more often used (1 rad = 0.01 Gy; 1 rad results in the absorption of 0.01 J/kg of tissue). The SI unit measuring tissue damage caused by radiation is the sievert (Sv). This takes into account both the energy and the biological effects of the type of radiation involved in the radiation dose.

Table **19.11.1*:*** *Units Used for Measuring Radiation*

Measurement Purpose	Unit	Quantity Measured	Description
activity of source	becquerel (Bq)	radioactive decays or emissions	amount of sample that undergoes 1 decay/second
	curie (Ci)		amount of sample that undergoes $\mathbf{3.7 \times 10^{10}}$ **decays/second**
absorbed dose	gray (Gy)	energy absorbed per kg of tissue	1 Gy = 1 J/kg tissue
	radiation absorbed dose (rad)		1 rad = 0.01 J/kg tissue
biologically effective dose	sievert (Sv)	tissue damage	Sv = RBE × Gy
	roentgen equivalent for man (rem)		Rem = RBE × rad

The roentgen equivalent for man (rem) is the unit for radiation damage that is used most frequently in medicine (1 rem = 1 Sv). Note that the tissue damage units (rem or Sv) includes the energy of the radiation dose (rad or Gy) along with a biological factor referred to as the RBE (for relative biological effectiveness) that is an approximate measure of the relative damage done by the radiation. These are related by:

$$\textbf{number of rems} = \textbf{RBE} \times \textbf{number of rads} \tag{19.11.1}$$

with RBE approximately 10 for α radiation, 2(+) for protons and neutrons, and 1 for β and γ radiation.

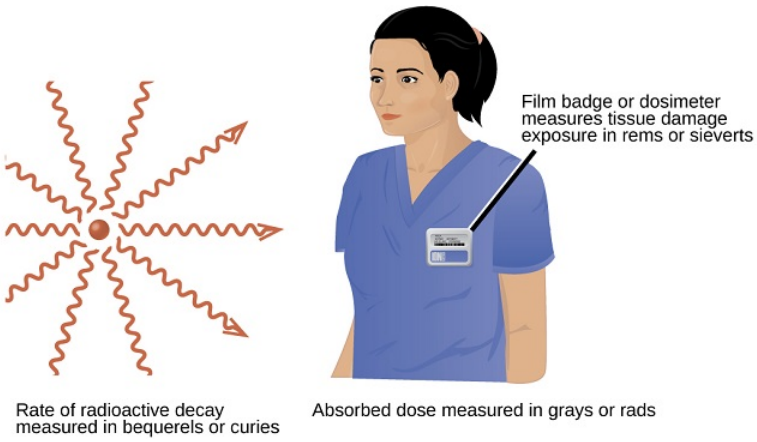


Figure* 19.11.7*: *Different units are used to measure the rate of emission from a radioactive source, the energy that is absorbed from the source, and the amount of damage the absorbed radiation does.*

Example 19.11.1: Amount of Radiation

Cobalt-60 ($t_{1/2}$ = 5.26 y) is used in cancer therapy since the γ rays it emits can be focused in small areas where the cancer is located. A 5.00-g sample of Co-60 is available for cancer treatment.

a. What is its activity in Bq?
b. What is its activity in Ci?

Solution

The activity is given by:

$$\text{Activity} = \lambda N = \left(\frac{\ln 2}{t_{1/2}}\right) N \tag{19.11.2}$$

$$= \left(\frac{\ln 2}{5.26\ \text{y}}\right) \times 5.00\ \text{g} = 0.659\ \frac{\text{g}}{\text{y}}\ \text{of}\ {}^{60}\text{Co that decay}$$

And to convert this to decays per second:

$$0.659\ \frac{\text{g}}{\text{y}} \times \frac{\text{y}}{365\ \text{day}} \times \frac{1\ \text{day}}{24\ \text{hours}} \times \frac{1\ \text{h}}{3,600\ \text{s}} \times \frac{1\ \text{mol}}{59.9\ \text{g}} \times \frac{6.02 \times 10^{23}\ \text{atoms}}{1\ \text{mol}} \times \frac{1\ \text{decay}}{1\ \text{atom}}$$

$$= 2.10 \times 10^{14}\ \frac{\text{decay}}{\text{s}}$$

(a) Since $1\ \text{Bq} = 1\ \frac{\text{decay}}{\text{s}}$, the activity in Becquerel (Bq) is:

$$2.10 \times 10^{14} \frac{\text{decay}}{\text{s}} \times \left(\frac{1\ \text{Bq}}{1\ \frac{\text{decay}}{\text{s}}}\right) = 2.10 \times 10^{14}\ \text{Bq}$$

(b) Since $1\ \text{Ci} = 3.7 \times 10^{11}\ \frac{\text{decay}}{\text{s}}$, the activity in curie (Ci) is:

$$2.10 \times 10^{14} \frac{\text{decay}}{\text{s}} \times \left(\frac{1\ \text{Ci}}{3.7 \times 10^{11}\ \frac{\text{decay}}{\text{s}}}\right) = 5.7 \times 10^{2}\ \text{Ci}$$

Exercise 19.11.1

Tritium is a radioactive isotope of hydrogen ($t_{1/2} = 12.32$ years) that has several uses, including self-powered lighting, in which electrons emitted in tritium radioactive decay cause phosphorus to glow. Its nucleus contains one proton and two neutrons, and the atomic mass of tritium is 3.016 amu. What is the activity of a sample containing 1.00mg of tritium (a) in Bq and (b) in Ci?

Answer a

$3.56 \times 10^{11}\text{Bq}$

Answer b

0.962 Ci

Effects of Long-term Radiation Exposure on the Human Body

The effects of radiation depend on the type, energy, and location of the radiation source, and the length of exposure. As shown in Figure 19.11.8, the average person is exposed to background radiation, including cosmic rays from the sun and radon from uranium in the ground (see the Chemistry in Everyday Life feature on Radon Exposure); radiation from medical exposure, including CAT scans, radioisotope tests, X-rays, and so on; and small amounts of radiation from other human activities, such as airplane flights (which are bombarded by increased numbers of cosmic rays in the upper atmosphere), radioactivity from consumer products, and a variety of radionuclides that enter our bodies when we breathe (for example, carbon-14) or through the food chain (for example, potassium-40, strontium-90, and iodine-131).

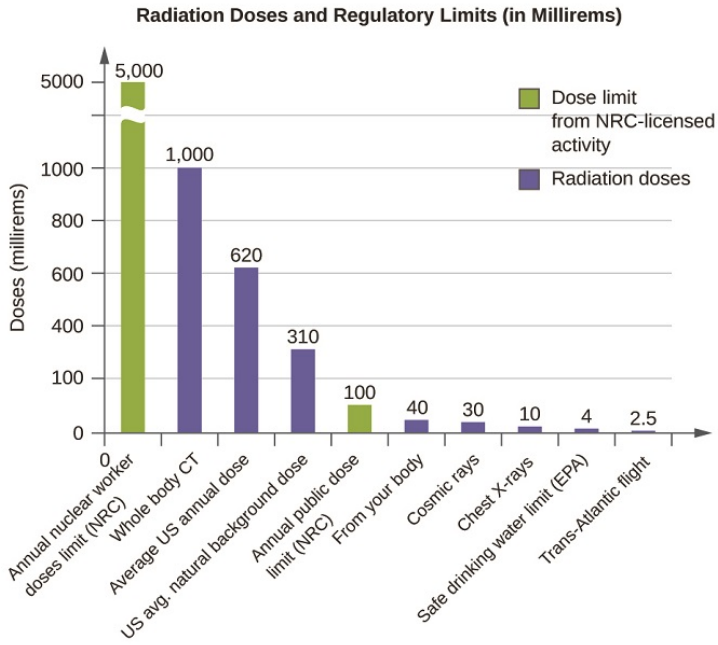


Figure* 19.11.8: The total annual radiation exposure for a person in the US is about 620 mrem. The various sources and their relative amounts are shown in this bar graph. (source: U.S. Nuclear Regulatory Commission).*

A short-term, sudden dose of a large amount of radiation can cause a wide range of health effects, from changes in blood chemistry to death. Short-term exposure to tens of rems of radiation will likely cause very noticeable symptoms or illness; a dose of about 500 rems is estimated to have a 50% probability of causing the death of the victim within 30 days of exposure. Exposure to radioactive emissions has a cumulative effect on the body during a person's lifetime, which is another reason why it is important to avoid any unnecessary exposure to radiation. Health effects of short-term exposure to radiation are shown in Table 19.11.2.

Table* 19.11.2: Health Effects of Radiation*

Exposure (rem)	Health Effect	Time to Onset (without treatment)
5–10	changes in blood chemistry	—
50	nausea	hours
55	fatigue	—
70	vomiting	—
75	hair loss	2–3 weeks
90	diarrhea	—
100	hemorrhage	—
400	possible death	within 2 months
1000	destruction of intestinal lining	—
	internal bleeding	—
	death	1–2 weeks
2000	damage to central nervous system	—
	loss of consciousness;	minutes
	death	hours to days

It is impossible to avoid some exposure to ionizing radiation. We are constantly exposed to background radiation from a variety of natural sources, including cosmic radiation, rocks, medical procedures, consumer products, and even our own atoms. We can minimize our exposure by blocking or shielding the radiation, moving farther from the source, and limiting the time of exposure.

Summary

We are constantly exposed to radiation from a variety of naturally occurring and human-produced sources. This radiation can affect living organisms. Ionizing radiation is the most harmful because it can ionize molecules or break chemical bonds, which damages the molecule and causes malfunctions in cell processes. It can also create reactive hydroxyl radicals that damage biological molecules and disrupt physiological processes. Radiation can cause somatic or genetic damage, and is most harmful to rapidly reproducing cells. Types of radiation differ in their ability to penetrate material and damage tissue, with alpha particles the least penetrating but potentially most damaging and gamma rays the most penetrating.

Various devices, including Geiger counters, scintillators, and dosimeters, are used to detect and measure radiation, and monitor radiation exposure. We use several units to measure radiation: becquerels or curies for rates of radioactive decay; gray or rads for energy absorbed; and rems or sieverts for biological effects of radiation. Exposure to radiation can cause a wide range of health effects, from minor to severe, and including death. We can minimize the effects of radiation by shielding with dense materials such as lead, moving away from the source, and limiting time of exposure.

Footnotes

1. 1 Source: US Environmental Protection Agency

Glossary

becquerel (Bq)

SI unit for rate of radioactive decay; 1 Bq = 1 disintegration/s

curie (Ci)

larger unit for rate of radioactive decay frequently used in medicine; 1 Ci = 3.7×10^{10} disintegrations/s

Geiger counter

instrument that detects and measures radiation via the ionization produced in a Geiger-Müller tube

gray (Gy)

SI unit for measuring radiation dose; 1 Gy = 1 J absorbed/kg tissue

ionizing radiation

radiation that can cause a molecule to lose an electron and form an ion

millicurie (mCi)

larger unit for rate of radioactive decay frequently used in medicine; 1 Ci = 3.7×10^{10} disintegrations/s

nonionizing radiation

radiation that speeds up the movement of atoms and molecules; it is equivalent to heating a sample, but is not energetic enough to cause the ionization of molecules

radiation absorbed dose (rad)

SI unit for measuring radiation dose, frequently used in medical applications; 1 rad = 0.01 Gy

radiation dosimeter

device that measures ionizing radiation and is used to determine personal radiation exposure

relative biological effectiveness (RBE)

measure of the relative damage done by radiation

roentgen equivalent man (rem)

unit for radiation damage, frequently used in medicine; 1 rem = 1 Sv

scintillation counter

instrument that uses a scintillator—a material that emits light when excited by ionizing radiation—to detect and measure radiation

sievert (Sv)

SI unit measuring tissue damage caused by radiation; takes into account energy and biological effects of radiation

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CHAPTER OVERVIEW

1.16: Back Matter

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CHAPTER OVERVIEW

10: Introduction to Energy

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In previous science classes you may have learned that one way to distinguish chemical changes from physical changes is that physical changes - such as the melting and freezing of water - are reversible but that chemical changes are not. In this unit we will see that this simple answer is not necessarily what it seems.

10.1: Conservation of Mass - There is No New Matter

10.2: Energy

10.3: Energy and Chemical and Physical Change

10.4: Internal Energy

10.5: Work and Heat

10.6: Enthalpy and Chemical Reactions

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10.1: Conservation of Mass - There is No New Matter

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It may seem as though burning destroys matter, but the same amount, or mass, of matter still exists after a campfire as before. Look at Figure 10.1.1 below. It shows that when wood burns, it combines with oxygen and changes not only to ashes, but also to carbon dioxide and water vapor. The gases float off into the air, leaving behind just the ashes. Suppose you had measured the mass of the wood before it burned and the mass of the ashes after it burned. Also suppose you had been able to measure the oxygen used by the fire and the gases produced by the fire. What would you find? The total mass of matter after the fire would be the same as the total mass of matter before the fire.

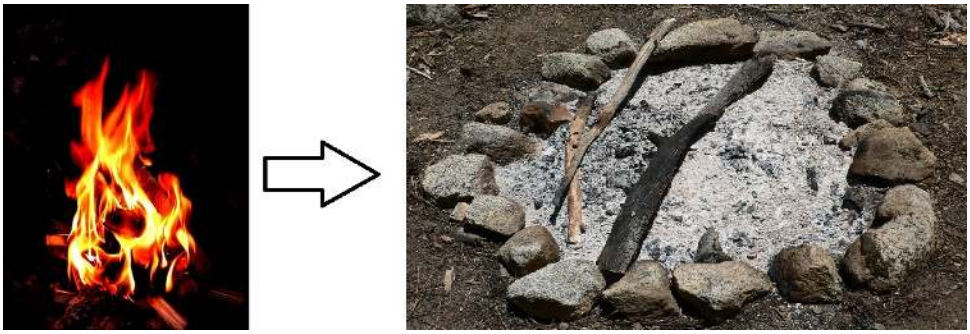


Figure 10.1.1: Burning is a chemical process. The flames caused as a result of a fuel undergoing combustion (burning). Images used with permission (CC BY-SA 2.5; Einar Helland Berger for fire and Walter Siegmund for ash).

Law of Conservation of Mass

The law of conservation of mass was created in 1789 by a French chemist, Antoine Lavoisier. The **law of conservation of mass** states that matter cannot be created or destroyed in a chemical reaction. For example, when wood burns, the mass of the soot, ashes, and gases, equals the original mass of the charcoal and the oxygen when it first reacted. So the mass of the product equals the mass of the reactant. A reactant is when two or more elements chemically interact to make a new substance and a product is the substance that is formed as the result of a chemical reaction (Video 10.1.1). Mass and matter may not be able to be created or destroyed, but it can change forms to other substances like liquids, gasses, solids, etc.



Video* 10.1.1*: *This is a nice little demonstration showing the Conservation of Mass in action.*

It's important to know the law well because if you're in a situation where there's a 300 kg tree that is burning down, when it is done burning down, there are only ashes left and all of them together weigh 10 kg. Well, it makes you wonder where the other 290 kg went. The missing 290 kg was released into the atmosphere as smoke so the only thing left that you could see was the 10 kg of ash, and if you knew the law of conservation of mass then you would know that the other 290 kg had to go somewhere because it had to equal the mass of the tree before it burnt down.

Example 10.1.1

If heating 10.0 grams of calcium carbonate ($CaCO_3$) produces 4.4 g of carbon dioxide (CO_2) and 5.6 g of calcium oxide (CaO), show that these observations are in agreement with the law of conservation of mass.

Solution

$$\text{Mass of the reactants} = \text{Mass of the products}$$

$$10.0\,\text{g of } CaCO_3 = 4.4\,\text{g of } CO_2 + 5.6\,\text{g of CaO}$$

$$10.0\,\text{g of reactant} = 10.0\,\text{g of products}$$

Because the mass of the reactant is equal to the mass of the products, the observations are in agreement with the law of conservation of mass.

Exercise 10.1.1

Potassium hydroxide (**KOH**) readily reacts with carbon dioxide (CO_2) to produce Potassium carbonate (K_2CO_3) and water (H_2O). How many grams of potassium carbonate is produced if 224.4 g of **KOH** reacted with 88.0 g of CO_2. The reaction also produced 36.0 g of water.

Answer

276.4 g of potassium carbonate

The Law is also applicable to both chemical and physical changes, for example if you have an ice cube that melts into a liquid and if you heat that liquid up, it becomes a gas. It looks like it disappeared, but it but it is still there.

Summary

- Burning and other changes in matter do not destroy matter.
- The mass of matter is always the same before and after the changes occur.
- The law of conservation of mass states that matter cannot be created or destroyed.

Contributors and Attributions

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10.2: Energy

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Learning Objectives

- Define heat and work.
- Distinguish between kinetic energy and potential energy.
- State the law of conservation of matter and energy.

Just like matter, energy is a term that we are all familiar with and use on a daily basis. Before you go on a long hike, you eat an *energy* bar; every month, the *energy* bill is paid; on TV, politicians argue about the *energy* crisis. But what is energy? If you stop to think about it, energy is very complicated. When you plug a lamp into an electric socket, you see energy in the form of light, but when you plug a heating pad into that same socket, you only feel warmth. Without energy, we couldn't turn on lights, we couldn't brush our teeth, we couldn't make our lunch, and we couldn't travel to school. In fact, without energy, we couldn't even wake up because our bodies require energy to function. We use energy for every single thing that we do, whether we're awake or asleep.

Ability to Do Work or Produce Heat

When we speak of *using* energy, we are really referring to *transferring* energy from one place to another. When you use energy to throw a ball, you transfer energy from your body to the ball, and this causes the ball to fly through the air. When you use energy to warm your house, you transfer energy from the furnace to the air in your home, and this causes the temperature in your house to rise. Although energy is used in many kinds of different situations, all of these uses rely on energy being transferred in one of two ways. Energy can be *transferred* as *heat* or as *work*.

When scientists speak of ***heat***, they are referring to energy that is transferred from an object with a higher temperature to an object with a lower temperature as a result of the temperature difference. Heat will "flow" from the hot object to the cold object until both end up at the same temperature. When you cook with a metal pot, you witness energy being transferred in the form of heat. Initially, only the stove element is hot – the pot and the food inside the pot are cold. As a result, heat moves from the hot stove element to the cold pot. After a while, enough heat is transferred from the stove to the pot, raising the temperature of the pot and all of its contents (Figure **10.2.1**).



Figure* 10.2.1*: *Energy is transferred as heat from the hot stove element to the cooler pot until the pot and its contents become just as hot as the element. The energy that is transferred into the pot as heat is then used to cook the food.*

Heat is only one way in which energy can be transferred. Energy can also be transferred as **work**. The scientific definition of work is *force (any push or pull) applied over a distance*. Whenever you push an object and cause it to move, you've done work, and you've transferred some of *your* energy to the object. At this point, it's important to warn you of a common misconception. Sometimes we think that the amount of work done can be measured by the amount of effort put in. This may be true in everyday life, but it isn't true in science. By definition, scientific work requires that force be applied *over a distance*. It does not matter how hard you push or how hard you pull. If you have not moved the object, you haven't done any work.

So far, we've talked about the two ways in which energy can be transferred from one place, or object, to another. Energy can be transferred as heat, and energy can be transferred as work. But the question still remains – *what IS energy*? We'll try to at least partially tackle that question in the next section.

Kinetic Energy

Machines use energy, our bodies use energy, energy comes from the sun, energy comes from volcanoes, energy causes forest fires, and energy helps us to grow food. With all these seemingly different types of energy, it's hard to believe that there are really only two different *forms* of energy – *kinetic energy* and *potential energy*. **Kinetic energy** is energy associated with motion. When an object is moving, it has kinetic energy. When the object stops moving, it has no kinetic energy. While all moving objects have kinetic energy, not all moving objects have the same amount of kinetic energy. The amount of kinetic energy possessed by an object is determined by its mass and its speed. The heavier an object is and the faster it is moving, the more kinetic energy it has.

Kinetic energy is very common, and it's easy to spot examples of it in the world around you. Sometimes we even try to capture kinetic energy and use it to power things like our home appliances. If you're from California, you might have driven through the Tehachapi Pass near Mojave or the Montezuma Hills in Solano County and seen the windmills lining the slopes of the mountains (Figure 10.2.2). These are two of the larger wind farms in North America. As wind rushes along the hills, the kinetic energy of the moving air particles turns the windmills, trapping the wind's kinetic energy so that people can use it in their houses and offices.



Figure 10.2.2: A wind farm in Solano County harnesses the kinetic energy of the wind. Attribution: BDS2006 at the English Wikipedia, CC-BY-SA-3.0 (http://creativecommons.org/licenses/by-sa/3.0/)], via Wikimedia Commons

Potential Energy

Potential energy is *stored* energy. It is energy that remains available until we choose to use it. Think of a battery in a flashlight. If you leave a flashlight on, the battery will run out of energy within a couple of hours, and your flashlight will die. If, however, you only use the flashlight when you need it, and you turn it off when you don't, the battery will last for days or even months. The battery contains a certain amount of energy, and it will power the flashlight for a certain amount of time, but because the battery stores *potential* energy, you can choose to use the energy all at once, or you can save it and only use a small amount at a time.

Any stored energy is potential energy. Unfortunately, there are a lot of different ways in which energy can be stored, and that can make potential energy very difficult to recognize. In general, an object has potential energy because of its *position relative to another object*. For example when you hold a rock above the earth, it has potential energy because of its position relative to the ground. You can tell that this is *potential energy* because the energy is *stored* for as long as you hold the rock in the air. Once you drop the rock, though, the stored energy is released as kinetic energy as the rock falls.

Chemical Energy

There are other common examples of potential energy. A ball at the top of a hill stores potential energy until it is allowed to roll to the bottom. When you hold two magnets next to each other, they store potential energy too. For some examples of potential energy, though, it's harder to see how "position" is involved. In chemistry, we are often interested in what is called **chemical potential energy**. Chemical potential energy is energy stored in the atoms, molecules, and chemical bonds that make up matter. How does this depend on position?

As you learned earlier, the world, and all of the chemicals in it are made up of atoms and molecules. These store potential energy that is dependent on their positions relative to one another. Of course, you can't see atoms and molecules. Nevertheless, scientists do know a lot about the ways in which atoms and molecules interact, and this allows them to figure out how much potential energy is stored in a specific quantity (like a cup or a gallon) of a particular chemical. *Different chemicals have different amounts of potential energy* because they are made up of different atoms, and those atoms have different positions relative to one another.

> Since different chemicals have different amounts of potential energy, scientists will sometimes say potential energy depends not only on ***position***, but also on ***composition***. Composition affects potential energy because it determines which molecules and atoms end up next to each other. For example, the total potential energy in a cup of pure water is different than the total potential energy in a cup of apple juice, because the cup of water and the cup of apple juice are *composed* of different amounts of different chemicals.

At this point, you might be wondering just how useful chemical potential energy is. If you want to release the potential energy stored in an object held above the ground, you just drop it. But how do you get potential energy out of chemicals? It's actually not that difficult. You use the fact that different chemicals have *different amounts of potential energy*. If you start with chemicals that

have a lot of potential energy and allow them to react and form chemicals with less potential energy, all the extra energy that was in the chemicals at the beginning but not at the end is released.

Units of Energy

Energy is measured in one of two common units: the calorie and the joule. The joule (J) is the SI unit of energy. The calorie is familiar because it is commonly used when referring to the amount of energy contained within food. A **calorie** (cal) is the quantity of heat required to raise the temperature of 1 gram of water by $1°C$. For example, raising the temperature of $100\ g$ of water from $20°C$ to $22°C$ would require $100 \times 2 = 200\ cal$.

Calories contained within food are actually kilocalories (kcal). In other words, if a certain snack contains 85 food calories, it actually contains $85\ kcal$ or $85,000\ cal$. In order to make the distinction, the dietary calorie is written with a capital C.

$$1\ \text{kilocalorie} = 1\ \text{Calorie} = 1000\ \text{calories} \tag{10.2.1}$$

To say that the snack "contains" 85 Calories means that $85\ kcal$ of energy are released when that snack is processed by your body.

Heat changes in chemical reactions are typically measured in joules rather than calories. The conversion between a joule and a calorie is shown below.

$$1\ J = 0.2390\ cal \text{ or } 1\ cal = 4.184\ J \tag{10.2.2}$$

We can calculate the amount of heat released in kilojoules when a 400. Calorie hamburger is digested.

$$400\ Cal = 400\ kcal \times \frac{4.184\ kJ}{1\ kcal} = 1.67 \times 10^3\ kJ \tag{10.2.3}$$

Summary

- Any time we use energy, we transfer energy from one object to another.
- Energy can be transferred in one of two ways – as heat, or as work.
- Heat is the term given to energy that is transferred from a hot object to a cooler object due to the difference in their temperatures.
- Work is the term given to energy that is transferred as a result of a force applied over a distance.
- Energy comes in two fundamentally different forms – kinetic energy and potential energy.
- Kinetic energy is the energy of motion.
- Potential energy is stored energy that depends on the position of an object relative to another object.
- Chemical potential energy is a special type of potential energy that depends on the positions of different atoms and molecules relative to one another.
- Chemical potential energy can also be thought of as depending on chemical composition.
- Energy can be converted from one form to another. The total amount of mass and energy in the universe is conserved.

Contributors and Attributions

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10.3: Energy and Chemical and Physical Change

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Learning Objectives

- Define endothermic and exothermic reactions.
- Describe how heat is transferred in endothermic and exothermic reactions.
- Determine whether a reaction is endothermic or exothermic through observations, temperature changes, or an energy diagram.

So far we've talked about how energy exists as either *kinetic energy* or *potential energy* and how energy can be transferred as either *heat* or *work*. While it's important to understand the difference between kinetic energy and potential energy and the difference between heat and work, the truth is, energy is constantly changing. Kinetic energy is constantly being turned into potential energy, and potential energy is constantly being turned into kinetic energy. Likewise, energy that is transferred as work might later end up transferred as heat, while energy that is transferred as heat might later end up being used to do work.

Even though energy can change form, it must still follow one fundamental law – *Energy cannot be created or destroyed, it can only be changed from one form to another*. This law is known as the **Law of Conservation of Energy**. In a lot of ways, energy is like money. You can exchange quarters for dollar bills and dollar bills for quarters, but no matter how often you convert between the two, you will not end up with any more or any less money than you started with. Similarly, you can transfer (or spend) money using cash, or transfer money using a credit card, but you still spend the same amount of money, and the store still makes the same amount of money.

A campfire is an example of basic thermochemistry. The reaction is initiated by the application of heat from a match. The reaction converting wood to carbon dioxide and water (among other things) continues, releasing heat energy in the process. This heat energy can then be used to cook food, roast marshmallows, or just keep warm when it's cold outside.



An image of a campfire with colored flames, made by the burning of a garden hose in a copper pipe. (CC SA-BY 3.0; Jared)

Exothermic and Endothermic Processes

When physical or chemical changes occur, they are generally accompanied by a transfer of energy. The **law of conservation of energy** states that in any physical or chemical process, energy is neither created nor destroyed. In other words, the entire energy in the universe is conserved. In order to better understand the energy changes taking place during a reaction, we need to define two parts of the universe, called the system and the surroundings. The **system** is the specific portion of matter in a given space that is being studied during an experiment or an observation. The **surroundings** is everything in the universe that is not part of the system. In practical terms for a laboratory chemist, the system is the particular chemicals being reacted, while the surroundings is the immediate vicinity within the room. During most processes, energy is exchanged between the system and the surroundings. If the system loses a certain amount of energy, that same amount of energy is gained by the surroundings. If the system gains a certain amount of energy, that energy is supplied by the surroundings.

A chemical reaction or physical change is **endothermic** if heat is absorbed by the system from the surroundings. In the course of an endothermic process, the system gains heat from the surroundings and so the temperature of the surroundings decreases. The quantity of heat for a process is represented by the letter ***q***. The sign of ***q*** for an endothermic process is positive because the system is gaining heat. A chemical reaction or physical change is **exothermic** if heat is released by the system into the surroundings. Because the surroundings is gaining heat from the system, the temperature of the surroundings increases. The sign of ***q*** for an exothermic process is negative because the system is losing heat.

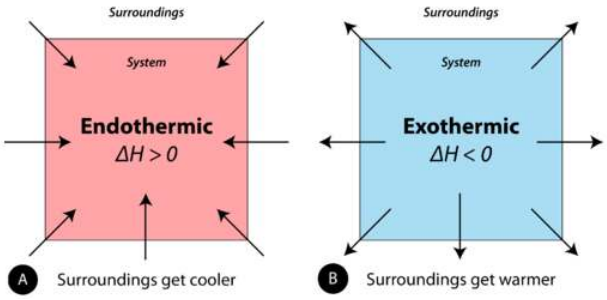


Figure 10.3.1: (A) Endothermic reaction. (B) Exothermic reaction.

During phase changes, energy changes are usually involved. For example, when solid dry ice vaporizes (physical change), carbon dioxide molecules absorb energy. Meanwhile, when liquid water becomes ice energy is released. Remember that all chemical reactions involve a change in the bonds of the reactants. The bonds in the reactants are broken and the bonds of the products are formed. Chemical bonds have **potential energy** or "stored energy". Because we are changing the bonding, this means we are also changing how much of this "stored energy" there is in a reaction.

Energy changes are frequently shown by drawing an energy diagram. Energy diagrams show the stored/hidden energy of the reactants and products as well as the activation energy. If, on an energy diagram, the products have more stored energy than the reactants started with, the reaction is endothermic.. You had to give the reaction energy. If, on the energy diagram, the products have less stored energy than the reactants started with, the reaction is exothermic.

Example 10.3.1

Label each of the following processes as endothermic or exothermic.

a. water boiling
b. gasoline burning
c. ice forming on a pond

Solution

a. endothermic - you must put a pan of water on the stove and give it heat in order to get water to boil. Because you are adding heat/energy, the reaction is endothermic.
b. exothermic - when you burn something, it feels hot to you because it is giving off heat into the surroundings.
c. exothermic - think of ice forming in your freezer instead. You put water into the freezer, which takes heat out of the water, to get it to freeze. Because heat is being pulled out of the water, it is exothermic. Heat is leaving.

Exercise 10.3.1

Label each of the following processes as endothermic or exothermic.

a. water vapor condensing
b. gold melting

Answer (a)

exothermic

Answer (b)

endothermic

Summary

Phase changes involve changes in energy. All chemical reactions involve changes in energy. This may be a change in heat, electricity, light, or other forms of energy. Reactions that absorb energy are endothermic. Reactions that release energy are exothermic.

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10.4: Internal Energy

Learning Objectives

- Define and calculate changes in the internal energy of the system.

Internal Energy

Internal Energy is defined as the sum of all the energy in a system. This energy can take the form or work or heat. We use the symbol ΔE to represent any changes in the internal energy of the system and account for these changes through work and heat

$$\Delta E = w + q \tag{10.4.1}$$

We know that if we have an exothermic reaction the system loses heat and the sign of q is negative. If we have an endothermic reaction heat is gained by the system and the sign of q is positive. Any work done by the system uses energy and the system loses energy, so the sign of w is negative. If work is done on the system the system gains energy and the sign of w is positive.

Energy	Change	Sign
q	Heat is gained by the system (endothermic)	+q
	Heat is lost by the system (exothermic)	-q
w	Work is done on the system (compression)	+w
	Work is done by the system (expansion)	-w

By conservation of energy any change in the energy of the system must account for any energy the system gained and any energy the system lost.

Example 10.4.4:

What is the change in internal energy for a gas if the gas gains 10 kJ of heat and expands, performing 5 kJ of work?

Solution

We can use

$$\Delta E = q + w \tag{10.4.2}$$

As the gas (our system) **gained** 10 kJ of heat, q is positive

$$q = +10\,kJ \tag{10.4.3}$$

The system did work, using energy in the process, so the system **lost** energy and w is negative.

$$w = -5\,kJ \tag{10.4.4}$$

Putting these together

$$\Delta E = q + w = 10\,kJ + (-5\,kJ) = 10\,kJ - 5\,kJ = +5\,kJ \tag{10.4.5}$$

So the system gained 5 kJ of energy overall.

Key Takeaways

- Any change in the internal energy of a system is the sum of the heat and the work.
- The overall change in the internal energy of a system will be the net total of any energy gained and any energy lost.

Exercises 10.4.1

1. A gas is compressed, decreasing the volume, is the sign of the work positive or negative? Explain.
2. A gas expands, increasing the volume, is the sign of the work positive or negative? Explain.

3. A gas exchanges 22 kJ of energy with the surroundings in an exothermic reaction, what is the sign of q?
4. A gas exchanges 25 kJ of energy with the surrounding in an endothermic reaction, what is the sign of q?
5. A gas is heated with 36 J of energy and expands, doing 33 J of work, what is sign and value of ΔE?
6. A gas is cooled, losing 43 J of energy and is compressed using 22 J of work, what is the sign and value of ΔE?
7. A gas undergoes an endothermic process and expands, for this process $|q| > |w|$, what is the sign of ΔE?
8. A gas undergoes an exothermic process and is compressed, for this process $|q| > |w|$, what is the sign of ΔE?
9. For an endothermic process that does work, if $|w| > |q|$ what is the sign of ΔE?
10. For an endothermic process that does work, if $|q| > |w|$ what is the sign of ΔE?
11. For an exothermic process where work is done on the gas, if $|w| > |q|$ what is the sign of ΔE?
12. For an exothermic process where work is done on the gas, if $|q| > |w|$ what is the sign of ΔE?

Answers

1. As work was done on the gas the gas gained energy, so the sign of the work would be positive.
2.
3. As the reaction was exothermic heat left the system, the sign of q is therefore negative, q = -22 kJ
4.
5. As the gas was heated it gained energy, therefore q is positive and q = +36 J. The gas did work so it lost energy, therefore w is negative and w = -33 J. $\Delta E = q + w = +36\ J + (-33\ J) = +3\ J$.
6. $\Delta E = -65\ J$
7. As the process is endothermic $q > 0$, as the gas expanded it did work, so $w < 0$. As the magnitude of q ($|q|$) is greater than the magnitude of w ($|w|$) we have a positive ΔE, $\Delta E = +|q| + (-|w|) = q - w$ and $|q| > |w|$.
8. $\Delta E < 0$
9. $\Delta E < 0$
10.
11. $\Delta E > 0$
12.

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10.5: Work and Heat

Learning Objectives

- Define a type of work in terms of pressure and volume.
- Define *heat*.
- Relate the amount of heat to a temperature change.

Work

We have already defined work as a force acting through a distance. It turns out that there are other equivalent definitions of work that are also important in chemistry.

When a certain volume of a gas expands, it works against an external pressure to expand (Fig. 7.3.1 - Volume versus Pressure)

That is, the gas must perform work. Assuming that the external pressure P_{ext} is constant, the amount of work done by the gas is given by the equation

$$w = -P_{ext} \times \Delta V$$

where ΔV is the change in volume of the gas. This term is always the final volume minus the initial volume,

$$\Delta V = V_{final} - V_{initial}$$

and can be positive or negative, depending on whether V_{final} is larger (is expanding) or smaller (is contracting) than $V_{initial}$. The negative sign in the equation for work is important and implies that as volume expands (ΔV is positive), the gas in the system is *losing* energy as work. On the other hand, if the gas is contracting, ΔV is negative, and the two negative signs make the work positive, so energy is being added to the system.

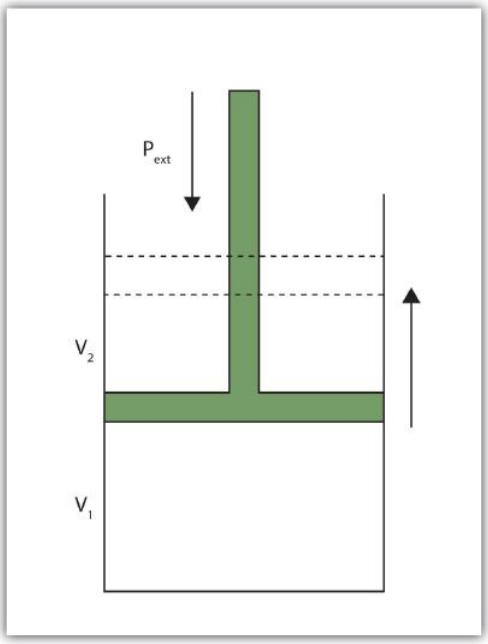


Fig. 7.3.1 Volume versus Pressure

When a gas expands against an external pressure, the gas does work.

Finally, let us consider units. Volume changes are usually expressed in units like liters, while pressures are usually expressed in atmospheres. When we use the equation to determine work, the unit for work comes out as liter·atmospheres, or L·atm. This is not a very common unit for work. However, there is a conversion factor between L·atm and the common unit of work, joules:

$$1 \text{ L·atm} = 101.32 \text{ J}$$

Using this conversion factor and the previous equation for work, we can calculate the work performed when a gas expands or contracts.

Example 10.5.1:

What is the work performed by a gas if it expands from 3.44 L to 6.19 L against a constant external pressure of 1.26 atm? Express the final answer in joules.

Solution

First we need to determine the change in volume, ΔV. A change is always the final value minus the initial value:

$$\Delta V = V_{\text{final}} - V_{\text{initial}} = 6.19\ \text{L} - 3.44\ \text{L} = 2.75\ \text{L}$$

Now we can use the definition of work to determine the work done:

$$w = -P_{\text{ext}} \cdot \Delta V = -(1.26\ \text{atm})(2.75\ \text{L}) = -3.47\ \text{L·atm}$$

Now we construct a conversion factor from the relationship between liter·atmospheres and joules:

$$-3.47\ \cancel{L \cdot atm} \times \times \frac{101.32\ J}{1\ \cancel{L \cdot atm}} = -351\ J \tag{10.5.1}$$

We limit the final answer to three significant figures, as appropriate.

Exercise 10.5.1

Test Yourself

What is the work performed when a gas expands from 0.66 L to 1.33 L against an external pressure of 0.775 atm?

Answer

−53 J

Heat

Heat is another aspect of energy. **Heat** is the transfer of energy from one body to another due to a difference in temperature. For example, when we touch something with our hands, we interpret that object as either hot or cold depending on how energy is transferred: If energy is transferred into your hands, the object feels hot. If energy is transferred from your hands to the object, your hands feel cold. Because heat is a measure of energy transfer, heat is also measured in joules.

For a given object, the amount of heat (q) involved is proportional to two things: the mass of the object (m) and the temperature change (ΔT) evoked by the energy transfer. We can write this mathematically as

$$q \alpha m \times \Delta T \tag{10.5.2}$$

where $\propto$ means "is proportional to." To make a proportionality an equality, we include a proportionality constant. In this case, the proportionality constant is labeled c and is called the **specific heat capacity**, or, more succinctly, **specific heat**:

$$q = m\,c\,\Delta T \tag{10.5.3}$$

where the mass, specific heat, and change in temperature are multiplied together. Specific heat is a measure of how much energy is needed to change the temperature of a substance; the larger the specific heat, the more energy is needed to change the temperature. The units for specific heat are

$$\frac{J}{g \cdot C} \text{ or } \frac{J}{g \cdot K} \tag{10.5.4}$$

depending on what the unit of ΔT is. You may note a departure from the insistence that temperature be expressed in Kelvin. That is because a *change* in temperature has the same value whether the temperatures are expressed in degrees Celsius or kelvins.

Example 10.5.2:

Calculate the heat involved when 25.0 g of Fe increase temperature from 22°C to 76°C. The specific heat of Fe is 0.449 J/g·°C.

Solution

First we need to determine ΔT. A change is always the final value minus the initial value:

ΔT = 76°C − 22°C = 54°C

Now we can use the expression for q, substitute for all variables, and solve for heat:

$$q = (25.0\,g)(0.449\frac{J}{g\cdot^\circ C})(54^\circ C) = 610\,J \tag{10.5.5}$$

Note how the g and °C units cancel, leaving J, a unit of heat. Also note that this value of q is inherently positive, meaning that energy is going into the system.

Exercise 10.5.2

Test Yourself

Calculate the heat involved when 76.5 g of Ag increase temperature from 17.8 °C to 144.5 °C. The specific heat of Ag is 0.233 J/g·°C.

Answer

2,260 J

As with any equation, when you know all but one variable in the expression for q, you can determine the remaining variable by using algebra.

Example 10.5.3:

It takes 5,408 J of heat to raise the temperature of 373 g of Hg by 104°C. What is the specific heat of Hg?

Solution

We can start with the equation for q, but now different values are given, and we need to solve for specific heat. Note that ΔT is given directly as 104°C. Substituting,

$$5408\,J = (373\,g)\,c\,(104^\circ C) \tag{10.5.6}$$

We divide both sides of the equation by 373 g and 104°C:

$$c = \frac{5408\,J}{(373\,g)(104^\circ C)} \tag{10.5.7}$$

Combining the numbers and bringing together all the units, we get

$$c = 0.139\frac{J}{g\cdot^\circ C} \tag{10.5.8}$$

Exercise 10.5.3

Test Yourself

Gold has a specific heat of 0.129 J/g·°C. If 1,377 J are needed to increase the temperature of a sample of gold by 99.9°C, what is the mass of the gold?

Answer

107 g

Table 7.3.1: *Specific Heats of Various Substances, lists the specific heats of some substances. Specific heat is a physical property of substances, so it is a characteristic of the substance. The general idea is that the lower the specific heat, the less energy is required to change the temperature of the substance by a certain amount.*

Substance	Specific Heat (J/g·°C)
water	4.184
iron	0.449
gold	0.129
mercury	0.139
aluminum	0.900
ethyl alcohol	2.419
magnesium	1.03
helium	5.171
oxygen	0.918

Table 7.3.1 Specific Heats of Various Substances

Key Takeaways

- Work can be defined as a gas changing volume against a constant external pressure.
- Heat is the transfer of energy due to temperature differences.
- Heat can be calculated in terms of mass, temperature change, and specific heat.

Exercise 10.5.1

1. Give two definitions of work.
2. What is the sign on work when a sample of gas increases its volume? Explain why work has that sign.
3. What is the work when a gas expands from 3.00 L to 12.60 L against an external pressure of 0.888 atm?
4. What is the work when a gas expands from 0.666 L to 2.334 L against an external pressure of 2.07 atm?
5. What is the work when a gas contracts from 3.45 L to 0.97 L under an external pressure of 0.985 atm?
6. What is the work when a gas contracts from 4.66 L to 1.22 L under an external pressure of 3.97 atm?
7. Like work, the sign on heat can be positive or negative. What is happening to the total energy of a system if heat is positive?
8. Like work, the sign on heat can be positive or negative. What is happening to the total energy of a system if heat is negative?
9. What is the heat when 55.6 g of Fe increase temperature from 25.6°C to 177.9°C? The heat capacity of Fe is in Table 7.3.1 "Specific Heats of Various Substances".
10. What is the heat when 0.444 g of Au increases temperature from 17.8°C to 222.5°C? The heat capacity of Au is in Table 7.3.1 "Specific Heats of Various Substances".
11. What is the heat when 245 g of H_2O cool from 355 K to 298 K? The heat capacity of H_2O is in Table 7.3.1 "Specific Heats of Various Substances".
12. What is the heat when 100.0 g of Mg cool from 725 K to 552 K? The heat capacity of Mg is in Table 7.3.1 "Specific Heats of Various Substances".
13. It takes 452 J of heat to raise the temperature of a 36.8 g sample of a metal from 22.9°C to 98.2°C. What is the heat capacity of the metal?

14. It takes 2,267 J of heat to raise the temperature of a 44.5 g sample of a metal from 33.9°C to 288.3°C. What is the heat capacity of the metal?
15. An experimenter adds 336 J of heat to a 56.2 g sample of Hg. What is its change in temperature? The heat capacity of Hg is in Table 7.3.1 "Specific Heats of Various Substances".
16. To a 0.444 g sample of H_2O, 23.4 J of heat are added. What is its change in temperature? The heat capacity of H_2O is in Table 7.3.1 "Specific Heats of Various Substances".
17. An unknown mass of Al absorbs 187.9 J of heat and increases its temperature from 23.5°C to 35.6°C. What is the mass of the aluminum? How many moles of aluminum is this?

Answers

1. Work is a force acting through a distance or a volume changing against some pressure.
2.
3. −864 J
4.
5. 248 J
6.
7. When heat is positive, the total energy of the system is increasing.
8.
9. 3.80×10^3 J
10.
11. −58,400 J
12.
13. 0.163 J/g·°C
14.
15. 43.0°C
16.
17. 17.3 g; 0.640 mol

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10.6: Enthalpy and Chemical Reactions

Learning Objectives

- Define *enthalpy*.
- Properly express the enthalpy change of chemical reactions.
- Explain how enthalpy changes are measured experimentally.

Now that we have shown how energy, work, and heat are related, we are ready to consider energy changes in chemical reactions. A fundamental concept is that *every chemical reaction occurs with a concurrent change in energy*. Now we need to learn how to properly express these energy changes.

Our study of gases in Chapter 6, and our definition of work in Section 7.3, indicate that conditions like pressure, volume, and temperature affect the energy content of a system. What we need is a definition of energy that holds when some of these conditions are specified (somewhat similar to our definition of standard temperature and pressure in our study of gases). We define the **enthalpy change** (ΔH) as the heat of a process when pressure is held constant:

$$\Delta H \equiv q \text{ at constant pressure} \tag{10.6.1}$$

The letter H stands for "enthalpy," a kind of energy, while the Δ implies a change in the quantity. We will always be interested in the change in H, rather than the absolute value of H itself.

When a chemical reaction occurs, there is a characteristic change in enthalpy. The enthalpy change for a reaction is typically written after a balanced chemical equation and on the same line. For example, when two moles of hydrogen react with one mole of oxygen to make two moles of water, the characteristic enthalpy change is 570 kJ. We write the equation as

$$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(\ell) \tag{10.6.2}$$

with $\Delta H = -570\ kJ$

A chemical equation that includes an enthalpy change is called a **thermochemical equation**. A thermochemical equation is assumed to refer to the equation in molar quantities, which means it must be interpreted in terms of moles, not individual molecules.

Example 10.6.1

Write the thermochemical equation for the reaction of $PCl_3(g)$ with $Cl_2(g)$ to make $PCl_5(g)$, which has an enthalpy change of −88 kJ.

Solution

The thermochemical equation is

$$PCl_3(g) + Cl_2(g) \rightarrow PCl_5(g) \qquad \Delta H = -88 \text{ kJ}$$

Exercise 10.6.1

Write the thermochemical equation for the reaction of $N_2(g)$ with $O_2(g)$ to make $2NO(g)$, which has an enthalpy change of 181 kJ.

Answer

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

You may have noticed that the ΔH for a chemical reaction may be positive or negative. The number is assumed to be positive if it has no sign; a + sign can be added explicitly to avoid confusion. A chemical reaction that has a positive ΔH is said to be **endothermic**, while a chemical reaction that has a negative ΔH is said to be **exothermic**.

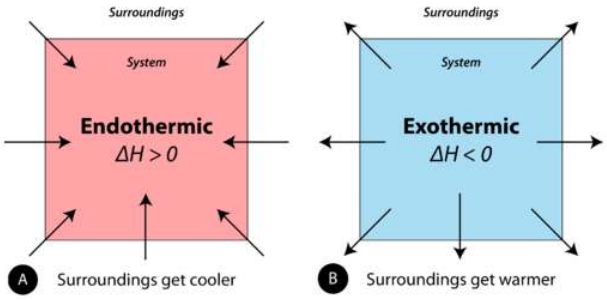


***Figure* 10.6.1:** *(A) Endothermic reaction. (B) Exothermic reaction.*

"Endothermic vs Exothermic Reactions" by Sharon Bewick, Richard Parsons, Therese Forsythe, Shonna Robinson, and Jean Dupon., CK-12

What does it mean if the Δ*H* of a process is positive? It means that the system in which the chemical reaction is occurring is gaining energy. If one considers the energy of a system as being represented as a height on a vertical energy plot, the enthalpy change that accompanies the reaction can be diagrammed as in part (a) of Fig. 7.4.2 Reaction Energy: the energy of the reactants has some energy, and the system increases its energy as it goes to products. The products are higher on the vertical scale than the reactants. Endothermic, then, implies that the system *gains*, or absorbs, energy.

An opposite situation exists for an exothermic process, as shown in part (b) of Fig. 7.4.2 Reaction Energy. If the enthalpy change of a reaction is negative, the system is losing energy, so the products have less energy than the reactants, and the products are lower on the vertical energy scale than the reactants are. Exothermic, then, implies that the system *loses*, or gives off, energy.

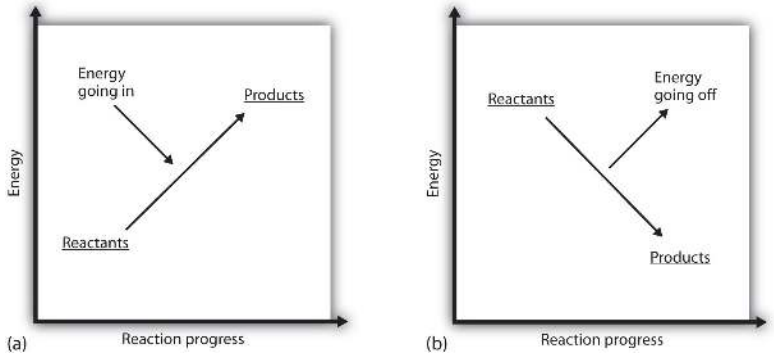


***Figure* 10.6.2:** *Reaction Energy (a) In an endothermic reaction, the energy of the system increases (i.e., moves higher on the vertical scale of energy). (b) In an exothermic reaction, the energy of the system decreases (i.e., moves lower on the vertical scale of energy).*

Example 10.6.2

Consider this thermochemical equation.

$$2\ CO(g) + O_2(g) \rightarrow 2\ CO_2(g)$$

with $\Delta H = -565$ kJ

Is it exothermic or endothermic? How much energy is given off or absorbed?

Solution

By definition, a chemical reaction that has a negative Δ*H* is exothermic, meaning that this much energy—in this case, 565 kJ—is given off by the reaction.

Exercise 10.6.2

Consider this thermochemical equation.

$$CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g) \qquad \Delta H = 42\ \text{kJ}$$

Is it exothermic or endothermic? How much energy is given off or absorbed?

Answer

Endothermic; 42 kJ are absorbed.

How are ΔH values measured experimentally? Actually, ΔH is not measured; q is measured. But the measurements are performed under conditions of constant pressure, so ΔH is equal to the q measured.

Experimentally, q is measured by taking advantage of the equation

$$q = mc\Delta T \tag{10.6.3}$$

We premeasure the mass of the chemicals in a system. Then we let the chemical reaction occur and measure the change in temperature (ΔT) of the system. If we know the specific heat of the materials in the system (typically, we do), we can calculate q. That value of q is numerically equal to the ΔH of the process, which we can scale up to a molar scale. The container in which the system resides is typically insulated, so any energy change goes into changing the temperature of the system, rather than being leaked from the system. The container is referred to as a **calorimeter**, and the process of measuring changes in enthalpy is called **calorimetry**.

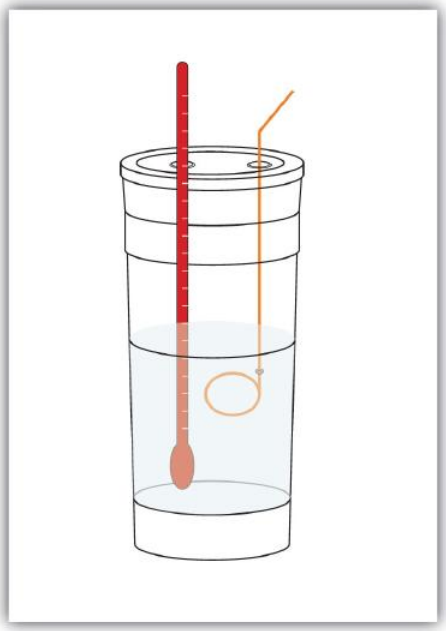


***Figure* 10.6.3:** *Calorimeters. A simple calorimeter can be constructed from some nested foam coffee cups, a cover, a thermometer, and a stirrer.*

For example, suppose 4.0 g of NaOH, or 0.10 mol of NaOH, are dissolved to make 100.0 mL of aqueous solution, while 3.65 g of HCl, or 0.10 mol of HCl, are dissolved to make another 100.0 mL of aqueous solution. The two solutions are mixed in an insulated calorimeter, a thermometer is inserted, and the calorimeter is covered (See Fig. 7.4.2 - Calorimeters for an example setup). The thermometer measures the temperature change as the following chemical reaction occurs:NaOH (aq) + HCl(aq) → NaCl(aq) + $H_2O(\ell)$

An observer notes that the temperature increases from 22.4°C to 29.1°C. Assuming that the heat capacities and densities of the solutions are the same as those of pure water, we now have the information we need to determine the enthalpy change of the chemical reaction. The total amount of solution is 200.0 mL, and with a density of 1.00 g/mL, we thus have 200.0 g of solution. Using the equation for q, we substitute for our experimental measurements and the specific heat of water (in Table 7.3.1 of Section 7.3).

$$q = (200.0 \cancel{g})\left(4.184 \frac{J}{\cancel{g} \cdot \cancel{^\circ C}}\right)(6.7 \cancel{^\circ C}) \tag{10.6.4}$$

Solving for q, we get

$$q = 5600\ J \equiv \Delta H\ for\ the\ reaction \tag{10.6.5}$$

The heat q is equal to the ΔH for the reaction because the chemical reaction occurs at constant pressure. However, the reaction is giving off this amount of energy, so the actual sign on ΔH is negative:

ΔH = −5,600 J for the reaction

Thus, we have the following thermochemical equation for the chemical reaction that occurred in the calorimeter:

$$\frac{1}{10}NaOH(aq) + \frac{1}{10}HCl(aq) \rightarrow \frac{1}{10}NaCl(aq) + \frac{1}{10}H_2O(l) \quad \Delta H = -5600\ J \tag{10.6.6}$$

The 1/10 coefficients are present to remind us that we started with one-tenth of a mole of each reactant, so we make one-tenth of a mole of each product. Typically, however, we report thermochemical equations in terms of moles, not one-tenth of a mole. To scale up to molar quantities, we must multiply the coefficients by 10. However, when we do this, we get 10 times as much energy. Thus, we have

$$\text{NaOH (aq) + HCl(aq) } \rightarrow \text{ NaCl(aq) + } H_2O(\ell) \qquad \Delta H = -56{,}000 \text{ J}$$

The ΔH can be converted into kJ units, so our final thermochemical equation is

$$\text{NaOH (aq) + HCl(aq) } \rightarrow \text{ NaCl(aq) + } H_2O(\ell) \qquad \Delta H = -56 \text{ kJ}$$

We have just taken our experimental data from calorimetry and determined the enthalpy change of a chemical reaction. Similar measurements on other chemical reactions can determine the ΔH values of any chemical reaction you want to study.

Example 10.6.3

A 100 mL solution of 0.25 mol of $Ca^{2+}(aq)$ was mixed with 0.50 mol of $F^-(aq)$ ions, and CaF_2 was precipitated:

$$Ca^{2+}(aq) + 2F^-(aq) \rightarrow CaF_2(s)$$

The temperature of the solution increased by 10.5°C. What was the enthalpy change for the chemical reaction? What was the enthalpy change for the production of 1 mol of CaF_2? Assume that the solution has the same density and specific heat as water.

Solution

Because we are given ΔT directly, we can determine the heat of the reaction, which is equal to ΔH:

$$q = (100 \cancel{g})\left(4.184 \frac{J}{\cancel{g} \cdot \cancel{^\circ C}}\right)(10.5 \cancel{^\circ C}) \tag{10.6.7}$$

Solving for q, we get

q = 4,400 J

Therefore, ΔH = −4,400 J.

According to the stoichiometry of the reaction, exactly 0.25 mol of CaF_2 will form, so this quantity of heat is for 0.25 mol. For 1 mol of CaF_2, we need to scale up the heat by a factor of four:

q = 4,400 J × 4 = 17,600 J for 1 mol CaF_2

On a molar basis, the change in enthalpy is

ΔH = −17,600 J = −17.6 kJ

Exercise 10.6.3

In a calorimeter at constant pressure, 0.10 mol of $CH_4(g)$ and 0.20 mol of $O_2(g)$ are reacted.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell)$$

The reaction warms 750.0 g of H_2O by 28.4°C. What is ΔH for the reaction on a molar scale?

Answer

−891 kJ

Key Takeaways

- Every chemical reaction occurs with a concurrent change in energy.
- The change in enthalpy equals heat at constant pressure.
- Enthalpy changes can be expressed by using thermochemical equations.
- Enthalpy changes are measured by using calorimetry.

Exercise 10.6.1

1. Under what circumstances are q and ΔH the same?
2. Under what circumstances are q and ΔH different?
3. Hydrogen gas and chlorine gas react to make hydrogen chloride gas with an accompanying enthalpy change of −184 kJ. Write a properly balanced thermochemical equation for this process.
4. Propane (C_3H_8) reacts with elemental oxygen gas to produce carbon dioxide and liquid water with an accompanying enthalpy change of −2,220 kJ. Write a properly balanced thermochemical equation for this process.
5. Nitrogen gas reacts with oxygen gas to make NO(g) while absorbing 180 kJ. Write a properly balanced thermochemical equation for this process.
6. Solid sodium reacts with chlorine gas to make solid sodium chloride while giving off 772 kJ. Write a properly balanced thermochemical equation for this process.
7. Hydrogen gas and chlorine gas react to make hydrogen chloride gas with an accompanying enthalpy change of −184 kJ. Is this process endothermic or exothermic?
8. Propane (C_3H_8) reacts with elemental oxygen gas to produce carbon dioxide while giving off 2,220 kJ of energy. Is this process endothermic or exothermic?
9. Nitrogen gas reacts with oxygen gas to make NO(g) while absorbing 180 kJ. Is this process exothermic or endothermic?
10. Sodium metal can react with nitrogen to make sodium azide (NaN_3) with a ΔH of 21.72 kJ. Is this process exothermic or endothermic?
11. Draw an energy level diagram for the chemical reaction in Exercise 8. (See Fig. 7.4.1 "Reaction Energy" for an example.)
12. Draw an energy level diagram for the chemical reaction in Exercise 9. (See Fig. 7.4.1 "Reaction Energy" for an example.)
13. In a 250 mL solution, 0.25 mol of KOH(aq) and 0.25 mol of HNO_3(aq) are combined. The temperature of the solution increases from 22.5°C to 35.9°C. Assume the solution has the same density and heat capacity of water. What is the heat of the reaction, and what is the ΔH of the reaction on a molar basis?
14. In a 600 mL solution, 0.50 mol of $Ca(OH)_2$(aq) and 0.50 mol of H_2SO_4(aq) are combined. The temperature of the solution increases by 22.3°C. What is the heat of the reaction, and what is the ΔH of the reaction on a molar basis? Assume the solution has the same density and heat capacity of water.
15. To warm 400.0 g of H_2O, 0.050 mol of ethanol (C_2H_5OH) is burned. The water warms from 24.6°C to 65.6°C. What is the heat of the reaction, and what is the ΔH of the reaction on a molar basis?
16. To warm 100.0 g of H_2O, 0.066 mol beeswax is burned. The water warms from 21.4°C to 25.5°C. What is the heat of the reaction, and what is the ΔH of the reaction on a molar basis?

Answers

1. under conditions of constant pressure
2.

3. $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)\ \Delta H = -184$ kJ

4.

5. $N_2(g) + O_2(g) \rightarrow 2NO(g)\ \Delta H = 180$ kJ

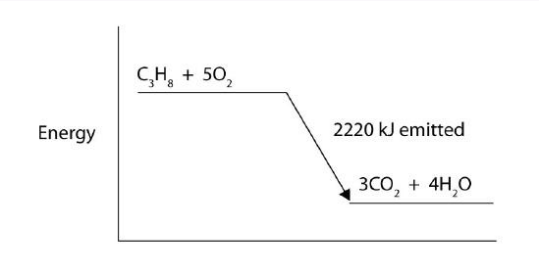
6.

7. exothermic

8.

9. endothermic

10.



11.

12.

13. heat of reaction = −14.0 kJ; $\Delta H = -56.0$ kJ/mol of reactants

14.

15. heat of reaction = −68.6 kJ; $\Delta H = -1{,}370$ kJ/mole of ethanol

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CHAPTER OVERVIEW

14: Solids and Liquids

In Chapter 6, we discussed the properties of gases. Here, we consider some properties of liquids and solids. As a review, the Table below lists some general properties of the three phases of matter.

Phase	Shape	Density	Compressibility
Gas	fills entire container	low	high
Liquid	fills a container from bottom to top	high	low
Solid	rigid	high	low

14.1: Prelude to Solids and Liquids
14.2: Intermolecular Forces
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14.1: Prelude to Solids and Liquids

There is an urban legend that glass is an extremely thick liquid rather than a solid, even at room temperature. Proponents claim that old windows are thicker at the bottom than at the top, suggesting that the glass flowed down over time. Unfortunately, the proponents of this idea have no credible evidence that this is true, as old windows were likely not subject to the stricter manufacturing standards that exist today. Also, when mounting a piece of glass that has an obviously variable thickness, it makes structural sense to put the thicker part at the bottom, where it will support the object better.



Figure **14.1.1** A woman cleaning glass © Thinkstock. Is this woman cleaning a solid or a liquid? Contrary to some claims, glass is a solid, not a very thick liquid.

Liquids flow when a small force is placed on them, even if only very slowly. Solids may deform under a small force, but they return to their original shape when the force is relaxed. This is how glass behaves: it goes back to its original shape (unless it breaks under the applied force). Observers also point out that telescopes with glass lenses to focus light still do so even decades after manufacture—a circumstance that would not be so if the lens were liquid and flowed. Thus, glass is a solid at room temperature.

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14.2: Intermolecular Forces

Learning Objective

- Relate phase to intermolecular forces.

Why does a substance have the phase that it does? The preferred phase of a substance at a given set of conditions is a balance between the energy of the particles and intermolecular forces (or intermolecular interactions) between the particles. If the forces between particles are strong enough, the substance is a liquid or, if stronger, a solid. If the forces between particles are weak and sufficient energy is present, the particles separate from each other, so the gas phase is the preferred phase. The energy of the particles is mostly determined by temperature, so temperature is the main variable that determines what phase is stable at any given point.

What forces define intermolecular interactions? There are several. A force present in all substances with electrons is the **dispersion force** (sometimes called the *London dispersion force*, after the physicist Fritz London, who first described this force in the early 1900s). This interaction is caused by the instantaneous position of an electron in a molecule, which temporarily makes that point of the molecule negatively charged and the rest of the molecule positively charged. In an instant, the electron is now somewhere else, but the fleeting imbalance of electric charge in the molecule allows molecules to interact with each other. As you might expect, the greater the number of electrons in a species, the stronger the dispersion force; this partially explains why smaller molecules are gases and larger molecules are liquids and solids at the same temperature. (Mass is a factor as well.)

Molecules with a permanent dipole moment experience **dipole-dipole interactions,** which are generally stronger than dispersion forces if all other things are equal. The oppositely charged ends of a polar molecule, which have partial charges on them, attract each other (Figure **14.2.1**). Thus, a polar molecule such as CH_2Cl_2 has a significantly higher boiling point (313 K, or 40°C) than a nonpolar molecule like CF_4 (145 K, or −128°C), even though it has a lower molar mass (85 g/mol vs. 88 g/mol).

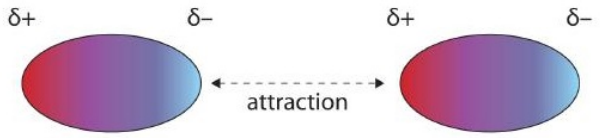


Figure **14.2.1**: Dipole-Dipole Interactions. Oppositely charged ends of polar molecules attract each other.
2 ovals with partial positive left & right sides are attracted to each other. The right of oval 1 is attracted to the left of oval 2.

An unusually strong form of dipole-dipole interaction is called **hydrogen bonding**. Hydrogen bonding is found in molecules with an H atom bonded to an N atom, an O atom, or an F atom. Such covalent bonds are very polar, and the dipole-dipole interaction between these bonds in two or more molecules is strong enough to create a new category of intermolecular force. Hydrogen bonding is the reason water has unusual properties. For such a small molecule (its molar mass is only 18 g/mol), H_2O has relatively high melting and boiling points. Its boiling point is 373 K (100°C), while the boiling point of a similar molecule, H_2S, is 233 K (−60°C). This is because H_2O molecules experience hydrogen bonding, while H_2S molecules do not. This strong attraction between H_2O molecules requires additional energy to separate the molecules in the condensed phase, so its boiling point is higher than would be expected. Hydrogen bonding is also responsible for water's ability as a solvent, its high heat capacity, and its ability to expand when freezing; the molecules line up in such a way that there is extra space between the molecules, increasing its volume in the solid state (Figure **14.2.2**).

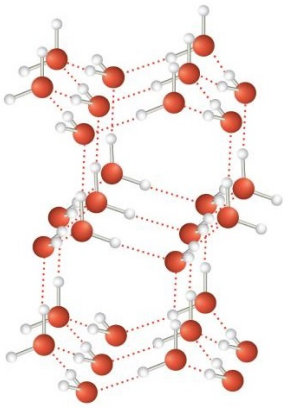


Figure 14.2.2: Hydrogen Bonding. When water solidifies, hydrogen bonding between the molecules forces the molecules to line up in a way that creates empty space between the molecules, increasing the overall volume of the solid. This is why ice is less dense than liquid water.

Example 14.2.1

Identify the most significant intermolecular force in each substance.

a. C_3H_8
b. CH_3OH
c. H_2S

Solution

1. Although C–H bonds are polar, they are only minimally polar. The most significant intermolecular force for this substance would be dispersion forces.
2. This molecule has an H atom bonded to an O atom, so it will experience hydrogen bonding.
3. Although this molecule does not experience hydrogen bonding, the Lewis electron dot diagram and VSEPR indicate that it is bent, so it has a permanent dipole. The most significant force in this substance is dipole-dipole interaction.

Exercise 14.2.1

Identify the most significant intermolecular force in each substance.

a. HF
b. HCl

Answers

a. hydrogen bonding
b. dipole-dipole interactions

The preferred phase a substance adopts can change with temperature. At low temperatures, most substances are solids (only helium is predicted to be a liquid at absolute zero). As the temperature increases, those substances with very weak intermolecular forces become gases directly (in a process called *sublimation*, which will be discussed in Section 10.3). Substances with weak interactions can become liquids as the temperature increases. As the temperature increases even more, the individual particles will have so much energy that the intermolecular forces are overcome, so the particles separate from each other, and the substance becomes a gas (assuming that their chemical bonds are not so weak that the compound decomposes from the high temperature). Although it is difficult to predict the temperature ranges for which solid, liquid, or gas is the preferred phase for any random substance, all substances progress from solid to liquid to gas (in that order) as temperature increases.

Summary

- All substances experience dispersion forces between their particles.
- Substances that are polar experience dipole-dipole interactions.

- Substances with covalent bonds between an H atom and N, O, or F atoms experience hydrogen bonding.
- The preferred phase of a substance depends on the strength of the intermolecular force and the energy of the particles.

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14.3: Phase Transitions - Melting, Boiling, and Subliming

Learning Objective

- Describe what happens during a phase change.
- Calculate the energy change needed for a phase change.

Substances can change phase—often because of a temperature change. At low temperatures, most substances are solid; as the temperature increases, they become liquid; at higher temperatures still, they become gaseous.

The process of a solid becoming a liquid is called **melting** (an older term that you may see sometimes is *fusion*). The opposite process, a liquid becoming a solid, is called **solidification**. For any pure substance, the temperature at which melting occurs—known as the **melting point**—is a characteristic of that substance. It requires energy for a solid to melt into a liquid. Every pure substance has a certain amount of energy it needs to change from a solid to a liquid. This amount is called the **enthalpy of fusion (or heat of fusion)** of the substance, represented as ΔH_{fus}. Some ΔH_{fus} values are listed in Table **14.3.1**; it is assumed that these values are for the melting point of the substance. Note that the unit of ΔH_{fus} is kilojoules per mole, so we need to know the quantity of material to know how much energy is involved. The ΔH_{fus} is always tabulated as a positive number. However, it can be used for both the melting and the solidification processes, minding that melting is always endothermic (so ΔH will be positive), while solidification is always exothermic (so ΔH will be negative).

Table **14.3.1**: Enthalpies of Fusion for Various Substances

Substance (Melting Point)	ΔH_{fus} (kJ/mol)
Water (0°C)	6.01
Aluminum (660°C)	10.7
Benzene (5.5°C)	9.95
Ethanol (−114.3°C)	5.02
Mercury (−38.8°C)	2.29

Example 14.3.1

What is the energy change when 45.7 g of $\mathbf{H_2O}$ melt at 0°C?

Solution

The ΔH_{fus} of $\mathbf{H_2O}$ is 6.01 kJ/mol. However, our quantity is given in units of grams, not moles, so the first step is to convert grams to moles using the molar mass of $\mathbf{H_2O}$, which is 18.0 g/mol. Then we can use ΔH_{fus} as a conversion factor. Because the substance is melting, the process is endothermic, so the energy change will have a positive sign.

$$45.7\ \cancel{g\ H_2O} \times \frac{1\ \cancel{mol\ H_2O}}{18.0\ \cancel{g}} \times \frac{6.01 kJ}{\cancel{mol}} = 15.3\ kJ$$

Without a sign, the number is assumed to be positive.

Exercise 14.3.1

What is the energy change when 108 g of $\mathbf{C_6H_6}$ freeze at 5.5°C?

Answer

−13.8 kJ

During melting, energy goes exclusively to changing the phase of a substance; it does not go into changing the temperature of a substance. Hence melting is an **isothermal** process because a substance stays at the same temperature. Only when all of a substance is melted does additional energy go to changing its temperature.

What happens when a solid becomes a liquid? In a solid, individual particles are stuck in place because the intermolecular forces cannot be overcome by the energy of the particles. When more energy is supplied (e.g., by raising the temperature), there comes a point at which the particles have enough energy to move around, but not enough energy to separate. This is the liquid phase: particles are still in contact, but are able to move around each other. This explains why liquids can assume the shape of their containers: the particles move around and, under the influence of gravity, fill the lowest volume possible (unless the liquid is in a zero-gravity environment—see Figure **14.3.1**.



Figure **14.3.1**: Liquids and Gravity. (a) A liquid fills the bottom of its container as it is drawn downward by gravity and the particles slide over each other. (b) A liquid floats in a zero-gravity environment. The particles still slide over each other because they are in the liquid phase, but now there is no gravity to pull them down. Source: Photo on the left © Thinkstock. Photo on the right courtesy of NASA, http://www.nasa.gov/mission_pages/st...image_009.html.

The phase change between a liquid and a gas has some similarities to the phase change between a solid and a liquid. At a certain temperature, the particles in a liquid have enough energy to become a gas. The process of a liquid becoming a gas is called **boiling (or vaporization)**, while the process of a gas becoming a liquid is called **condensation**. However, unlike the solid/liquid conversion process, the liquid/gas conversion process is noticeably affected by the surrounding pressure on the liquid because gases are strongly affected by pressure. This means that the temperature at which a liquid becomes a gas, the **boiling point**, can change with surrounding pressure. Therefore, we define the **normal boiling point** as the temperature at which a liquid changes to a gas when the surrounding pressure is exactly 1 atm, or 760 torr. Unless otherwise specified, it is assumed that a boiling point is for 1 atm of pressure.

Like the solid/liquid phase change, the liquid/gas phase change involves energy. The amount of energy required to convert a liquid to a gas is called the **enthalpy of vaporization** (or heat of vaporization), represented as ΔH_{vap}. Some ΔH_{vap} values are listed in Table **14.3.2**; it is assumed that these values are for the normal boiling point temperature of the substance, which is also given in the table. The unit for ΔH_{vap} is also kilojoules per mole, so we need to know the quantity of material to know how much energy is involved. The ΔH_{vap} is also always tabulated as a positive number. It can be used for both the boiling and the condensation processes as long as you keep in mind that boiling is always endothermic (so ΔH will be positive), while condensation is always exothermic (so ΔH will be negative).

Table **14.3.1**: Enthalpies of Vaporization for Various Substances

Substance (Normal Boiling Point)	ΔH_{vap} (kJ/mol)
Water (100°C)	40.68
Bromine (59.5°C)	15.4
Benzene (80.1°C)	30.8
Ethanol (78.3°C)	38.6
Mercury (357°C)	59.23

Example 14.3.2

What is the energy change when 66.7 g of $Br_2(g)$ condense to a liquid at 59.5°C?

Solution

The ΔH_{vap} of Br_2 is 15.4 kJ/mol. Even though this is a condensation process, we can still use the numerical value of ΔH_{vap} as long as we realize that we must take energy out, so the ΔH value will be negative. To determine the magnitude of the energy change, we must first convert the amount of Br_2 to moles. Then we can use ΔH_{vap} as a conversion factor.

$$66.7\ \cancel{g\ Br_2} \times \frac{1\ \cancel{mol\ Br_2}}{159.8\ \cancel{g}} \times \frac{15.4 kJ}{\cancel{mol}} = 6.43\ kJ$$

Because the process is exothermic, the actual value will be negative: $\Delta H = -6.43$ kJ.

Exercise 14.3.2

What is the energy change when 822 g of $C_2H_5OH(\ell)$ boil at its normal boiling point of 78.3°C?

Answer

689 kJ

As with melting, the energy in boiling goes exclusively to changing the phase of a substance; it does not go into changing the temperature of a substance. So boiling is also an isothermal process. Only when all of a substance has boiled does any additional energy go to changing its temperature.

What happens when a liquid becomes a gas? We have already established that a liquid is composed of particles in contact with each other. When a liquid becomes a gas, the particles separate from each other, with each particle going its own way in space. This is how gases tend to fill their containers. Indeed, in the gas phase most of the volume is empty space; only about 1/1,000th of the volume is actually taken up by matter (Figure **14.3.1**). It is this property of gases that explains why they can be compressed, a fact that is considered in Chapter 6.

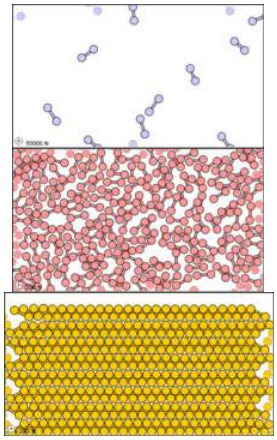


Figure **14.3.2**: Sub-microscopic view of the diatomic molecules of the element bromine (a) in the gaseous state (above 58°C); (b) in liquid form (between -7.2 and 58.8°C); and (c) in solid form (below -7.2°C). As a solid, the molecules are fixed, but fluctuate. As a liquid, the molecules are in contact but are also able to move around each other. As a gas, most of the volume is actually empty space. The particles are not to scale; in reality, the dots representing the particles would be about 1/100th of the size depicted.

Under some circumstances, the solid phase can transition directly to the gas phase without going through a liquid phase, and a gas can directly become a solid. The solid-to-gas change is called **sublimation**, while the reverse process is called **deposition.** Sublimation is isothermal, like the other phase changes. There is a measurable energy change during sublimation—this energy change is called the **enthalpy of sublimation**, represented as ΔH_{sub}. The relationship between the ΔH_{sub} and the other enthalpy changes is as follows:

$$\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$$

As such, ΔH_{sub} is not always tabulated because it can be simply calculated from ΔH_{fus} and ΔH_{vap}.

There are several common examples of sublimation. A well-known product, dry ice, is actually solid CO_2. Dry ice is dry because it sublimes, with the solid bypassing the liquid phase and going straight to the gas phase. The sublimation occurs at temperature of −77°C, so it must be handled with caution. If you have ever noticed that ice cubes in a freezer tend to get smaller over time, it is because the solid water is very slowly subliming. "Freezer burn" isn't actually a burn; it occurs when certain foods, such as meats, slowly lose solid water content because of sublimation. The food is still good, but looks unappetizing. Reducing the temperature of a freezer will slow the sublimation of solid water.



Figure **14.3.3**: Freezer burn on a piece of beef. (Public Domain; RolloM.)

Chemical equations can be used to represent a phase change. In such cases, it is crucial to use phase labels on the substances. For example, the chemical equation for the melting of ice to make liquid water is as follows:

$$H_2O(s) \rightarrow H_2O(\ell)$$

No chemical change is taking place; however, a physical change is taking place.

Summary

- Phase changes can occur between any two phases of matter.
- All phase changes occur with a simultaneous change in energy.
- All phase changes are isothermal.

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14.4: Properties of Liquids

Learning Objective

- Define the vapor pressure of liquids.
- Explain the origin of both surface tension and capillary action.

There are some properties that all liquids, including water, have. All liquids have a certain portion of particles with enough energy to enter the gas phase, and if these particles are at the surface of the liquid, they do so (Figure **14.4.1**). The formation of a gas from a liquid at temperatures below the boiling point is called **evaporation**. At these temperatures, the material in the gas phase is called **vapor**, rather than gas; the term *gas* is reserved for when the gas phase is the stable phase.

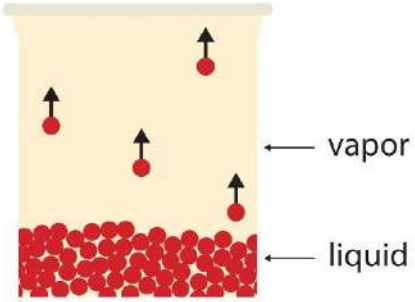


Figure **14.4.1**: Evaporation. Some particles of a liquid have enough energy to escape the liquid phase to become a vapor.

If the available volume is large enough, eventually all the liquid will become vapor. But if the available volume is not enough, eventually some of the vapor particles will reenter the liquid phase (Figure **14.4.2** Equilibrium). At some point, the number of particles entering the vapor phase will equal the number of particles leaving the vapor phase, so there is no net change in the amount of vapor in the system. We say that the system is *at equilibrium*. The partial pressure of the vapor at equilibrium is called the *vapor pressure of the liquid*.

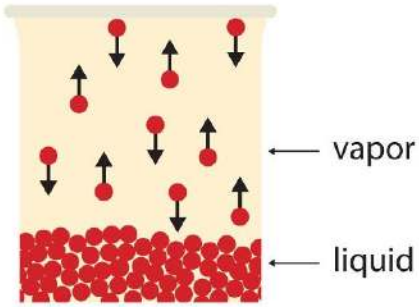


Figure **14.4.2**: Equilibrium. At some point, the number of particles entering the vapor phase will be balanced by the number of particles returning to the liquid. This point is called equilibrium.

Understand that the liquid has not stopped evaporating. The reverse process—condensation—is occurring as fast as evaporation, so there is no net change in the amount of vapor in the system. The term **dynamic equilibrium** represents a situation in which a process still occurs, but the opposite process also occurs at the same rate, so that there is no net change in the system.

The vapor pressure for a substance is dependent on the temperature of the substance; as the temperature increases, so does the vapor pressure. Figure **14.4.3** - Plots of Vapor Pressure versus Temperature for Several Liquids, is a plot of vapor pressure versus temperature for several liquids. Having defined vapor pressure, we can also redefine the *boiling point* of a liquid: the temperature at which the vapor pressure of a liquid equals the surrounding environmental pressure. The normal vapor pressure, then, is the temperature at which the vapor pressure is 760 torr, or exactly 1 atm. Thus boiling points vary with surrounding pressure, a fact that can have large implications on cooking foods at lower- or higher-than-normal elevations. Atmospheric pressure varies significantly with altitude.

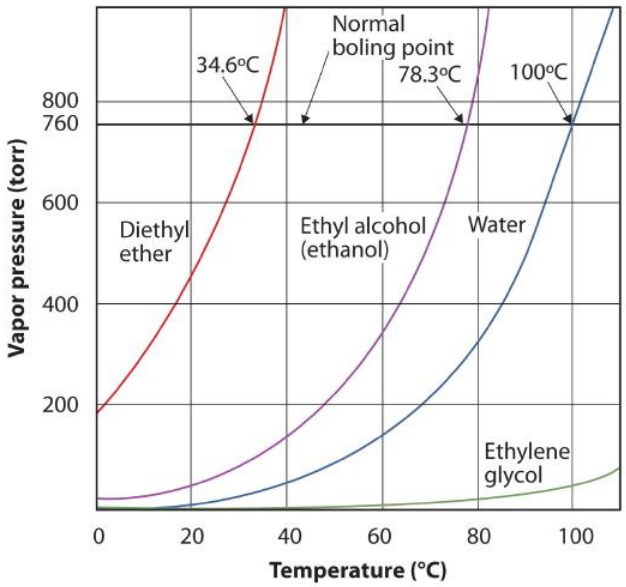


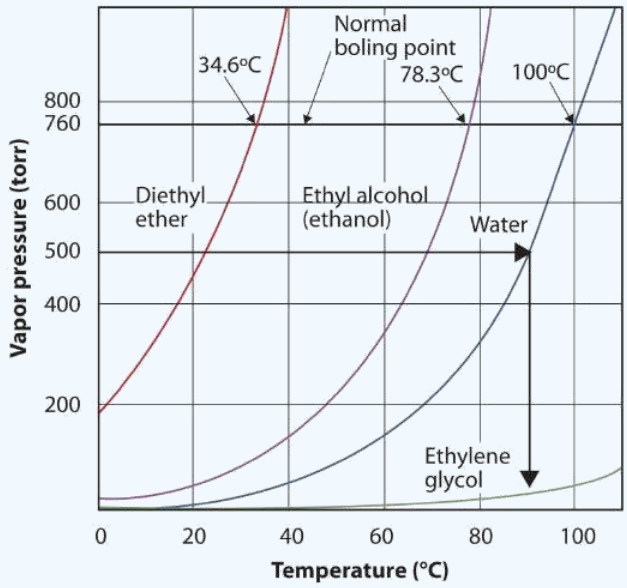
Figure **14.4.3**: Plots of Vapor Pressure versus Temperature for Several Liquids. The vapor pressure of a liquid depends on the identity of the liquid and the temperature, as this plot shows.

Example 14.4.1

Use Figure **14.4.3** to estimate the boiling point of water at 500 torr, which is the approximate atmospheric pressure at the top of Mount Everest.

Solution

See the accompanying figure. Five hundred torr is between 400 and 600, so we extend a line from that point on the *y*-axis across to the curve for water and then drop it down to the *x*-axis to read the associated temperature. It looks like the point on the water vapor pressure curve corresponds to a temperature of about 90°C, so we conclude that the boiling point of water at 500 torr is 90°C.



By reading the graph properly, you can estimate the boiling point of a liquid at different temperatures.

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? Exercise 14.4.1

Use Figure **14.4.3** to estimate the boiling point of ethanol at 400 torr.

Answer

about 65°C

The vapor pressure curve for water is not exactly zero at the melting point 0°C. Even ice has a vapor pressure—that is why it sublimes over time. However, the vapor pressures of solids are typically much lower than that of liquids. At −1°C, the vapor pressure of ice is 4.2 torr. At a freezer temperature of 0°F (−17°C), the vapor pressure of ice is only 1.0 torr; so-called deep freezers can get down to −23°C, where the vapor pressure of ice is only 0.6 torr.

All liquids share some other properties as well. **Surface tension** is an effect caused by an imbalance of forces on the atoms at the surface of a liquid, as shown in Figure **14.4.4**. The blue particle in the bulk of the liquid experiences intermolecular forces from all around, as illustrated by the arrows. However, the yellow particle on the surface does not experience any forces above it because there are no particles above it. This leads to an imbalance of forces, called surface tension.

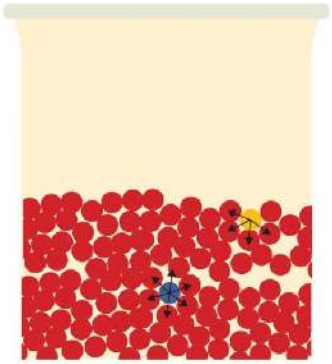


Figure **14.4.4** Surface Tension. Surface tension comes from the fact that particles at the surface of a liquid do not experience interactions from all directions, leading to an imbalance of forces on the surface.

Surface tension is responsible for several well-known behaviors of liquids, including water. Liquids with high surface tension tend to bead up when present in small amounts (Figure **14.4.5**).



Figure **14.4.5** Effects of Surface Tension © Thinkstock. Water on the surface of this apple beads up due to the effect of surface tension.

Surface tension causes liquids to form spheres in free fall or zero gravity. Surface tension is also responsible for the fact that small insects can "walk" on water. Because of surface tension, it takes energy to break the surface of a liquid, and if an object (such as an insect) is light enough, there is not enough force due to gravity for the object to break through the surface, so the object stays on top of the water (Figure **14.4.6**). Carefully done, this phenomenon can also be illustrated with a thin razor blade or a paper clip.



Figure **14.4.6** Walking on Water. Small insects can actually walk on top of water because of surface tension effects. (Unsplash License; Miguel Alcântara via unsplash)

The fact that small droplets of water bead up on surfaces does not mean that water—or any other liquid—does not interact with other substances. Sometimes the attraction can be very strong. **Adhesion** is the tendency of a substance to interact with other substances because of intermolecular forces, while **cohesion** is the tendency of a substance to interact with itself. If cohesive forces within a liquid are stronger than adhesive forces between a liquid and another substance, then the liquid tends to keep to itself; it will bead up. However, if adhesive forces between a liquid and another substance are stronger than cohesive forces, then the liquid will spread out over the other substance, trying to maximize the interface between the other substance and the liquid. It is said that the liquid *wets* the other substance.

Adhesion and cohesion are important for other phenomena as well. In particular, if adhesive forces are strong, then when a liquid is introduced to a small-diameter tube of another substance, the liquid will move up or down in the tube, as if ignoring gravity. Because tiny tubes are called capillaries, this phenomenon is called **capillary action.** For example, one type of capillary action, *capillary rise*, is seen when water or water-based liquids rise up in thin glass tubes (like the capillaries sometimes used in blood tests), forming an upwardly curved surface called a **meniscus**. Capillary action is also responsible for the "wicking" effect that towels and sponges use to dry wet objects; the matting of fibers forms tiny capillaries that have good adhesion with water. Cotton is a good material for this; polyester and other synthetic fabrics do not display similar capillary action, which is why you seldom find rayon bath towels. A similar effect is observed with liquid fuels or melted wax and their wicks. Capillary action is thought to be at least partially responsible for transporting water from the roots to the tops of trees, even tall ones.

On the other hand, some liquids have stronger cohesive forces than adhesive forces. In this case, in the presence of a capillary, the liquid is forced down from its surface; this is an example of a type of capillary action called *capillary depression*. In this case, the meniscus curves downward. Mercury has very strong cohesive forces; when a capillary is placed in a pool of mercury, the surface of the mercury liquid is depressed (Figure **14.4.7**).

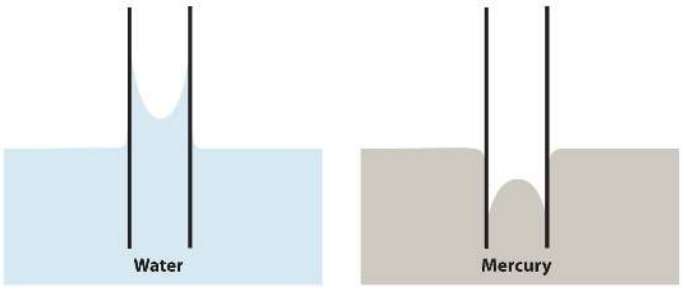


Figure **14.4.7**: Capillary Action. (a) Capillary rise is seen when adhesion is strong, such as with water in a thin glass tube. (b) Capillary depression is seen when cohesive forces are stronger than adhesive forces, such as with mercury and thin glass tubes.

Chemistry is Everywhere: Waxing a Car

Responsible car owners are encouraged to wax their cars regularly. In addition to making the car look nicer, it also helps protect the surface, especially if the surface is metal. Why?

The answer has to do with cohesion and adhesion (and, to a lesser extent, rust). Water is an important factor in the rusting of iron, sometimes used extensively in outer car bodies. Keeping water away from the metal is one way to minimize rusting. A coat of paint helps with this. However, dirty or scratched paint can attract water, and adhesive forces will allow the water to wet the surface, maximizing its contact with the metal and promoting rust.



Figure 14.4.8: Waxing a car. Droplets of water on a freshly waxed car do not wet the car well because of low adhesion between water and the waxed surface. This helps protect the car from rust. (Unsplash License; Yuvraj Singh via Unspash)

Wax is composed of long hydrocarbon molecules that do not interact well with water. (Hydrocarbons are compounds with C and H atoms; for more information on hydrocarbons, see Chapter 16). That is, a thin layer of wax will not be wetted by water. A freshly waxed car has low adhesive forces with water, so water beads up on the surface, as a consequence of its cohesion and surface tension. This minimizes the contact between water and metal, thus minimizing rust.

Summary

- All liquids evaporate.
- If volume is limited, evaporation eventually reaches a dynamic equilibrium, and a constant vapor pressure is maintained.
- All liquids experience surface tension, an imbalance of forces at the surface of the liquid.
- All liquids experience capillary action, demonstrating either capillary rise or capillary depression in the presence of other substances.

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14.5: Solids

Learning Objective

- Describe the general properties of a solid.
- Describe the six different types of solids.

A solid is like a liquid in that particles are in contact with one another. Solids are unlike liquids in that the intermolecular forces are strong enough to hold the particles in place. At low enough temperatures, all substances are solids (helium is the lone exception), but the temperature at which the solid state becomes the stable phase varies widely among substances, from 20 K (−253°C) for hydrogen to over 3,900 K (3,600°C) for carbon.

The solid phase has several characteristics. First, solids maintain their shape. They do not fill their entire containers like gases do, and they do not adopt the shape of their containers like liquids do. They cannot be easily compressed like gases can, and they have relatively high densities.

Solids may also demonstrate a variety of properties. For example, many metals can be beaten into thin sheets or drawn into wires, while compounds such as NaCl will shatter if they are struck. Some metals, such as sodium and potassium, are rather soft, while others, such as diamond, are very hard and can easily scratch other substances. Appearances differ as well: most metals are shiny and silvery, but sulfur (a nonmetal) is yellow, and ionic compounds can take on a rainbow of colors. Solid metals conduct electricity and heat, while ionic solids do not. Many solids are opaque, but some are transparent. Some dissolve in water, but some do not. Figure **14.5.1**, shows two solids that exemplify the similar and dissimilar properties of solids.



Figure **14.5.1**: Properties of Solids. (a) Sodium metal is silvery, soft, opaque, and conducts electricity and heat well. (b) NaCl is transparent, hard, colorless, and does not conduct electricity or heat well in the solid state. These two substances illustrate the range of properties that solids can have. Source: Photo on left courtesy of Images of Elements, http://images-of-elements.com/sodium.php. Photo on right courtesy of Choba Poncho, commons.wikimedia.org/wiki/File:Sodiumchloride_crystal_01.jpg.

Solids can have a wide variety of physical properties. We will review the different types of solids and the bonding that gives them their properties.

First, we must distinguish between two general types of solids. An **amorphous solid** is a solid with no long-term structure or repetition. Examples include glass and many plastics, both of which are composed of long chains of molecules with no order from one molecule to the next. A **crystalline solid** is a solid that has a regular, repeating three-dimensional structure. A crystal of NaCl (Figure **14.5.1**) is one example: at the atomic level, NaCl is composed of a regular three-dimensional array of Na^+ ions and Cl^- ions.

There is only one type of amorphous solid. However, there are several different types of crystalline solids, depending on the identity of the units that compose the crystal.

An **ionic solid** is a crystalline solid composed of ions (even if the ions are polyatomic). NaCl is an example of an ionic solid (Figure **14.5.2** - An Ionic Solid). The Na^+ ions and Cl^- ions alternate in three dimensions, repeating a pattern that goes on throughout the sample. The ions are held together by the attraction of opposite charges—a very strong force. Hence most ionic

solids have relatively high melting points; for example, the melting point of NaCl is 801°C. Ionic solids are typically very brittle. To break them, the very strong ionic attractions need to be broken; a displacement of only about 1×10^{-10} m will move ions next to ions of the same charge, which results in repulsion. Ionic solids do not conduct electricity in their solid state; however, in the liquid state and when dissolved in some solvent, they do conduct electricity. This fact originally promoted the idea that some substances exist as ionic particles.

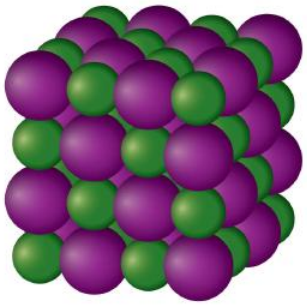


Figure **14.5.2**: An Ionic Solid. NaCl is a solid composed of a three-dimensional array of alternating Na^+ ions (green) and Cl^- ions (purple) held together by the attraction of opposite charges.

A **molecular solid** is a crystalline solid whose components are covalently bonded molecules. Many molecular substances, especially when carefully solidified from the liquid state, form solids where the molecules line up with a regular fashion similar to an ionic crystal, but they are composed of molecules instead of ions. Because the intermolecular forces between molecules are typically less strong than in ionic solids, molecular solids typically melt at lower temperatures and are softer than ionic solids. Ice is an example of a molecular solid. In the solid state, the molecules line up in a regular pattern (Figure **14.5.3**). Some very large molecules, such as biological molecules, will form crystals only if they are very carefully solidified from the liquid state or, more often, from a dissolved state; otherwise, they will form amorphous solids.

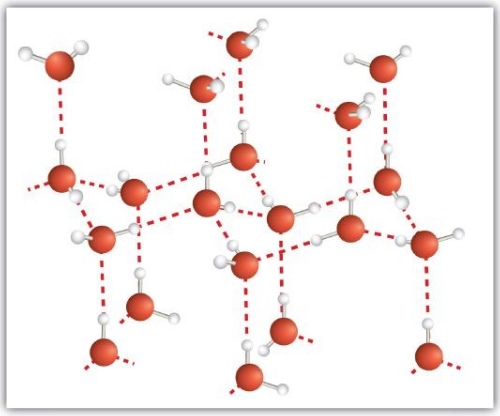


Figure **14.5.3**: Molecular Solids. Water molecules line up in a regular pattern to form molecular solids. The dotted lines show how the polar O–H covalent bonds in one molecule engage in hydrogen bonding with other molecules. The O atoms are red, and the H atoms are white.

Some solids are composed of atoms of one or more elements that are covalently bonded together in a seemingly never-ending fashion. Such solids are called **covalent network solids**. Each piece of the substance is essentially one huge molecule, as the covalent bonding in the crystal extends throughout the entire crystal. The two most commonly known covalent network solids are carbon in its diamond form and silicon dioxide (SiO_2). Figure **14.5.4** - Covalent Network Solids, shows the bonding in a covalent network solid. Generally, covalent network solids are poor conductors of electricity, although their ability to conduct heat is variable: diamond is one of the most thermally conductive substances known, while SiO_2 is about 100 times less thermally conductive. Most covalent network solids are very hard, as exemplified by diamond, which is the hardest known substance. Covalent network solids have high melting points by virtue of their network of covalent bonds, all of which would have to be broken for them to transform into a liquid. Indeed, covalent network solids are among the highest-melting substances known: the

melting point of diamond is over 3,500°C, while the melting point of SiO_2 is around 1,650°C. These characteristics are explained by the network of covalent bonds throughout the sample.

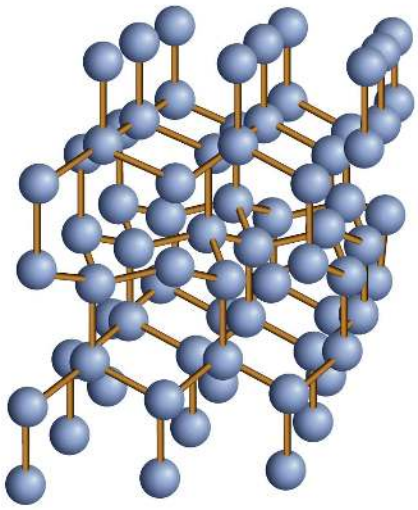


Figure **14.5.4**: Covalent Network Solids. Diamond is a covalent network solid, with each C atom making four covalent bonds to four other C atoms. A diamond is essentially one huge molecule.

A **metallic solid** is a solid with the characteristic properties of a metal: shiny and silvery in color and a good conductor of heat and electricity. A metallic solid can also be hammered into sheets and pulled into wires. A metallic solid exhibits metallic bonding, a type of intermolecular interaction caused by the sharing of the *s* valence electrons by all atoms in the sample. It is the sharing of these valence electrons that explains the ability of metals to conduct electricity and heat well. It is also relatively easy for metals to lose these valence electrons, which explains why metallic elements usually form cations when they make compounds.

✔ Example 14.5.1

Predict the type of crystal exhibited by each solid.

a. MgO
b. Ag
c. CO_2

Solution

a. A combination of a metal and a nonmetal makes an ionic compound, so MgO would exist as ionic crystals in the solid state.
b. Silver is a metal, so it would exist as a metallic solid in the solid state.
c. CO_2 is a covalently bonded molecular compound. In the solid state, it would form molecular crystals. (You can actually see the crystals in dry ice with the naked eye.)

? Exercise 14.5.1

Predict the type of crystal exhibited by each solid.

a. I_2
b. $Ca(NO_3)_2$

Answers

a. molecular crystals
b. ionic crystals

Food and Drink Application: The Rocks We Eat

The foods and beverages we eat and drink all have different phases: solid, liquid, and gas. (How do we ingest gases? Carbonated beverages have gas, which sometimes cause a person to belch.) However, among the solids we eat, three in particular are, or are produced from, rocks. Yes, rocks!

The first one is NaCl, or common salt. Salt is the only solid that we ingest that is actually mined as a rock (hence the term *rock salt*; it really is a rock). Salt provides both Na^+ ions and Cl^- ions, both of which are necessary for good health. Salt preserves food, a function that was much more important before the days of modern food preparation and storage. The fact that saltiness is one of the major tastes the tongue can detect suggests a strong evolutionary link between ingesting salt and survival. There is some concern today that there is too much salt in the diet; it is estimated that the average person consumes at least three times as much salt daily as is necessary for proper bodily function.

The other two rocks we eat are related: sodium bicarbonate ($NaHCO_3$) and sodium carbonate (Na_2CO_3). However, we do not mine these substances directly from the ground; we mine trona, whose chemical formula is $Na_3H(CO_3)_2$. This substance is dissolved in water and treated with CO_2 gas to make either Na_2CO_3 or $NaHCO_3$. Another process, called the Solvay process, is also used to make Na_2CO_3. In the Solvay process, NH_3 and CO_2 are added to solutions of NaCl to make $NaHCO_3$ and NH_4Cl; the $NaHCO_3$ precipitates and is heated to produce Na_2CO_3. Either way, we get these two products from the ground (i.e., rocks).

$NaHCO_3$ is also known as baking soda, which is used in many baked goods. Na_2CO_3 is used in foods to regulate the acid balance. It is also used in laundry (where it is called washing soda) to interact with other ions in water that tend to reduce detergent efficiency.



Figure **14.5.5**: Salt Mining © Thinkstock. Salt mining can be at the surface or below ground. Here salt is mined from surface deposits. Part of the processing facility can be seen in the background.

Summary

- Solids can be divided into amorphous solids and crystalline solids.
- Crystalline solids can be ionic, molecular, covalent network, or metallic.

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CHAPTER OVERVIEW

17: 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 which we can affect the extent of chemical reactions.

17.1: Prelude to Chemical Equilibrium
17.2: Chemical Equilibrium
17.3: The Equilibrium Constant
17.4: Heterogeneous Equilibria
17.6: Calculating Equilibrium Values
17.7: Solubility Equilibria

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17.1: 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 this chapter.

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17.2: 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 H_2 and the I_2 react to make HI.

However, this is not the case. The reverse chemical reaction is also taking place:

$$2HI \rightarrow H_2 + I_2$$

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:

$$H_2 + I_2 \rightleftharpoons 2HI$$

The double arrow implies that the reaction is going in both directions. Note that the reaction must still be balanced.

Example 17.2.1

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:

$$CaCO_3 + \rightleftharpoons CaO + CO_2$$

Exercise 17.2.1

Write the equilibrium equation between elemental hydrogen and elemental oxygen as reactants and water as the product.

Answer

$$2H_2 + O_2 + \rightleftharpoons 2H_2O$$

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 canceled 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

$$H_2 + I_2 \rightleftharpoons 2HI$$

is the same thing as representing the same equilibrium as

$$2HI \rightleftharpoons H_2 + I_2$$

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.

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17.3: 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:

$$K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

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

$$K_{eq} = \frac{[B]}{[A]}$$

(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:

$$K_{eq} = \frac{[B]}{[A]} = \frac{4.0}{2.0} = 2.0$$

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:

$$K_{eq} = \frac{[B]}{[A]} = \frac{6.0}{3.0} = 2.0$$

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 become 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 17.3.1

Given the following reaction:

$$\mathrm{H_2 + I_2 \rightleftharpoons 2\,HI} \tag{17.3.1}$$

If the equilibrium [HI] is 0.75 M and the equilibrium [H_2] is 0.20 M, what is the equilibrium [I_2] if the K_{eq} is 0.40?

Solution

We start by writing the K_{eq} expression. Using the *products over reactants* approach, the K_{eq} expression is as follows:

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

Note that [HI] is squared because of the coefficient 2 in the balanced chemical equation. Substituting for the equilibrium [H_2] and [HI] and for the given value of K_{eq}:

$$0.40 = \frac{(0.75)^2}{(0.20)[I_2]}$$

To solve for [I_2], 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 [I_2]. This brings [I_2] 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,

[I_2] = 7.0 M

The concentration unit is assumed to be molarity. This value for [I_2] 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 17.3.1

Given the following reaction:

$$\mathrm{H_2 + I_2 \rightleftharpoons 2\,HI} \tag{17.3.2}$$

If the equilibrium [HI] is 0.060 M and the equilibrium [I_2] is 0.90 M, what is the equilibrium [H_2] if the K_{eq} 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 17.3.2

The following reaction is at equilibrium:

$$\mathrm{N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3} \tag{17.3.3}$$

The K_{eq} at a particular temperature is 13.7. If the equilibrium [N_2] is 1.88 M and the equilibrium [NH_3] is 6.62 M, what is the equilibrium [H_2]?

Solution

We start by writing the K_{eq} expression from the balanced chemical equation:

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

Substituting for the known equilibrium concentrations and the K_{eq}, this becomes

$$13.7 = \frac{(6.62)^2}{(1.88)[H_2]^3}$$

Rearranging algebraically and then evaluating the numerical expression, we get

$$[H_2]^3 = \frac{(6.62)^2}{(1.88)(13.7)} = 1.7015219754$$

To solve for $[H_2]$, we need to take the cube root of the equation. Performing this operation, we get

$[H_2] = 1.19$ 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 17.3.2

The following reaction is at equilibrium:

$$\mathrm{N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3} \tag{17.3.4}$$

The K_{eq} at a particular temperature is 13.7. If the equilibrium $[N_2]$ is 0.055 M and the equilibrium $[H_2]$ is 1.62 M, what is the equilibrium $[NH_3]$?

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 17.3.3

What is the K_P for this reaction, given the equilibrium partial pressures of 0.664 atm for NO_2 and 1.09 for N_2O_4?

$$\mathrm{2\,NO_2\,(g) \rightleftharpoons N_2O_4\,(g)} \tag{17.3.5}$$

Solution

Write the K_P expression for this reaction:

$$K_P = \frac{P_{N_2O_4}}{P_{NO_2}^2}$$

Then substitute the equilibrium partial pressures into the expression and evaluate:

$$K_P = \frac{(1.09)}{(0.664)^2} = 2.47$$

Exercise 17.3.3

What is the K_P for this reaction, given the equilibrium partial pressures of 0.44 atm for H_2, 0.22 atm for Cl_2, and 2.98 atm for HCl?

$$\mathrm{H_2 + Cl_2 \rightleftharpoons 2\,HCl} \tag{17.3.6}$$

Answer

91.7

There is a simple relationship between K_{eq} (based on concentration units) and K_P (based on pressure units):

$$K_P = K_{eq} \cdot (RT)^{\Delta n}$$

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 $n_{gas,prods} - n_{gas,rcts}$. Note that this equation implies that if the number of moles of gas are the same in reactants and products, $K_{eq} = K_P$.

Example 17.3.4

What is the K_P at 25°C for this reaction if the K_{eq} is 4.2×10^{-2}?

$$\mathrm{N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3} \tag{17.3.7}$$

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:

$\Delta n = 2 - 4 = -2$ 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:

$K_P = (4.2 \times 10^{-2})(0.08205)(298)^{-2}$

Solving,

$K_P = 7.0 \times 10^{-5}$

Exercise 17.3.4

What is the K_P at 25°C for this reaction if the K_{eq} is 98.3?,-

$$\mathrm{I_2\,(g) \rightleftharpoons 2\,I\,(g)} \tag{17.3.8}$$

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:

$$\mathrm{2\,NaHCO_3\,(s) \rightleftharpoons Na_2CO_3\,(s) + CO_2\,(g) + H_2O\,(l)} \tag{17.3.9}$$

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.

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17.4: Heterogeneous Equilibria

Learning Objectives

- To understand how different phases affect equilibria.

When the products and reactants of an equilibrium reaction form a single phase, whether gas or liquid, the system is a homogeneous equilibrium. In such situations, the concentrations of the reactants and products can vary over a wide range. In contrast, a system whose reactants, products, or both are in more than one phase is a heterogeneous equilibrium, such as the reaction of a gas with a solid or liquid.

As noted in the previous section, the equilibrium constant expression is actually a ratio of activities. To simplify the calculations in general chemistry courses, the activity of each substance in the reaction is often approximated using a ratio of the molarity of a substance compared to the standard state of that substance. For substances that are liquids or solids, the standard state is just the concentration of the substance within the liquid or solid. Because the molar concentrations of pure liquids and solids normally do not vary greatly with temperature, the ratio of the molarity to the standard state for substances that are liquids or solids always has a value of 1. For example, for a compound such as $CaF_2(s)$, the term going into the equilibrium expression is $[CaF_2]/[CaF_2]$ which cancels to unity. Thus, when the activities of the solids and liquids (including solvents) are incorporated into the equilibrium expression, they do not change the value.

Consider the following reaction, which is used in the final firing of some types of pottery to produce brilliant metallic glazes:

$$\mathrm{CO_2(g) + C(s) \rightleftharpoons 2\,CO(g)} \tag{17.4.1}$$

The glaze is created when metal oxides are reduced to metals by the product, carbon monoxide. The equilibrium constant expression for this reaction is as follows:

$$K = \frac{a_{CO}^2}{a_{CO_2} a_C} = \frac{[CO]^2}{[CO_2][1]} = \frac{[CO]^2}{[CO_2]} \tag{17.4.2}$$

The equilibrium constant for this reaction can also be written in terms of the partial pressures of the gases:

$$K_p = \frac{(P_{CO})^2}{P_{CO_2}} \tag{17.4.3}$$

Incorporating all the constant values into K' or K_p allows us to focus on the substances whose concentrations change during the reaction.

Although the activities of pure liquids or solids are not written explicitly in the equilibrium constant expression, these substances must be present in the reaction mixture for chemical equilibrium to occur. Whatever the concentrations of CO and CO_2, the system described in Equation 17.4.1 will reach chemical equilibrium only if a stoichiometric amount of solid carbon or excess solid carbon has been added so that some is still present once the system has reached equilibrium. As shown in Figure 17.4.1, it does not matter whether 1 g or 100 g of solid carbon is present; in either case, the composition of the gaseous components of the system will be the same at equilibrium.

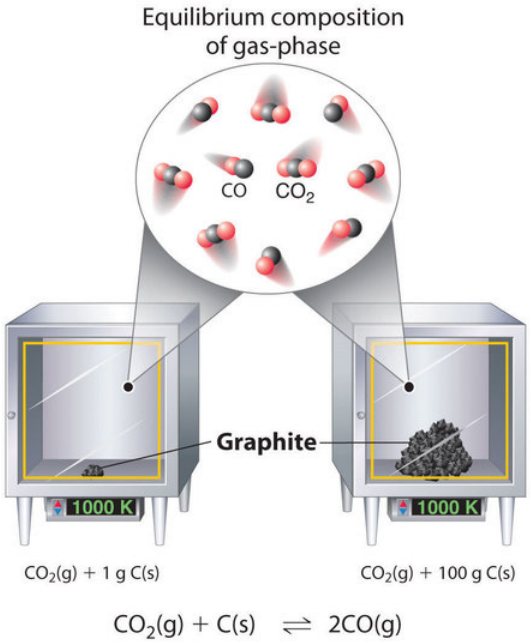


Figure 17.4.2: Effect of the Amount of Solid Present on Equilibrium in a Heterogeneous Solid–Gas System. In the system, the equilibrium composition of the gas phase at a given temperature, 1000 K in this case, is the same whether a small amount of solid carbon (left) or a large amount (right) is present.

Example 17.4.1

Write each expression for K, incorporating all constants, and K_p for the following equilibrium reactions.

a. $\mathrm{PCl_3(l) + Cl_2(g) \rightleftharpoons PCl_5(s)}$
b. $\mathrm{Fe_3O_4(s) + 4H_2(g) \rightleftharpoons 3Fe(s) + 4H_2O(g)}$

Given: balanced equilibrium equations.

Asked for: expressions for K and K_p.

Strategy:

Find K by writing each equilibrium constant expression as the ratio of the concentrations of the products and reactants, each raised to its coefficient in the chemical equation. Then express K_p as the ratio of the partial pressures of the products and reactants, each also raised to its coefficient in the chemical equation.

Solution

This reaction contains a pure solid (PCl_5) and a pure liquid (PCl_3). Their activities are equal to 1, so when incorporated into the equilibrium constant expression, they do not change the value. So

$$K = \frac{1}{(1)[Cl_2]}$$

and

$$K_p = \frac{1}{(1)P_{Cl_2}}$$

This reaction contains two pure solids (Fe_3O_4 and Fe), which are each assigned a value of 1 in the equilibrium constant expressions:

$$K = \frac{(1)[H_2O]^4}{(1)[H_2]^4}$$

and

$$K_p = \frac{(1)(P_{H_2O})^4}{(1)(P_{H_2})^4}$$

? Exercise 17.4.1

Write the expressions for K and K_p for the following reactions.

a. $\mathrm{CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)}$

b. $\underset{\textit{glucose}}{\mathrm{C_6H_{12}O_6\,(s)}} + \mathrm{6\,O_2\,(g) \rightleftharpoons 6\,CO_2\,(g) + 6\,H_2O\,(g)}$

Answer a

$K = [\mathrm{CO_2}]$ and $K_p = P_{\mathrm{CO_2}}$

Answer b

$K = \frac{[CO_2]^6[H_2O]^6}{[O_2]^6}$ and $K_p = \frac{(P_{CO_2})^6(P_{H_2O})^6}{(P_{O_2})^6}$

For reactions carried out in solution, the solvent is assumed to be pure, and therefore is assigned an activity equal to 1 in the equilibrium constant expression. The activities of the solutes are approximated by their molarities. The result is that the equilibrium constant expressions appear to only depend upon the concentrations of the solutes.

> *The activities of pure solids, pure liquids, and solvents are defined as having a value of '1'. Often, it is said that these activities are "left out" of equilibrium constant expressions. This is an unfortunate use of words. The activities are not "left out" of equilibrium constant expressions. Rather, because they have a value of '1', they do not change the value of the equilibrium constant when they are multiplied together with the other terms. The activities of the solutes are approximated by their molarities.*

Summary

An equilibrated system that contains products and reactants in a single phase is a homogeneous equilibrium; a system whose reactants, products, or both are in more than one phase is a heterogeneous equilibrium.

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17.6: Calculating Equilibrium Values

The numeric value of the equilibrium constant tells us something about the *ratio* of the reactants and products in the final equilibrium mixture. Likewise, the magnitude of the equilibrium constant tells us about the actual composition of that mixture.

In the three equilibrium systems, the first depicts a reaction in which the ratio of products to reactants is very *small*. Because the expression for the equilibrium constant is given by the pressure (or concentration) of products divided by the pressure (or concentration) of reactants, the equilibrium constant, *K*, for this system is also small. In the second example, the concentrations of reactants and products are shown to be *equal*, making the ratio (the equilibrium constant) equal to "1". In the last example, the products are shown to dominate the equilibrium mixture, making the ratio $^{(P_{Products})}/_{(P_{Reactants})}$ very large. In these examples, the stoichiometric ratios of the reactants and products are one and there is only one reactant and only one product; if multiple reactants or products are involved, the relationship between their concentrations would be more complex, but that ratio is always given by the expression for *K*. This fact allows us to take data for an equilibrium reaction and, if *K* is known, calculate concentrations for reactants and products. Likewise, if all of the equilibrium concentrations are known, we can use these to calculate a value for the equilibrium constant.

In these types of problems, an *ICE* table is often useful. This table has entries for *Initial* concentrations (or pressures), *Equilibrium* concentrations and any *Change* between the initial and equilibrium states. For example, consider the reaction between carbon monoxide and chlorine to form phosgene, a deadly compound that was used as a gas warfare agent in World War I.

$$\mathbf{CO}\ (g) + \mathbf{Cl_2}\ (g) \rightleftarrows \mathbf{COCl_2}\ (g)$$

Example 17.6.1:

A mixture of CO and Cl_2 has initial partial pressures of 0.60 atm for CO and 1.10 atm for Cl_2. After the mixture reaches equilibrium, the partial pressure of $COCl_2$ is 0.10 atm. Determine the value of *K*.

Solution

The initial pressures for carbon monoxide and chlorine are placed in the first row and the equilibrium pressure for phosgene is placed in the last row. ***Initially***, the pressure of phosgene was zero, so that goes in the first row; the change for phosgene is therefore "+ 0.10 atm".

Solutions to Example 10.3.1

	P_{CO}	P_{Cl_2}	P_{COCl_2}
=== Initial ===	0.60 atm	1.10 atm	0 atm
Change			
	+ 0.10 atm		
Equilibrium			
	0.10 atm		

Because one mole of CO is required to make one mole of $COCl_2$ the partial pressure of CO must have dropped by 0.10 atm (the ***Change***) in order to make $COCl_2$ with a partial pressure of 0.10 atm, giving a final (***Equilibrium***) pressure of 0.50 atm for carbon monoxide. Likewise, one mole of chlorine is required to make one mole of $COCl_2$ making the ***Change*** for chlorine 0.10 atm and the ***Equilibrium*** partial pressure 1.00 atm. The completed table is shown below:

Solutions to Example 10.3.1

	P_{CO}	P_{Cl_2}	P_{COCl_2}
=== Initial ===	0.60 atm	1.10 atm	0 atm
Change	-0.10 atm	-0.10 atm	+ 0.10 atm
Equilibrium	0.50 atm	1.00 atm	0.10 atm

The equilibrium expression for the phosgene-forming reaction is given by the following equation:

$$\frac{P_{COCl_2}}{P_{CO}P_{Cl_2}} = K$$

Substituting the values from the Table into this equation:

$$\frac{P_{COCl_2}}{P_{CO}P_{Cl_2}} = \frac{(0.10)}{(0.50)(1.00)} = 0.20$$

Notice that equilibrium constants for gas phase reactions are not typically written with units, although units are sometimes used in equilibrium constants calculated from molar concentrations. Many textbooks differentiate between equilibrium constants calculated from partial pressures and molar concentrations by affixing subscripts; K_P and K_C. In this book, we will simply use K and K_C to represent the two; a value for K will always denote a constant calculated from partial pressure data.

? Exercise 17.6.1

1. For the reaction shown below, all four gasses are introduced into a vessel, each with an initial partial pressure of 0.500 atm, and allowed to come to equilibrium; at equilibrium, the partial pressure of SO_3 is found to be 0.750 atm. Determine the value of *K*.

$$\mathbf{SO_2}\ \textit{(g)} + \mathbf{NO_2}\ \textit{(g)} \rightleftarrows \mathbf{SO_3}\ \textit{(g)} + \mathbf{NO}\ \textit{(g)}$$

2. For the reaction shown above, the initial partial pressures of SO_3 and NO are 0.500 atm under conditions where the equilibrium constant is, $K = 9.00$. The equilibrium partial pressure for SO_2 is found to be 0.125 atm. Calculate the equilibrium partial pressure for SO_3.

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17.7: Solubility Equilibria

In Chapter 5 we learned about a class of reactions that involved the formation of a solid that was "insoluble" in water, and precipitated from the solution. In these "precipitation reactions", one ionic salt was described as "insoluble", driving the reaction towards the formation of products. Silver chloride is a classic example of this. If you mix silver nitrate (almost *all* nitrate salts are "soluble" in water) with sodium chloride, a copious white precipitate of silver chloride formed and the silver nitrate was deemed "insoluble".

Nonetheless, if you took the clear solution from above the silver chloride precipitate and did a chemical analysis, there will be sodium ions, nitrate ions, and *traces* of chloride ions and silver ions. The concentrations of silver and chloride ions would be about 1.67×10^{-5} M, far below the concentrations we typically work with, hence we say that silver chloride is "insoluble in water". That, of course, is not true. Solubility is an equilibrium in which ions leave the solid surface and go into solution at the same time that ions are re-deposited on the solid surface. For silver chloride, we could write the equilibrium expression as:

$$\mathrm{AgCl\,(s) + H_2O\,(l) \rightleftharpoons Ag^+\,(aq) + Cl^-\,(aq)}$$

In order to write the expression for the equilibrium constant for this solubility reaction, we need to recall the rules stated in Section 10.2 of this chapter; Rule #4 states, "Reactants or products that are present as solids or liquids or the solvent, all have an activity value of 1, and so they do not affect the value of the equilibrium expression." Because silver chloride is a solid, and water is the solvent, the expression for the equilibrium constant is simply,

$$K_{sp} = [Ag^+][Cl^-]$$

Note that we have denoted the equilibrium constant as K_{sp}, where "sp" refers to solubility equilibrium, or "solubility product" (the product of the concentrations of the ions). We can calculate the value of K_{sp} for silver chloride from the analytical data that we cited above; an aqueous solution above solid silver chloride has a concentration of silver and chloride ions of 1.67×10^{-5} M, at 25° C. Because the concentrations of silver and chloride ions are both 1.67×10^{-5} M, the value of K_{sp} under these conditions must be:

$$K_{sp} = [Ag^+][Cl^-] = (1.67 \times 10^{-5})^2 = 2.79 \times 10^{-10}$$

This is very small, considering that K_{sp} for sodium chloride is about 29!

For a salt such as PbI_2 chemical analysis tells us that the lead concentration in a saturated solution (the maximum equilibrium solubility under a specified set of conditions, such as temperature, pressure, etc.) is about 1.30×10^{-3} M. In order to calculate K_{sp} for lead (II) iodide, you must first write the chemical equation and then the equilibrium expression for K_{sp} and then simply substitute for the ionic concentrations.

$$\mathrm{PbI_2\,(s) \rightleftharpoons Pb^{2+}\,(aq) + 2\,I^-\,(aq)}$$

As you do this, remember that there are *two* iodide ions for every lead ion, therefore the concentrations for lead (II) and iodide are 1.30×10^{-3} M and 2.60×10^{-3} M, respectively.

$$K_{sp} = [Pb^{2+}][I^-]^2 = (1.30 \times 10^{-3})(2.60 \times 10^{-3})^2 = 8.79 \times 10^{-9}$$

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CHAPTER OVERVIEW

20: Organic Chemistry

Organic chemistry is a very vast and complex subject. There are millions of known organic compounds, which is far more than the number of inorganic compounds. The reason lies within the uniqueness of carbon's structure and bonding capabilities. Carbon has four valence electrons and therefore makes four separate covalent bonds in compounds. Carbon has the ability to bond to itself repeatedly, making long chains of carbon atoms as well as ringed structures. These bonds can be single, double, or triple covalent bonds. Carbon readily makes covalent bonds with other elements, primarily hydrogen, oxygen, nitrogen, halogens, and several other nonmetals.

Topic hierarchy

20.01: Organic Chemistry
20.02: Straight-Chain Alkanes
20.03: Branched Alkanes
20.04: Isomers
20.05: Alkenes and Alkynes
20.06: Aromatic Hydrocarbons
20.07 Functional Groups
20.08: Alcohols
20.09: Aldehydes and Ketones
20.10: Carboxylic Acids
20.11: Esters
20.12: Addition Reactions
20.13: Substitution Reactions
20.14: Oxidation Reactions
20.15: Condensation Reactions
20.16: Polymerization - Addition Polymers
20.17: Polymerization - Condensation Polymers

Contributors

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20.01: Organic Chemistry

How many carbon-containing molecules are there? The current estimate is around 20 million different known organic compounds. Why the uncertainty? Every day, scientists are coming up with new compounds. Some of these materials are of interest for a research project, while others are destined to be developed for a commercial market. As soon as we think we know how many organic compounds exist, more are discovered and our number quickly becomes out of date.

Organic Chemistry

At one time in history, it was thought that only living things were capable of synthesizing the carbon-containing compounds present in cells. For that reason, the term organic was applied to those compounds. Eventually it was proved that carbon-containing compounds could be synthesized from inorganic substances, but the term "organic" has remained. Currently, **organic compounds** are defined as covalently bonded compounds containing carbon, excluding carbonates and oxides. By this definition, compounds such as carbon dioxide (CO_2) and sodium carbonate (Na_2CO_3) are considered to be inorganic. **Organic chemistry** is the study of all organic compounds.

Organic chemistry is a very vast and complex subject. There are millions of known organic compounds—far more than the number of inorganic compounds. The reason lies within the uniqueness of carbon's structure and bonding capabilities. Carbon has four valence electrons, and therefore makes four separate covalent bonds in compounds. Carbon has the ability to bond to itself repeatedly, making long chains of carbon atoms, as well as ringed structures. These bonds can be single, double, or triple covalent bonds. Carbon readily makes covalent bonds with other elements—primarily hydrogen, oxygen, nitrogen, halogens, and several other nonmetals. The figures below show ball-and-stick models of two of the many organic compounds.



Figure **20.1.1**: Stearic acid is composed of many carbon (black) and hydrogen (white) atoms, along with two oxygen (red) atoms.

The related field of biochemistry overlaps to some extent with organic chemistry. **Biochemistry** is the study of the chemistry of living systems. Many biochemical compounds are considered to be organic chemicals. Both of the molecules shown above are biochemical materials in terms of their use in the body, but organic chemicals in terms of their structure and chemical reactivity.

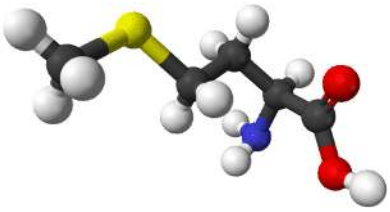


Figure **20.1.2**: Methionine is composed of carbon, hydrogen, oxygen, nitrogen (blue), and sulfur (yellow) atoms.

Summary

- Organic compounds are defined as covalently bonded compounds containing carbon, excluding carbonates and oxides. (By this definition, compounds such as carbon dioxide (CO_2) and sodium carbonate (Na_2CO_3) are considered to be inorganic.)
- Organic chemistry is the study of all organic compounds.
- Biochemistry is the study of the chemistry of living systems.

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20.02: Straight-Chain Alkanes

As our country looks at the prospect of oil shortages in the future, we are searching for alternative transportation fuel sources. One very viable possibility is propane gas. Power and acceleration capacities for propane-powered vehicles are comparable to gasoline-powered vehicles, and fuel efficiency is greater. Propane has a higher octane rating than regular gasoline, leading to much longer engine life. When properly structured, propane engines can produce lower amounts of air pollution. We are seeing a growing use of propane in buses, trucks, and police cars. Maybe your next car will burn propane.

Straight-Chain Alkanes

Hydrocarbons

A **hydrocarbon** is an organic compound that is made up of only carbon and hydrogen. A hydrocarbon is the simplest kind of organic molecule, and is the basis for all other more complex organic compounds. Hydrocarbons can be divided into two broad categories: aliphatic and aromatic. **Aliphatic hydrocarbons** are hydrocarbons that do not contain the benzene group or a benzene ring. **Aromatic hydrocarbons** contain one or more benzene rings. In this section, we will focus on the aliphatic hydrocarbons.

Alkanes

An **alkane** is a hydrocarbon in which there are only single covalent bonds. The simplest alkane is methane, with the molecular formula $\mathbf{CH_4}$. The carbon is the central atom and makes four single covalent bonds to hydrogen atoms.

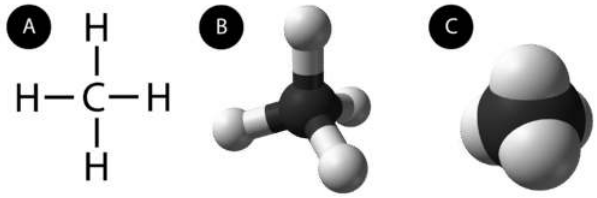
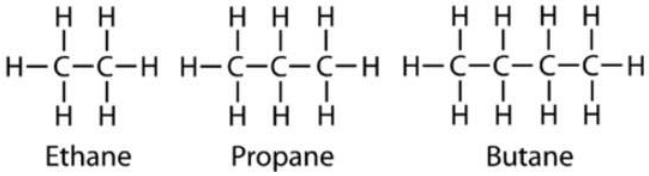


Figure **20.2.1**: Methane is the simplest hydrocarbon and is shown with a structural formula, a ball-and-stick model, and a space-filling model.

The next simplest alkane is called ethane ($\mathbf{C_2H_6}$), and consists of two carbon atoms with a single covalent bond between them. Each carbon is then able to bond to three hydrogen atoms. The alkane series progresses from there, increasing the length of the carbon chain by one carbon at a time. Structural formulas for ethane, propane ($\mathbf{C_3H_8}$), and butane ($\mathbf{H_4H_{10}}$) are shown below.



These alkanes are called straight-chain alkanes because the carbon atoms are connected in one continuous chain with no branches. Naming and writing structural and molecular formulas for the straight-chain alkanes is straightforward. The name of each alkane consists of a prefix that specifies the number of carbon atoms and the ending *-ane*. The molecular formula follows the pattern of $\mathbf{C_nH_{2n_2}}$ where n is the number of carbons in the chain. The table below lists the first ten members of the alkane series.

Table **20.2.1**: First Ten Members of the Alkane Series

Name	Molecular Formula	Condensed Structural Formula	Boiling Point (°C)
Methane	CH_4	CH_4	-161.0
Ethane	C_2H_6	CH_3CH_3	-88.5
Propane	C_3H_8	$CH_3CH_2CH_3$	-42.0
Butane	C_4H_{10}	$CH_3CH_2CH_2CH_3$	0.5
Pentane	C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$	36.0
Hexane	C_6H_{14}	$CH_3CH_2CH_2CH_2CH_2CH_3$	68.7
Heptane	C_7H_{16}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	98.5
Octane	C_8H_{18}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	125.6
Nonane	C_9H_{20}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	150.7
Decane	$C_{10}H_{22}$	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	174.0

Note that the table shows a variation of a structural formula called a condensed structural formula. In this formula, the covalent bonds are understood to exist between each carbon and the hydrogens associated with it, as well as between carbon atoms. This table also shows that the boiling points of the alkanes steadily increase as the length of the carbon chain increases. This is due to an increase in the strength of the intermolecular attractive forces and is a general feature of other organic molecules as well.

Summary

- A hydrocarbon is an organic compound that is made up of only carbon and hydrogen; it is the simplest kind of organic molecule.
- Aliphatic hydrocarbons are hydrocarbons that do not contain the benzene group or a benzene ring.
- Aromatic hydrocarbons contain one or more benzene rings.
- An alkane is a hydrocarbon in which there are only single covalent bonds.

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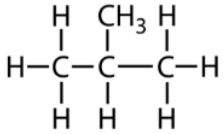
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20.03: Branched Alkanes

Tracing your family tree can be both fun and exciting. In order to do this correctly, it helps to know the exact names of your family members. Just a first, middle, or last name is not enough. A traceable family tree is one in which all relatives are carefully and precisely identified. After all, you would prefer that great-great-great-uncle to be royalty, and not a horse thief!

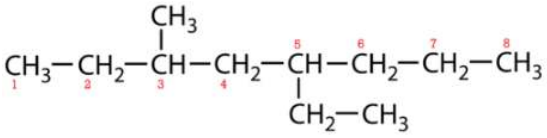
Branched Alkanes

Beginning with butane, there is an alternate structure possible that is not a straight chain. The structural formula below shows a structure with a three-carbon chain that has a $-CH_3$ group attached to the middle carbon.



The name of this molecule is 2-methylpropane. The molecular formula is still C_4H_{10}, which is the same formula as butane. A **structural isomer** is one of multiple molecules that have the same molecular formula, but different structural formulas. Butane and 2-methylpropane are structural isomers.

2-methylpropane is an example of a type of alkane called a branched alkane. The IUPAC system of nomenclature for branched alkanes follows a set of steps which will be applied to the example molecule below.



1. Find the longest continuous chain of carbon atoms in the molecule. This is called the parent chain. In the example, the longest chain is eight carbon atoms, and so the parent hydrocarbon is octane.
2. Number the carbon atoms in the parent chain. To do this, start at the end that will give the smallest numbers possible to the carbon atoms where the branches originate. In the example above, the branches are on carbons 3 and 5 when the chain is numbered left-to-right. If it were to be numbered right-to-left, the branches would be on carbons 4 and 6, so the left-to-right order is preferable.
3. The atoms attached to the parent chain (branches) are called substituents. A substituent that is a hydrocarbon is called an **alkyl group**. The names of alkyl groups use the same prefixes as the alkanes, but with a *-yl* suffix. So a 1-carbon alkyl group is a methyl group, a 2-carbon alkyl group is an ethyl group, and so on. The substituents are named by placing the number from the parent carbon chain in front of the name of the substituent. In the current example, we have 3-methyl and 4-ethyl substituents.
4. Use a prefix to indicate the appearance of more than one of the same substituent in the structural formula. Two of the same group is *di-*, three is *tri-*, four is *tetra-*, etc. For example, if methyl groups were attached to both carbons 2 and 3, that part of the name would be 2,3-dimethyl-. This rule does not apply to the structure pictured above.
5. Multiple different substituents are listed in alphabetical order. Ignore any of the prefixes from rule 4. In the current example, the 5-ethyl- comes before the 3-methyl-.
6. Commas are used to separate multiple numbers. Hyphens come between the number and the name of the substituent. The parent name comes immediately after the last substituent. There are no blank spaces in the name.

The correct name for the above structure, according to the IUPAC system, is 5-ethyl-3-methyloctane.

Summary

- A structural isomer is one of multiple molecules that have the same molecular formula, but different structural formulas.
- Nomenclature rules for branched hydrocarbons are given.

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20.04: Isomers

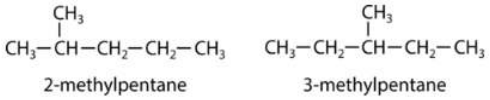
As we delve into the complexities of organic chemistry, we will see how molecular shape affects reactions. One common reaction for alkenes is the addition of hydrogen across the double bond to form the corresponding alkane. Because of the geometry of the reaction, the different 2-butene shapes have different heats of reaction. These differences are important, both from a theoretical standpoint, as well as from the point of view of industrial applications. Greater energy requirements mean a higher cost and a more expensive product.

Isomers

One of the interesting aspects of organic chemistry is that it is three-dimensional. A molecule can have a shape in space that may contribute to its properties. Molecules can differ in the way the atoms are arranged—the same combination of atoms can be assembled in more than one way. These compounds are known as **isomers**. Isomers are molecules with the same molecular formulas, but different arrangements of atoms. We will look at some isomer possibilities for alkanes and alkenes.

Structural Isomers

A **structural isomer** is one in which two or more organic compounds have the same molecular formulas, but different structures. The two pentane molecules below differ only in the location of the methyl group.



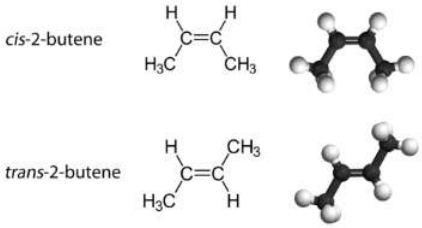
Alkenes can also demonstrate structural isomerism. In alkenes, there are multiple structural isomers based on where in the chain the double bond occurs. The condensed structural formulas of 1-butene and 2-butene show this.



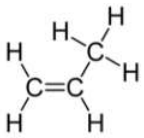
The number in the name of the alkene refers to the lowest numbered carbon in the chain that is part of the double bond.

Geometric Isomers

With a molecule such as 2-butene, a different type of isomerism called geometric isomerism can be observed. **Geometric isomers** are isomers in which the order of atom bonding is the same, but the arrangement of atoms in space is different. The double bond in an alkene is not free to rotate because of the nature of the pi bond. Therefore, there are two different ways to construct the 2-butene molecule. The image below shows the two geometric isomers, called *cis*-2-butene and *trans*-2-butene.



The *cis* isomer has the two single hydrogen atoms on the same side of the molecule, while the *trans* isomer has them on opposite sides of the molecule. In both molecules, the bonding order of the atoms is the same. In order for geometric isomers to exist, there must be a rigid structure in the molecule to prevent free rotation around a bond. If the double bond in an alkene was capable of rotating, the two geometric isomers above would not exist. In addition, the two carbon atoms must each have two different groups attached in order for there to be geometric isomers. Propene has no geometric isomers because one of the carbon atoms has two single hydrogens bonded to it.



Physical and chemical properties of geometric isomers are generally different. While *cis*-2-butene is a polar molecule, *trans*-2-butene is nonpolar. Heat or irradiation with light can be used to bring about the conversion of one geometric isomer to another. The input of energy must be large enough to break the pi bond between the two carbon atoms, which is weaker than the sigma bond. At that point, the now single bond is free to rotate, and the isomers can interconvert.

As with alkenes, alkynes display structural isomerism beginning with 1-butyne and 2-butyne. However, there are no geometric isomers with alkynes, because there is only one other group bonded to the carbon atoms that are involved in the triple bond.

Summary

- Isomers are molecules with the same molecular formulas, but different arrangements of atoms.
- A structural isomer is one in which two or more organic compounds have the same molecular formulas, but different structures.
- Geometric isomers are isomers in which the order of atom bonding is the same, but the arrangement of atoms in space is different.
- Examples of alkane and alkene isomers are given.

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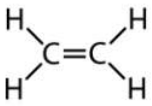
20.05: Alkenes and Alkynes

One of the most effective ways to cut metal is with an oxy-acetylene torch. Very high temperatures are obtained when acetylene burns in oxygen. Mixed 1:1 with oxygen, a temperature of over $3000°C$ can be achieved. The amount of energy released is high—the net heat of combustion is $1300\ kJ/mol$. Safety precautions need to be observed, as the gas is very explosive. The oxy-acetylene torch is one of the top tools for welding and cutting.

Alkenes and Alkynes

Alkenes

An **alkene** is a hydrocarbon with one or more carbon-carbon double covalent bonds. The simplest alkene is composed of two carbon atoms and is called ethene (shown below). Each carbon is bonded to two hydrogen atoms, in addition to the double bond between them.

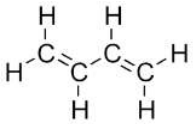


The hybridization of each carbon atom is sp^2 with trigonal planar geometry. All the atoms of the molecule lay in one plane. Like the alkane series, the names of alkenes are based on the number of atoms in the parent chain. Naming follows the same rules as for alkanes, with the addition of using a number to indicate the location of the double bond. Propene (C_3H_6) has three carbons total, while butene (C_4H_8) has four. The general formula for alkenes with one double bond is C_nH_{2n}. Alkenes are called unsaturated hydrocarbons. An **unsaturated hydrocarbon** is a hydrocarbon that contains less than the maximum number of hydrogen atoms that can possibly bond with the number of carbon atoms present.

The location of the carbon-carbon double bond can vary. The 4-carbon alkene generic name is butene. Since the double bond can be located in more than one place, we have 1-butene and 2-butene:



Molecules with multiple double bonds are also quite common. The formula below shows a four-carbon chain with double bonds between carbons 1 and 2, and between carbons 3 and 4. This molecule is called 1,3-butadiene.



Alkynes

An **alkyne** is a hydrocarbon with one or more carbon-carbon triple covalent bonds. The simplest alkyne consists of two carbon atoms and is called ethyne (common name: acetylene).



The ethyne molecule is linear, with sp hybridization for each carbon atom. The general formula of alkynes with one triple bond is C_nH_{2n-2}. Alkynes are also unsaturated hydrocarbons. Other alkynes exist, such as 2-pentyne:



Summary

- An alkene is a hydrocarbon with one or more carbon-carbon double covalent bonds.
- An alkyne is a hydrocarbon with one or more carbon-carbon triple covalent bonds.

- An unsaturated hydrocarbon is a hydrocarbon that contains less than the maximum number of hydrogen atoms that can possibly bond with the number of carbon atoms present.
- Structures of alkene and alkyne are given.

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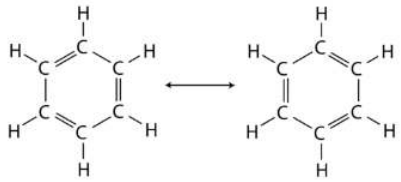
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20.06: Aromatic Hydrocarbons

Friedrich Kekulé was a German chemist in the 1800s. Supposedly, he was thinking about the structure of benzene one night as he fell asleep. While asleep, he dreamed of a snake eating its own tail. He used this idea to propose the cyclic structure of benzene. Whether or not he actually had this dream has been debated ever since. Whatever really happened, the tale persists today.

Aromatic Hydrocarbons

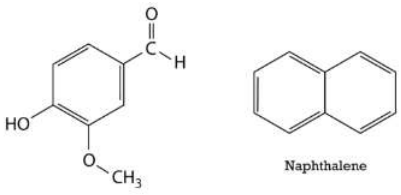
Benzene is the parent compound of the large family of organic compounds known as aromatic compounds. Unlike cyclohexane, benzene only contains six hydrogen atoms, giving the impression that the ring is unsaturated, and that each carbon atom participates in one double bond. Two different structures with alternating single and double bonds around the ring can be written for benzene.



In benzene, the true bonding between carbon atoms is neither a single nor a double bond. Rather, all of the bonds are a hybrid of a single and double bond. In benzene, the pi bonding electrons are free to move completely around the ring. **Delocalized electrons** are electrons that are not confined to the bond between two atoms, but are instead allowed to move between three or more. The delocalization of the electrons in benzene can best be shown by showing benzene with a ring inside the hexagon, with the hydrogen atoms understood.

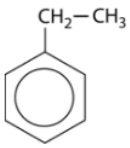


Delocalization of the electrons makes for a more stable molecule than a similar molecule that does not have delocalized electrons. Benzene is a more stable and less reactive compound than straight-chain hexenes. The sp^2 hybridization of the carbon atoms results in a planar molecule, as opposed to the puckered structure of cyclohexane. Benzene rings are common in a great number of natural substances and biomolecules. The figure below shows the structural formulas for vanilla and naphthalene. Naphthalene is a chemical which is commonly used in mothballs.

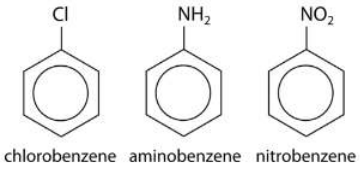


Nomenclature of Aromatic Compounds

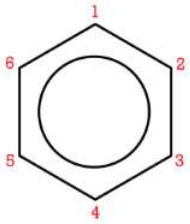
The simplest aromatic compounds are benzene rings with one substituent replacing one of the hydrogen atoms. If this substituent is an alkyl group, it is named first, followed in one word with "benzene". The molecule shown below is therefore called ethylbenzene.



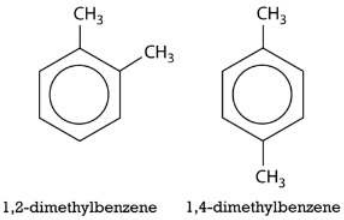
Substituents can be groups other than alkyl groups. If a chlorine atom were substituted for a hydrogen, the name becomes chlorobenzene. An $-NH_2$ group is called an amino group, so the corresponding molecule is called aminobenzene, often referred to as an aniline. An $-NO_2$ group is called a nitro group, and so the third example below is nitrobenzene.



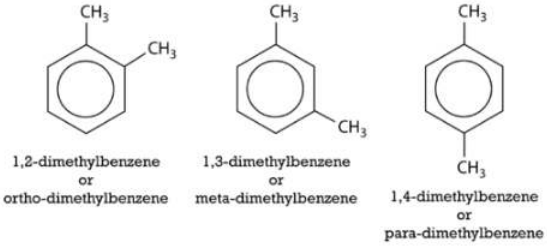
If more than one substituent is present, their location relative to one another can be indicated by numbering the positions on the benzene ring.



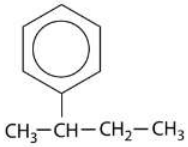
The number of the carbon location then precedes the name of the substituent in the overall name, with the numbers separated by a comma. As with branched alkanes, the system requires that the numbers be the lowest possible, and that prefixes be used for more than one of the same substituent. If there are different substituents, the first in alphabetical order is given the lower number and listed first. The structures below are called 1,2-dimethylbenzene and 1-ethyl-4-methylbenzene.



An alternate system for naming di-substituted benzene rings uses three different prefixes: *ortho*, *meta*, and *para*. If two groups are in the ortho position, they are on adjacent carbon atoms. The meta positioning refers to being in a 1,3 arrangement. The para positioning refers to being in a 1,4 arrangement. Shown below are the three possibilities for dimethylbenzene, also called xylene.



Lastly, a benzene ring missing one hydrogen atom $(-C_6H_5)$ can itself be considered the substituent on a longer chain of carbon atoms. That group is called a *phenyl* group and so the molecule below is called 2-phenylbutane.



Summary

- Benzene is the parent compound of the large family of organic compounds known as aromatic compounds.
- In benzene, the pi bonding electrons are free to move completely around the ring.
- Delocalized electrons are electrons that are not confined to the bond between two atoms, but are instead allowed to move between three or more.
- Nomenclature for benzene compounds is dictated.

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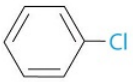
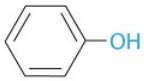
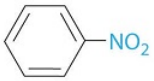
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20.07 Functional Groups

Learning Objectives

- To know the major classes of organic compounds and identify important functional groups.

You were previously introduced to several structural units that chemists use to classify organic compounds and predict their reactivities. These functional groups, which determine the chemical reactivity of a molecule under a given set of conditions, can consist of a single atom (such as Cl) or a group of atoms (such as CO_2H). The major families of organic compounds are characterized by their functional groups. Figure **1** summarizes five families introduced in earlier chapters, gives examples of compounds that contain each functional group, and lists the suffix or prefix used in the systematic nomenclature of compounds that contain each functional group.

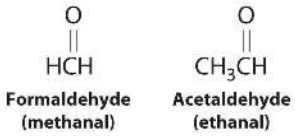
Class	General Formula	Example	Common Name (Systematic Name)	Common Suffix/Prefix (Systematic)
Hydrocarbons				
Alkanes	RH	CH_3CH_3	ethane	-ane
Alkenes	$RR'C{=}CR''R'''$	$H_2C{=}CH_2$	ethylene (ethene)	-ene
Alkynes	$RC{\equiv}CR'$	$HC{\equiv}CH$	acetylene (ethyne)	(-yne)
Arenes	ArH[a]		benzene	-ene
Halogen-Containing Compounds				
Alkyl halides	RX	CH_3CH_2Cl	ethyl chloride (chloroethane)	halide (halo-)
Aryl halides	ArX[a]		chlorobenzene	halo-
Oxygen-Containing Compounds				
Alcohols	ROH[a]	CH_3CH_2OH	ethyl alcohol (ethanol)	-ol
Phenols	ArOH[b]		phenol	-ol
Ethers	ROR′	$H_3CH_2COCH_2CH_3$	diethyl ether	ether
Aldehydes	RCHO	$CH_3\overset{\overset{O}{\|}}{C}H$	acetaldehyde (ethanal)	-aldehyde (-al)
Ketones	RR′C=O	$CH_3\overset{\overset{O}{\|}}{C}CH_3$	acetone (2-propanone)	-one
Carboxylic acids	RCO_2H	$CH_3\overset{\overset{O}{\|}}{C}OH$	acetic acid (ethanoic acid)	-ic acid (-oic acid)
Carboxylic Acid Derivatives				
Esters	RCO_2R'	$CH_3\overset{\overset{O}{\|}}{C}OCH_3$	methyl acetate (methyl ethanoate)	-ate (-oate)
Amides	RCONHR′	$CH_3\overset{\overset{O}{\|}}{C}NHCH_3$	*N*-methylacetamide	-amide
Nitrogen-Containing Compounds				
Amines	RNH_2, RNHR′, RNR′R″	$CH_3CH_2NH_2$	ethylamine	-amine
Nitriles	$RC{\equiv}N$	$H_3CC{\equiv}N$	acetonitrile	-nitrile
Nitro compounds	$ArNO_2$[a]		nitrobenzene	nitro-

https://chem.libretexts.org/@go/page/177480

[a] R indicates an alkyl group [b] Ar indicates an aryl group. Figure 1: Major Classes of Organic Compounds

The first family listed in Figure **1** is the hydrocarbons. These include alkanes, with the general molecular formula C_nH_{2n+2} where n is an integer; alkenes, represented by C_nH_{2n}; alkynes, represented by C_nH_{2n-2}; and arenes. Halogen-substituted alkanes, alkenes, and arenes form a second major family of organic compounds, which include the alkyl halides and the aryl halides. Oxygen-containing organic compounds, a third family, may be divided into two main types: those that contain at least one C–O bond, which include alcohols, phenols (derivatives of benzene), and ethers, and those that contain a carbonyl group (C=O), which include aldehydes, ketones, and carboxylic acids. Carboxylic acid derivatives, the fourth family listed, are compounds in which the OH of the $–CO_2H$ functional group is replaced by either an alkoxy (–OR) group, producing an ester, or by an amido (–NRR′, where R and R′ can be H and/or alkyl groups), forming an amide. Nitrogen-containing organic compounds, the fifth family, include amines; nitriles, which have a C≡N bond; and nitro compounds, which contain the $–NO_2$ group.

The systematic nomenclature of organic compounds indicates the positions of substituents using the lowest numbers possible to identify their locations in the carbon chain of the parent compound. If two compounds have the same systematic name, then they are the same compound. Although systematic names are preferred because they are unambiguous, many organic compounds are known by their common names rather than their systematic names. Common nomenclature uses the prefix form—for a compound that contains no carbons other than those in the functional group, and acet—for those that have one carbon atom in addition [two in the case of acetone, $(CH_3)_2C=O$]. Thus methanal and ethanal, respectively, are the systematic names for formaldehyde and acetaldehyde.



Recall that in the systematic nomenclature of aromatic compounds, the positions of groups attached to the aromatic ring are indicated by numbers, starting with 1 and proceeding around the ring in the direction that produces the lowest possible numbers. For example, the position of the first CH_3 group in dimethyl benzene is indicated with a 1, but the second CH_3 group, which can be placed in any one of three positions, produces 1,2-dimethylbenzene, 1,3-dimethylbenzene, or 1,4-dimethylbenzene (Figure **2**). In common nomenclature, in contrast, the prefixes ortho-, meta-, and para- are used to describe the relative positions of groups attached to an aromatic ring. If the CH_3 groups in dimethylbenzene, whose common name is xylene, are adjacent to each other, the compound is commonly called ortho-xylene, abbreviated o-xylene. If they are across from each other on the ring, the compound is commonly called para-xylene or p-xylene. When the arrangement is intermediate between those of ortho- and para- compounds, the name is meta-xylene or m-xylene.

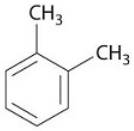
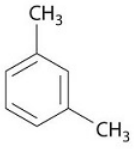
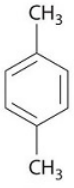
Prefix	Positions of Methyl Groups	Example	Common Name (Systematic Name)
ortho-	1,2		*o*-xylene (1,2-dimethylbenzene)
meta-	1,3		*m*-xylene (1,3-dimethylbenzene)
para-	1,4		*p*-xylene (1,4-dimethylbenzene)

Figure **2**: Common Nomenclature for Aromatic Ring Substitutions

We begin our discussion of the structure and reactivity of organic compounds by exploring structural variations in the simple saturated hydrocarbons known as alkanes. These compounds serve as the scaffolding to which the various functional groups are most often attached.

Summary

Functional groups determine the chemical reactivity of an organic molecule. Functional groups are structural units that determine the chemical reactivity of a molecule under a given set of conditions. Organic compounds are classified into several major categories based on the functional groups they contain. In the systematic names of organic compounds, numbers indicate the positions of functional groups in the basic hydrocarbon framework. Many organic compounds also have common names, which use the prefix form—for a compound that contains no carbons other than those in the functional group and acet—for those that have one additional carbon atom.

Conceptual Problems

1. Can two substances have the same systematic name and be different compounds?
2. Is a carbon–carbon multiple bond considered a functional group?

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20.08: Alcohols

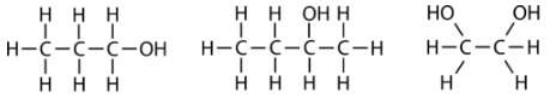
Water freezes at 0°C, which creates problems for cars in the winter. The water in the engine will freeze and crack the engine block. To prevent this, antifreeze is added to lower the freezing point of the liquid. The most common antifreeze is an alcohol known as propylene glycol. It has largely replaced the much more toxic ethylene glycol. Methanol can also be used as an antifreeze, mainly in windshield wiper fluid.

Alcohols

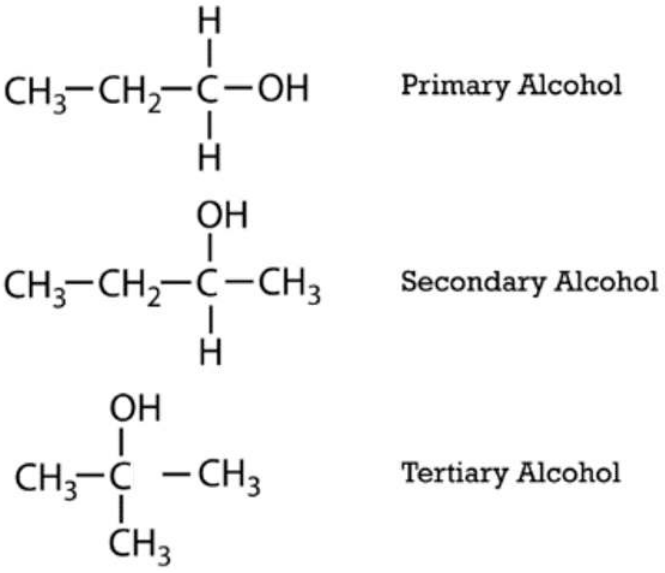
An **alcohol** is an organic compound that contains one or more hydroxyl (–OH) groups. The general formula for alcohols is R–OH. Do not confuse alcohols with inorganic bases that contain the hydroxide ion (OH^-). The –OH group in an alcohol is covalently bonded to a carbon atom and does not ionize in solution. The steps for naming alcohols are listed below.

1. Name the parent compound by finding the longest continuous carbon atom chain that also contains the hydroxyl group. If there is one hydroxyl group in the molecule, change the final *-e* in the name of the alkane to *-ol*. If there is more than one hydroxyl group, use the full name of the alkane and add a suffix to indicate the number of hydroxyl groups. For example, two hydroxyl groups is *-diol*, three is *-triol*, etc.
2. Number the carbon chain in a way that makes the sum of the hydroxyl numbers as low as possible.
3. Add the numerical prefix into the name before the name of the alcohol.
4. Separate numbers with commas and separate numbers from names or prefixes with a hyphen. There are no spaces in the name.

Following are three examples of alcohols and their IUPAC names.



Aliphatic alcohols can be classified according to the number of R groups attached to the carbon with the hydroxyl group. If one R group is attached to that carbon, the alcohol is a primary alcohol. If two R groups are attached, the alcohol is a secondary alcohol. If three R groups are attached, the alcohol is a tertiary alcohol. Shown below is an example of each. The primary alcohol is 1-propanol, the secondary alcohol is 2-butanol, and the tertiary alcohol is 2-methyl-2-propanol.



Properties of Alcohols

The smallest and lightest alcohols (methanol, ethanol, propanol) are completely soluble in water in all proportions. In a solution, the hydroxyl groups of alcohol molecules and the water molecules form hydrogen bonds with each other, resulting in complete

miscibility. However, as the length of the carbon chain increases, the solubility decreases. The solubility of 1-butanol is $7.4\ g$ per $100\ g$ of water, while that of 1-pentanol is $2.7\ g$ per $100\ g$ of water, and 1-octanol is $0.06\ g$ per $100\ g$ of water. The carbon chain portion of the larger alcohol molecule is nonpolar, and leads to the decreased solubility of the overall compound.

The presence of hydrogen bonds in alcohols also explains the relatively high boiling points of alcohols compared to alkanes of similar molar mass (see table below).

Table 20.8.1: Boiling Point Comparison of Alkanes and Alcohols

Compound	Formula	Molar Mass (g/mol)	Boiling Point (°C)
ethane	CH_3CH_3	32	-88
methanol	CH_3OH	30	64.7
propane	$CH_3CH_2CH_3$	44	-42.1
ethanol	CH_3CH_2OH	46	78.3

Only weak London dispersion forces hold molecules of nonpolar alkanes together in the liquid phase. Consequently, less energy is required to break these molecules away from the surface of the liquid and turn them into a vapor. The stronger hydrogen bonding between alcohol molecules means that more energy is required to convert the liquid to vapor, and boiling points are therefore high.

Summary

- An alcohol is an organic compound that contains one or more hydroxyl ($-OH$) groups.
- The lightest alcohols (methanol, ethanol, propanol) are completely soluble in water in all proportions; as the length of the carbon chain increases, the solubility decreases.
- The presence of hydrogen bonds in alcohols also explains the relatively high boiling points of alcohols compared to alkanes of similar molar mass.

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20.09: Aldehydes and Ketones

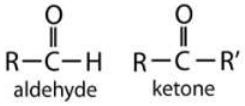
There's nothing like the smell of a fresh cinnamon roll; the taste is even better. What is that delicious taste owed to? This flavoring comes from the bark of a tree (actually, several different kinds of trees). One of the major compounds responsible for the taste and odor of cinnamon is cinnamaldehyde. Cinnamon has been widely used through centuries to treat a number of different disorders. In ancient times, doctors believed it could cure snakebite poisoning, freckles, and the common cold. Today, there are several research studies being carried out on the health benefits of cinnamon. So, enjoy that cinnamon roll—it just might have a health benefit or two.

Aldehydes and Ketones

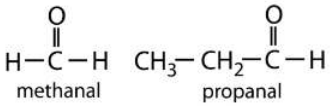
Aldehydes and ketones are two related categories of organic compounds that both contain the **carbonyl group**, shown below.



The difference between aldehydes and ketones is the placement of the carbonyl group within the molecule. An **aldehyde** is an organic compound in which the carbonyl group is attached to a carbon atom at the end of a carbon chain. A **ketone** is an organic compound in which the carbonyl group is attached to a carbon atom within the carbon chain. The general formulas for each are shown below.

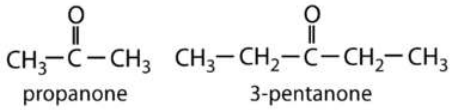


For aldehydes, the **R** group may be a hydrogen atom or any length carbon chain. Aldehydes are named by finding the longest continuous chain that contains the carbonyl group. Change the *-e* at the end of the name of the alkane to *-al*.



For ketones, **R** and **R′** must be carbon chains, of either the same or different lengths. The steps for naming ketones, followed by two examples, are shown below.

1. Name the parent compound by finding the longest continuous chain that contains the carbonyl group. Change the *-e* at the end of the name of the alkane to *-one*.
2. Number the carbon atoms in the chain in a way so that the carbonyl group has the lowest possible number.
3. Add the numerical prefix into the name before the name of the ketone.
4. Use a hyphen between the number and the name of the ketone.



Properties of Aldehydes and Ketones

Aldehydes and ketones can work weak hydrogen bonds with water through the carbonyl oxygen atom. The lower members of both series (3 carbons or fewer) are soluble in water in all proportions. As the length of the carbon chain increases, water solubility decreases. Similar to ethers, neither aldehydes nor ketones can hydrogen bond with themselves. As a result, their boiling points are generally lower than those of alcohols. Unlike alkanes however, aldehydes and ketones are polar molecules due to the more electronegative oxygen atom. The dipole-dipole interactions are stronger than the dispersion forces present in alkanes. The boiling points of aldehydes and ketones are intermediate between those of alkanes and alcohols. For example, the boiling point of ethane is **−89°C**, ethanal is **20°C**, and ethanol is **78°C**.

Methanal, commonly known as formaldehyde, was once commonly used as a biological preservative for dead animals. In recent years, formaldehyde has been shown to be a carcinogen, and so has been replaced by safer alternatives for preservation purposes. Aldehydes are currently used in the production of resins and plastics. The simplest ketone, propanone, is commonly called acetone. Acetone is a common organic solvent that was once used in most nail polish removers, but has largely been replaced by other solvents.

Summary

- Aldehydes and ketones are two related categories of organic compounds that both contain the carbonyl group.
- An aldehyde is an organic compound in which the carbonyl group is attached to a carbon atom at the end of a carbon chain.
- A ketone is an organic compound in which the carbonyl group is attached to a carbon atom within the carbon chain.
- Aldehydes and ketones generally have lower boiling points than those of alcohols.

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20.10: Carboxylic Acids

Vinegar (dilute acetic acid) is available in every grocery store in the country. The large one-gallon jugs can be found in households everywhere. One magazine published an article listing 150 ways to use vinegar, from getting dirt off of your computer to cleaning window blinds. A mixture of vinegar and baking soda is an excellent way to clean sink drains. You can also clean your carpets and your piano keys. Not bad for something that may have struck you as merely an ingredient in salad dressing!

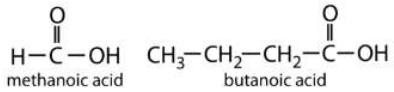
Carboxylic Acids

Organic acids such as acetic acid all contain a functional group called a **carboxyl group**.



The carboxyl group contains the C=O of the carbonyl group, with the carbon atom also being bonded to a hydroxyl (−OH) group. A **carboxylic acid** is an organic compound that contains the carboxyl functional group. The general formula for a carboxylic acid can be abbreviated as R−COOH. The carbon atom of the carboxyl group may be attached to a hydrogen atom or to a carbon chain. The naming of a carboxylic acid is as follows:

1. Name the parent compound by finding the longest continuous chain that contains the carboxyl group.
2. Change the *-e* at the end of the name of the alkane to *-oic acid*.



Properties of Carboxylic Acids

Carboxylic acids are all weak acids. In aqueous solution, the O−H bond of the hydroxyl group can break, yielding a negative carboxylate ion and the hydrogen ion.

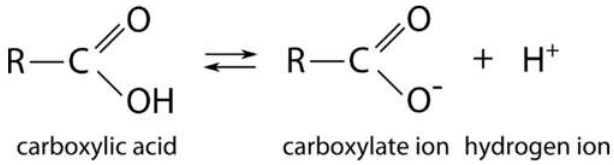


Figure 20.10.1: Equilibrium between carboxyl group and carboxylate ion.

The smaller members of the aliphatic carboxylic acid series are colorless, volatile liquids with strong odors. Ethanoic acid is commonly known as acetic acid; common household vinegar is a 5% solution of acetic acid. Larger carboxylic acids are solids with low melting points. There are numerous aromatic carboxylic acids, which are all crystalline solids. Carboxylic acids can form intermolecular hydrogen bonds, and thus have relatively high melting and boiling points compared to other organic compounds that cannot hydrogen bond. Carboxylic acids with shorter carbon chains are very soluble in water, while those with longer carbon chains are less soluble.

Many carboxylic acids occur naturally in plants and animals. Citrus fruits such as oranges and lemons contain citric acid.

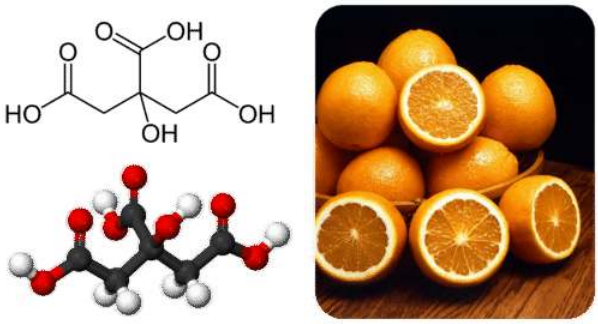


Figure **20.10.2**: Citric acid is a large carboxylic acid with three ionizable hydrogen atoms. It is found in citrus fruits and gives them their sour or tart flavor.

Ethanoic and citric acids are frequently added to foods to give them a tart flavor. Benzoic, propanoic, and sorbic acids are used as food preservatives because of their ability to kill microorganisms that can lead to spoilage. Methanoic and ethanoic acids are widely used in industry as starting points for the manufacture of paints, adhesives, and coatings.

Summary

- Organic acids, such as acetic acid, all contain a functional group called a carboxyl group.
- The carboxyl group contains the **C=O** of the carbonyl group, with the carbon atom also being bonded to a hydroxyl (**–OH**) group.
- A carboxylic acid is an organic compound that contains the carboxyl functional group.

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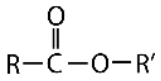
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20.11: Esters

Perfumes contain ingredients from a number of sources. Musk is obtained from animals, but the vast majority of perfume components are obtained from plants. Approximately 2,000 plant species have been used as sources for perfume materials. The needed chemicals are extracted using solvent extraction or distillation. The oils are diluted with ethanol to varying degrees, depending on the price of the finished product—the less ethanol present (meaning there is a higher percentage of the active scent ingredients), the more expensive the perfume.

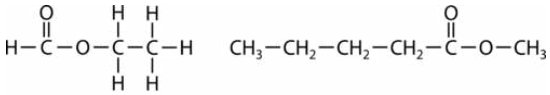
Esters

An **ester** is an organic compound that is a derivative of a carboxylic acid, in which the hydrogen atom of the hydroxyl group has been replaced with an alkyl group. The structure is the product of a carboxylic acid (the **R**-portion) and an alcohol (the **R′**-portion). The general formula for an ester is shown below.



The **R** group can either be a hydrogen or a carbon chain. The **R′** group must be a carbon chain since a hydrogen atom would make the molecule a carboxylic acid. The steps for naming esters, along with two examples, are shown below.

1. Identify and name the alkyl group (**R′**) that has replaced the hydrogen of the hydroxyl group. This is the first part of the ester name.
2. Name the carboxylic acid portion of the molecule (**R–COO**), but change the ending of the name from *-oic acid* to *-oate*. This is the second part of the ester name.
3. Leave a space between the alkyl group name and the name of the carboxylic acid derivative.



Esters have lower boiling points than the carboxylic acids from which they were derived because they cannot form hydrogen bonds with each other. This is because there are no hydrogen atoms bonded to oxygen atoms, as in the acid. Esters with shorter carbon chains are soluble in water, while those with longer chains are less soluble.

Esters are very commonly found in plants, and are responsible for many distinct odors and flavors. For example, methyl salicylate has the odor and flavor of oil of wintergreen, while propyl ethanoate has that of a pear.

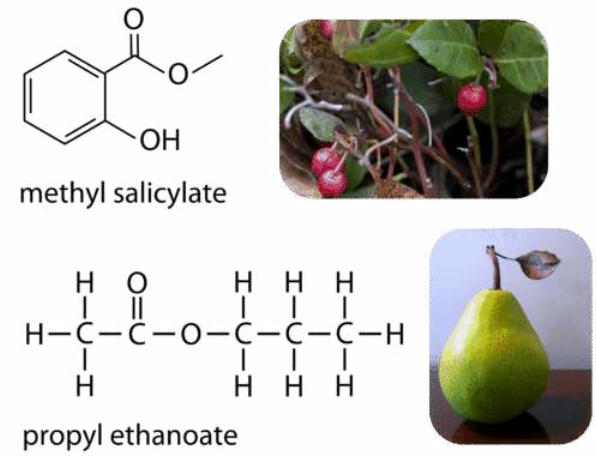


Figure **20.11.1**: Ester examples.

Summary

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20.12: Addition Reactions

There is some debate these days about the benefits of using margarine versus butter on your toast (or pancakes, or muffin). Margarine is less expensive than butter, and is lower in fat and cholesterol. Margarine is made from vegetable fats using hydrogenation to reduce the double bonds in the fatty acids. Hydrogen gas is bubbled through the liquid oil and reacts with the carbon-carbon double bonds present in the long-chain fatty acids. The product is less likely to spoil than butter.

Addition Reactions

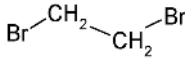
An **addition reaction** is a reaction in which an atom or molecule is added to an unsaturated molecule, making a single product. An addition reaction can be thought of as adding a molecule across the double bond or triple bond of an alkene or alkyne. Addition reactions are useful ways to introduce a new functional group into an organic molecule.

One type of addition reaction is called hydrogenation. **Hydrogenation** is a reaction that occurs when molecular hydrogen is added to an alkene to produce an alkane. The reaction is typically performed with the use of a platinum catalyst. Ethene reacts with hydrogen to form ethane.

$$\mathrm{CH_2{=}CH_2\,(g) + H_2\,(g) \xrightarrow{Pt} CH_3CH_3\,(g)}$$

Alkyl halides can be produced from an alkene by the addition of either the elemental halogen or the hydrogen halide. When the reactant is the halogen, the product is a disubstituted alkyl halide, as in the addition of bromine to ethene:

$$\mathrm{CH_2{=}CH_2\,(g) + Br_2\,(l) \rightarrow CH_2BrCH_2Br\,(g)\ \ (1,2\text{-dibromoethane})}$$



The addition of bromine to an unknown organic compound is indeed a test for saturation in the compound. Bromine has a distinctive brownish-orange color, while most bromoalkanes are colorless. When bromine is slowly added to the compound, the orange color will fade if it undergoes the addition reaction to the hydrocarbon. If the orange color remains, then the original compound was already saturated, and no reaction occurred.

A monosubstituted alkyl halide can be produced by the addition of a hydrogen halide to an alkene. Shown below is the formation of chloroethane.

$$\mathrm{CH_2{=}CH_2\,(g) + HCl\,(g) \rightarrow CH_3CH_2Cl\,(g)}$$

A **hydration reaction** is a reaction in which water is added to an alkene. Hydration reactions can take place when the alkene and water are heated to near **100°C** in the presence of a strong acid, which acts as a catalyst. Shown below is the hydration of ethene to produce ethanol.

$$\mathrm{CH_2{=}CH_2 + H_2O \rightarrow CH_3CH_2OH}$$

Under modest reaction conditions, benzene resists addition reactions because adding a molecule across a double bond in a benzene ring disrupts the ring of delocalized electrons; this greatly destabilizes the molecule. However, under conditions of high temperature and pressure, and with an appropriate catalyst, benzene will slowly react with three molecules of hydrogen to produce cyclohexane.

$$\mathrm{C_6H_6 + 3H_2 \xrightarrow{Pt} C_6H_{12}}$$



Summary

- An addition reaction is a reaction in which an atom or molecule is added to an unsaturated molecule, making a single product.
- Hydrogenation is a reaction that occurs when molecular hydrogen is added to an alkene to produce an alkane; the reaction is typically performed with the use of a platinum catalyst.

- A hydration reaction is a reaction in which water is added to an alkene.

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20.13: Substitution Reactions

Organic compounds can be used for a wide variety of applications. One organic compound is halothane, an alkyl halide. This material is used as a general anesthetic for surgical procedures. When it was first developed in 1956, it was very popular, but has had limited use more recently because of toxicity issues—specifically liver damage.

Substitution Reactions

A **substitution reaction** is a reaction in which one or more atoms replace another atom or group of atoms in a molecule. Alkyl halides are formed by the substitution of a halogen atom for a hydrogen atom. When methane reacts with chlorine gas, ultraviolet light can act as a catalyst for the reaction:

$$\mathrm{CH_4}\,(g) + \mathrm{Cl_2}\,(g) \overset{\text{UV light}}{\rightarrow} \mathrm{CH_3Cl}\,(g) + \mathrm{HCl}\,(g)$$

The reaction produces chloromethane and hydrogen chloride. When the mixture is allowed to react for longer periods of time further, substitution reactions may occur.

$$\mathrm{CH_3Cl}\,(g) + \mathrm{Cl_2}\,(g) \overset{\text{UV light}}{\rightarrow} \mathrm{CH_2Cl_2}\,(g) + \mathrm{HCl}\,(g)$$

The product above is dichloromethane. Further substitution produces trichloromethane and tetrachloromethane, commonly called carbon tetrachloride. A mixture of products occurs in the reaction, with the relative amounts dependent upon the time that the reaction is allowed to proceed. Chlorofluorocarbons are produced by reacting chloroalkanes with hydrofluoric acid (**HF**), because the fluorine atom bonds preferentially to the carbon.

$$\mathrm{CCl_4}\,(g) + \mathrm{HF}\,(g) \overset{\mathrm{FeBr_3}}{\rightarrow} \mathrm{CCl_3F}\,(g) + \mathrm{HCl}\,(g)$$

The fluorine atom substitutes for a chlorine atom in the reaction.

Benzene is a fairly stable and unreactive molecule due to the electron delocalization around the six-membered ring. The treatment of benzene with a halogen in the presence of an iron catalyst causes the substitution of a halogen atom for a hydrogen atom. The resulting molecule is called an aryl halide.

$$\mathrm{C_6H_6}\,(l) + \mathrm{Br_2}\,(l) \overset{\mathrm{FeBr_3}}{\rightarrow} \mathrm{C_6H_5Br}\,(l) + \mathrm{HBr}\,(g)$$



Alkyl groups can be introduced onto a benzene ring by the reaction of benzene with an alkyl halide, using aluminum chloride as the catalyst. In the reaction below, benzene reacts with chloroethane to produce ethylbenzene.

$$\mathrm{C_6H_6}\,(l) + \mathrm{CH_3CH_2Cl}\,(g) \overset{\mathrm{AlCl_3}}{\rightarrow} \mathrm{C_6H_5CH_2CH_3}\,(l) + \mathrm{HCl}\,(g)$$



The reaction of an alkyl halide with an inorganic hydroxide base at elevated temperature produces an alcohol. The molecular reaction to produce methanol from iodomethane and sodium hydroxide is shown below.

$$\mathrm{CH_3I}\,(l) + \mathrm{NaOH}\,(aq) \overset{100^\circ\mathrm{C}}{\rightarrow} \mathrm{CH_3OH}\,(l) + \mathrm{NaI}\,(aq)$$

Summary

- A substitution reaction is a reaction in which one or more atoms replace another atom or group of atoms in a molecule.
- Examples of substitution reactions are given.

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20.14: Oxidation Reactions

Benzoic acid is widely used as a food preservative, either as the carboxylic acid or as the sodium benzoate salt. This compound is most effective when added to acidic foods such as fruit juices and soft drinks. The major industrial source of benzoic acid is the partial oxidation of toluene with oxygen. The process is inexpensive and environmentally benign.

Oxidation Reactions

Oxidation can be defined as the addition of oxygen to a molecule, or the removal of hydrogen from a molecule. When an alkane is heated in the presence of an appropriate catalyst, it can be oxidized to the corresponding alkene in a reaction called a dehydrogenation reaction. Two hydrogen atoms are removed in the process. The alkene can be further oxidized to an alkyne by the removal of two more hydrogen atoms:

$$\text{oxidation: } CH_3CH_3 \xrightarrow{-H_2} CH_2{=}CH_2 \xrightarrow{-H_2} CH \equiv CH$$

The reactions are reversible, and so an alkyne can be reduced first to an alkene, and then to an alkane:

Double subscripts: use braces to clarify

The alkane is the most reduced form of a hydrocarbon, while the alkyne is the most oxidized form.

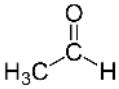
Oxidation reactions in organic chemistry often involve the addition of oxygen to a compound, which changes the particular functional group of that compound. The following sequence shows how methane can be oxidized first to methanol, then to methanal, then to methanoic acid, and finally to carbon dioxide.

$$\underset{\text{methane}}{CH_4} \xrightarrow{\text{gain of oxygen}} \underset{\text{methanol}}{CH_3OH} \xrightarrow{\text{loss of hydrogen}} \underset{\text{methanal}}{CH_2O} \xrightarrow{\text{gain of oxygen}} \underset{\text{methanoic acid}}{HCOOH} \xrightarrow{\text{loss of hydrogen}} \underset{\text{carbon dioxide}}{CO_2}$$

Each step in the process is either a gain of oxygen or a loss of hydrogen. Each step also releases energy, which explains why the complete combustion of alkanes to carbon dioxide is an extremely exothermic reaction.

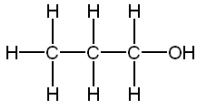
The oxidation of an alcohol can produce either an aldehyde or a ketone. Ethanol can be oxidized in the laboratory through a heating process combined with the addition of an oxidizing agent such as the dichromate ion, which catalyzes the reaction in an acidic solution. The reaction produces the aldehyde ethanal (acetaldehyde).

$$CH_3CH_2OH \xrightarrow[H^+]{Cr_2O_7^{2-}} CH_3CHO$$

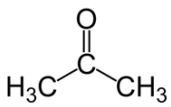


When the alcohol to be oxidized is a secondary alcohol, the oxidation product is a ketone rather than an aldehyde. The oxidation of the simplest secondary alcohol, 2-propanol, yields propanone.

$$CH_3CHOCH_3 \xrightarrow[H^+]{Cr_2O_7^{2-}} CH_3COCH_3$$



propanol



propanone (acetone)

Tertiary alcohols cannot be oxidized in this way, because the carbon to which the hydroxyl group is attached does not have another hydrogen atom attached to it.

When a primary alcohol is oxidized to an aldehyde, the reaction is difficult to stop because the aldehyde is easily oxidized further to the corresponding carboxylic acid. The oxidation of ethanal produces ethanoic (acetic) acid.

$$CH_3CHO \xrightarrow[H^+]{Cr_2O_7^{2-}} CH_3COOH$$

Ethanol-containing beverages, such as wine, are susceptible to such oxidation if kept for long periods of time after having been opened and exposed to the air. Wine that has become oxidized will have an unpleasant vinegary taste due to the production of acetic acid.

Unlike aldehydes, ketones are resistant to further oxidation because the carbonyl group is in the middle of the carbon chain, and so the ketone cannot be converted to a carboxylic acid.

Summary

- Oxidation can be defined as the addition of oxygen to a molecule, or the removal of hydrogen from a molecule.
- Primary alcohols can be oxidized to aldehydes, and then further oxidized to carboxylic acids.
- When the alcohol to be oxidized is a secondary alcohol, the oxidation product is a ketone rather than an aldehyde.
- Tertiary alcohols cannot be oxidized.

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20.15: Condensation Reactions

Vegetable oils are being explored for a variety of uses in which they could replace petroleum products. One such application is in the field of lubricants. Every moving part in machinery (such as engine pistons) needs lubrication to decrease friction and prolong the life of the equipment. Petroleum products serve this purpose now, but are not good for the environment. New techniques for making specialized esters from vegetable oil are being explored, with the purpose of making the compounds more stable and more useful as lubricants.

Condensation Reactions

A **condensation reaction** is a reaction in which two molecules combine to form a single molecule. A small molecule, often water, is usually removed during a condensation reaction. Amino acids are important biological molecules that have an amine functional group on one end of the molecule and a carboxylic acid functional group on the other end. When two amino acids combine in a condensation reaction, a covalent bond forms between the amine nitrogen of one amino acid and the carboxyl carbon of the second amino acid. A molecule of water is then removed as a second product.

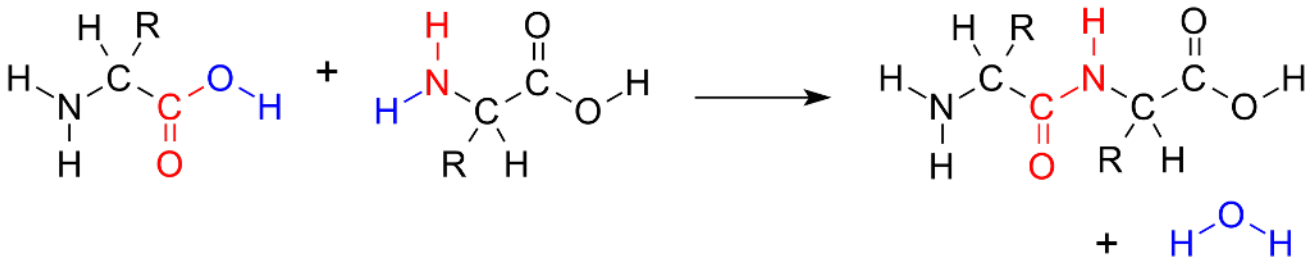
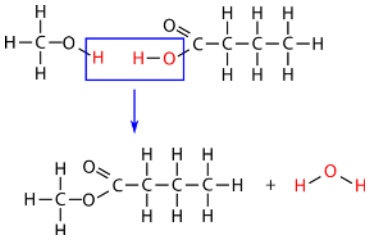


Figure 20.15.1: Amino acids join together to form a molecule called a dipeptide. The **–OH** from the carboxyl group of one amino acid combines with a hydrogen atom from the amine group of the other amino acid to produce water (blue).

This reaction forms a molecule called a dipeptide and the carbon-nitrogen covalent bond is called a peptide bond. When repeated numerous times, a lengthy molecule called a protein is eventually produced.

Esterification

An **esterification** is a condensation reaction in which an ester is formed from an alcohol and a carboxylic acid. Esterification is a subcategory of condensation reactions because a water molecule is produced in the reaction. The reaction is catalyzed by a strong acid, usually sulfuric acid. When the carboxylic acid butanoic acid is heated with an excess of methanol and a few drops of sulfuric acid, the ester methyl butanoate is produced. Methyl butanoate has the scent of pineapples. The reaction is shown below with both molecular and structural formulas.



The esterification reaction is reversible. When an ester is heated in the presence of a strong base such as sodium hydroxide, the ester breaks down. The products are an alcohol and the conjugate base of the carboxylic acid as a salt.

$$\underset{\text{ethyl ethanoate}}{CH_3COOCH_2CH_3} + NaOH \rightarrow \underset{\text{sodium acetate}}{CH_3COO^- Na^+} + \underset{\text{ethanol}}{CH_3CH_2OH}$$

The sodium hydroxide is not acting as a catalyst, but is consumed in the reaction.

Saponification describes the alkaline hydrolysis reaction of an ester. The term saponification originally described the hydrolysis of long-chain esters called fatty acid esters to produce soap molecules, which are the salts of fatty acids. One such soap molecule is

sodium stearate, formed from the hydrolysis of ethyl stearate.

$$\underset{\text{ethyl stearate}}{C_{17}H_{35}COOC_2H_5} + NaOH \rightarrow \underset{\text{sodium stearate (soap)}}{C_{17}H_{35}COO^- Na^+} + C_2H_5OH$$

Summary

- A condensation reaction is a reaction in which two molecules combine to form a single molecule.
- An esterification is a condensation reaction in which an ester is formed from an alcohol and a carboxylic acid.
- Saponification describes the alkaline hydrolysis reaction of an ester.

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20.16: Polymerization - Addition Polymers

We reap the benefits of using Styrofoam containers, but don't often consider where they end up. Styrofoam materials do not break down quickly under exposure to the elements. When buried in a landfill, styrofoam will remain intact for a long time. The good news is that there is not a lot of this pollutant found in landfills (maybe about 0.5% by weight of the total mass of garbage). There is no good way to recycle Styrofoam at present, but in the future, a creative scientist may change that.

Polymerization - Addition Polymers

Polymers are very different from the other kinds of organic molecules that you have seen so far. Whereas other compounds are of relatively low molar mass, polymers are giant molecules of very high molar mass. Polymers are the primary components of all sorts of plastics and related compounds. A **polymer** is a large molecule formed of many smaller molecules covalently bonded in a repeating pattern. The small molecules which make up the polymer are called **monomers**. Polymers generally form either from an addition reaction or a condensation reaction.

Addition Polymers

An **addition polymer** is a polymer formed by chain addition reactions between monomers that contain a double bond. Molecules of ethene can polymerize with each other under the right conditions to form the polymer called polyethylene.

$$n\mathrm{CH_2{=}CH_2} \rightarrow -(\mathrm{CH_2CH_2})_n-$$

The letter n stands for the number of monomers that are joined in repeated fashion to make the polymer, and can have a value in the hundreds or even thousands.

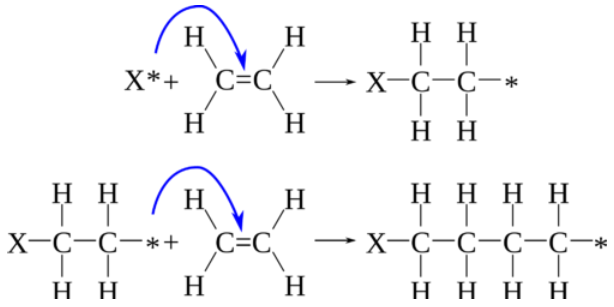


Figure **20.16.1**: Polyethylene synthesis.

The reactions above show the basic steps to form an addition polymer:

1. Initiation - a free radical initiator ($\mathrm{X^*}$) attacks the carbon-carbon double bond (first step above). The initiator can be something like hydrogen peroxide. This material can easily split to form two species with a free electron attached to each: $\mathrm{H{-}O{-}O{-}H \rightarrow 2H{-}O\cdot}$. This free radical attacks a carbon-carbon double bond. One of the pi electrons forms a single bond with the initiator while the other pi electron forms a new free radical on the carbon atom.
2. Propagation - the new free radical compound interacts with another alkane, continuing the process of chain growth (second step above).
3. Termination occurs whenever two free radicals come in contact with one another (not shown). The two free electrons form a covalent bond and the free radical on each molecule no longer exists.

Polyethylene can have different properties depending on the length of the polymer chains, and on how efficiently they pack together. Some common products made from different forms of polyethylene include plastic bottles, plastic bags, and harder plastic objects such as milk crates.

Several other kinds of unsaturated monomers can be polymerized, and are components in common household products. Polypropylene is stiffer than polyethylene, and is in plastic utensils and some other types of containers.

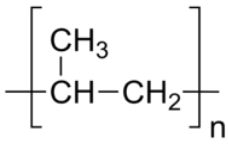


Figure 20.16.2: Polypropylene structure.

Polystyrene is used in insulation and in molded items such as coffee cups.

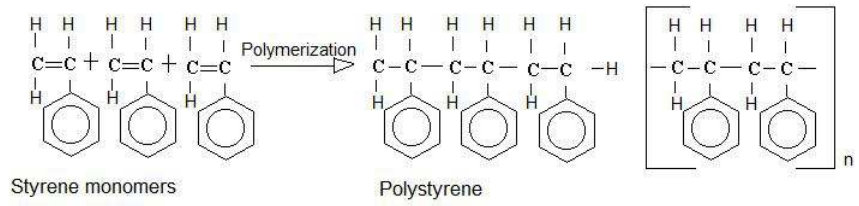


Figure 20.16.3: Polystyrene synthesis and structure.

Polyvinyl chloride (PVC) is extensively used for plumbing pipes.



Figure 20.16.4: Polyvinyl chloride.

Polyisoprene is a polymer of isoprene and is better known as rubber. It is produced naturally by rubber trees, but several variants have been developed which demonstrate improvements on the properties of natural rubber.

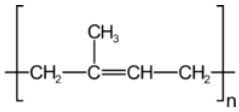


Figure 20.16.5: Polyisoprene.

Summary

- A polymer is a large molecule formed of many smaller molecules covalently bonded in a repeating pattern; they are the primary components of all sorts of plastics and related compounds.
- The small molecules which make up polymers are called monomers.
- Polymers generally form either from an addition reaction or a condensation reaction.
- An addition polymer is a polymer formed by chain addition reactions between monomers that contain a double bond.
- The basic steps to form an addition polymer are: (1) initiation, (2) propagation, (3) termination

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20.17: Polymerization - Condensation Polymers

Animal intestines and silk were used for all guitar strings for centuries, until modern technology and changes in musical taste brought about significant changes. There are two major types of guitar strings in use today. Steel strings (first developed around 1900) are found on acoustic and electric guitars. They have a bright, crisp sound that lends itself well to diverse music such as jazz, rock 'n' roll, and bluegrass. Nylon strings are a more recent development. During World War II, the silk and animal products needed to manufacture steel guitar strings were not available. Nylon quickly proved to be a more-than-adequate substitute. Now nylon strings are found on all classical guitars. Their sound is somewhat softer than the steel strings, making the tone quality well-suited for the classical genre of music.

Polymerization - Condensation Polymers

A **condensation polymer** is a polymer formed by condensation reactions. Monomers of condensation polymers must contain two functional groups so that each monomer can link up with two other monomers. One type of condensation polymer is called a polyamide. An amide is characterized by the functional group shown below wherein the carbon of a carbonyl group is bonded to the nitrogen of an amine.

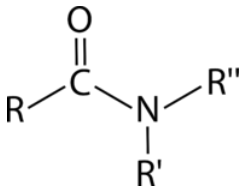


Figure 20.17.1: Amide.

One pair of monomers that can form a polyamide is that of adipic acid and hexanediamine. Adipic acid is a carboxylic acid with two carboxyl groups on either end of the molecule. Hexanediamine has amino groups on either end of a six-carbon chain. When these molecules react with each other, a molecule of water is eliminated, classifying it as a condensation reaction (see figure below).

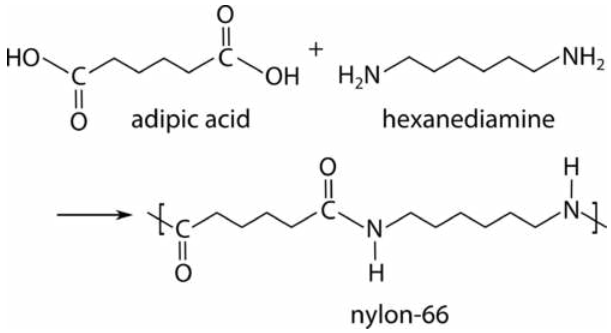


Figure 20.17.2: Nylon synthesis.

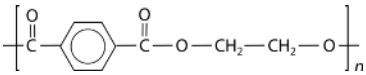
The polymer that results from the repetition of the condensation reaction is a polyamide called nylon-66. Nylon-66 was first invented in 1935 and has been used in all sorts of products. Polyamides, including Nylon-66, are commonly found in fibers and clothing, cooking utensils, fishing line, and carpeting—among many other applications.



Figure 20.17.3: Nylon spatula.

Polyester is another common type of condensation polymer. Recall that esters are formed from the reaction of an alcohol with a carboxylic acid. When both the acid and alcohol have two functional groups, the ester is capable of being polymerized. One such

polyester is called polyethylene terephthalate (PET) and is formed from the reaction of ethylene glycol with terephthalic acid. The structure of PET is shown below.



PET is used in tires, photographic film, food packaging, and clothing. Polyester fabric is used in permanent-press clothing. Its resistance to wrinkling comes from the cross-linking of the polymer strands.

Summary

- A condensation polymer is a polymer formed by condensation reactions.
- Polyamides and polyesters are common types of condensation polymers.

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CHAPTER OVERVIEW

21: Biochemistry

Topic hierarchy

21.01: Protein Structure
21.02: Enzymes
21.03: Monosaccharides
21.04: Disaccharides
21.05: Polysaccharides
21.06: Nucleic Acids
21.07: DNA and RNA
21.08: Genetic Code
21.09: Protein Synthesis
21.10: Lipids
21.11: Nonpolar Lipids
21.12: Phospholipids
21.13: Steroids

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21.01: Protein Structure

Learning Outcomes

- Describe the four levels of protein structure.
- Identify the two types of secondary structure in proteins.
- Describe the interactive forces in each level of protein structure.
- Distinguish between globular and fibrous proteins.
- Define denaturation of proteins.
- Identify ways in which proteins are denatured.

Hemoglobin is a complex protein which has a quaternary structure and contains iron. There are four subunits in the hemoglobin molecule - two alpha subunits and two beta subunits. Each subunit contains one iron ion, whose oxidation state changes from $+2$ to $+3$ and back again, depending upon the environment around the iron. When oxygen binds to the iron, the three-dimensional shape of the molecule changes. Upon release of the oxygen to the cells, the shape changes again.

With hemoglobin of normal structure, this shift in conformation does not present any problems. However, individuals with hemoglobin S do experience serious complications. This hemoglobin has one amino acid in the two beta chains that is different from the amino acid at that point in the primary structure of normal hemoglobin. The result of this one structural change is aggregation of the individual protein molecules when oxygen is released. Adjacent hemoglobin molecules come in contact with one another and clump up, causing the red cells to deform and break.

This abnormality, known as sickle cell, is genetic in nature. A person may inherit the gene from one parent and have sickle cell trait (only some of the hemoglobin is hemoglobin S), which is usually not life-threatening. Inheriting the gene from both parents will result in sickle cell disease, a very serious condition.

Proteins

A **polypeptide** is a sequence of amino acids between ten and one hundred in length. A **protein** is a peptide that is greater than one hundred amino acids in length. Proteins are very prevalent in living organisms. Hair, skin, nails, muscles, and the hemoglobin in red blood cells are some of the important parts of your body that are made of different proteins. The wide array of chemical and physiological properties of proteins is a function of their amino acid sequences. Since proteins generally consist of one hundred or more amino acids, the number of amino acid sequences that are possible is virtually limitless.

The three-dimensional structure of a protein is very critical to its function. This structure can be broken down into four levels. The **primary structure** is the amino acid sequence of the protein. The amino acid sequence of a given protein is unique and defines the function of that protein. Peptide bonds form the connections between the amino acids.

The **secondary structure** is a highly irregular sub-structure of the protein. The two most common types of protein secondary structure are the alpha helix (see figure below) and the beta sheet (see figure below). An alpha helix consists of amino acids that adopt a spiral shape. A beta pleated sheet (like a fan-folded paper) is alternating rows of amino acids that line up in a side-by-side fashion. In both cases, the secondary structures are stabilized by extensive hydrogen bonding between the side chains. The interaction of the various side chains in the amino acid, specifically the hydrogen bonding, leads to the adoption of a particular secondary structure. The hydrogen bonding occurs between amino acids that are close to each other in the primary structure.

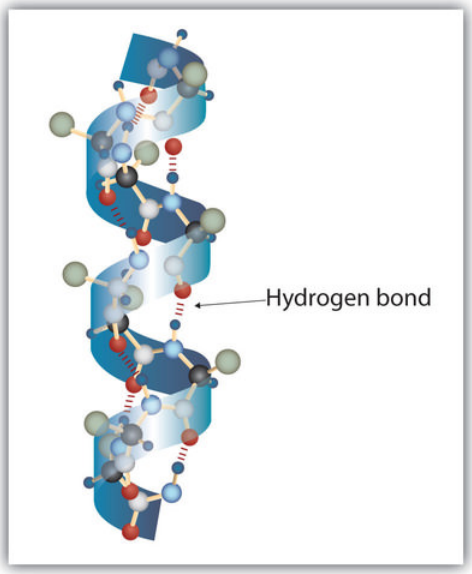


Figure **21.1.1**: Alpha helix.

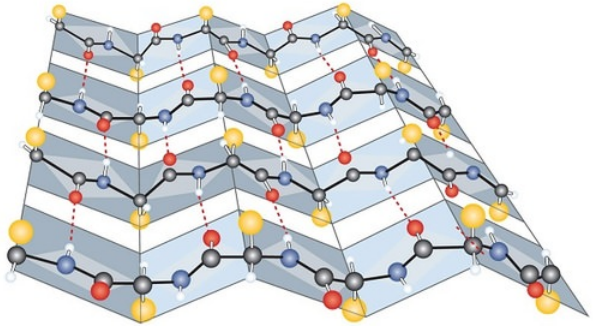
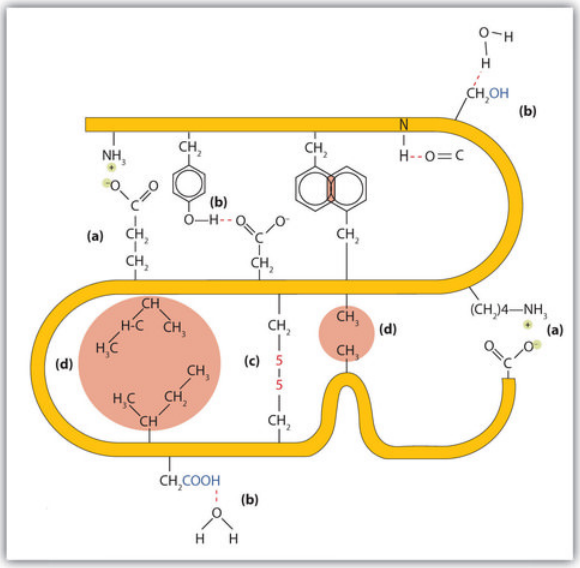


Figure **21.1.2**: Beta pleated sheet.

The **tertiary structure** is the overall three-dimensional structure of the protein. A typical protein consists of several sections of a specific secondary structure (alpha helix or beta sheet) along with other areas in which a more random structure occurs. These areas combine to produce the tertiary structure. The tertiary structure is stabilized by forces similar to the intermolecular forces previously seen between molecules. These attractive forces include London dispersion forces (hydrophobic), hydrogen bonding, dipole-dipole forces, ion-dipole interactions, ionic salt bridges, and disulfide bonds (see figure below).



Some protein molecules consist of multiple protein subunits. The **quaternary structure** of a protein refers to the specific interaction and orientation of the subunits of that protein. The quaternary structure is a result of the same types of interactions as seen in tertiary structure but between different subunits. Quaternary structures can have different numbers of subunits. For example, hemoglobin contains four subunits while insulin contains two subunits.

Hemoglobin is a very large protein found in red blood cells and whose function is to bind and carry oxygen throughout the bloodstream. Hemoglobin consists of four subunits - two α subunits (yellow) and two β subunits (gray) - which then come together in a specific and defined way through interactions of the side chains (see figure below). Hemoglobin also contains four iron atoms, located in the middle of each of the four subunits. The iron atoms are part of a structure called a porphyrin, shown in red in the figure.

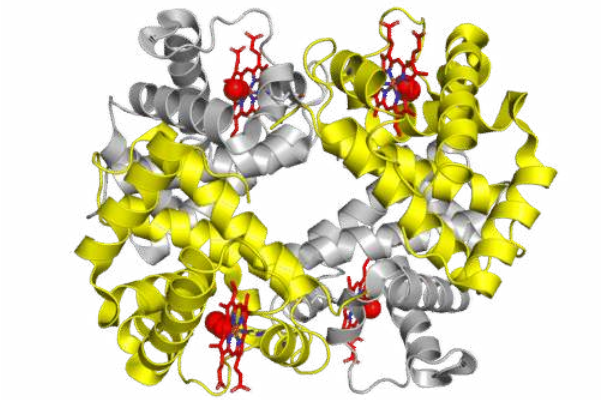


Figure **21.1.3**: Hemoglobin.

Some proteins consist of only one subunit and thus do not have a quaternary structure. The figure below diagrams the interaction of the four levels of protein structure.

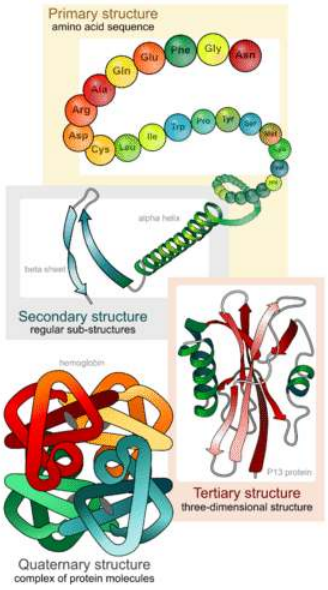


Figure **21.1.4**: The four levels of protein structure.

Globular and Fibrous Proteins

Once proteins form and have developed all levels of their structure, they can be classified as either fibrous or globular. These classifications give the basic shape of the entire protein molecule. While many proteins are globular proteins (see figure below), keratin proteins are fibrous (see figure below) and make up the hair, nails, and the outer layer of skin.

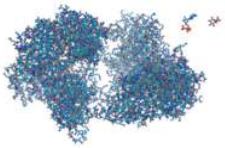


Figure **21.1.5**: Globular protein.

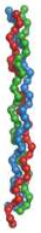


Figure **21.1.6**: Fibrous protein.

Denaturation of Proteins

The highly organized structures of proteins are truly masterworks of chemical architecture. But highly organized structures tend to have a certain delicacy, and this is true of proteins. Denaturation is the term used for any change in the three-dimensional structure of a protein that renders it incapable of performing its assigned function. A denatured protein cannot do its job because there is a change in the secondary, tertiary, or quaternary structure (see figure below). A wide variety of reagents and conditions, such as heat, organic compounds, pH changes, and heavy metal ions can cause protein denaturation. Anyone who has fried an egg has observed denaturation. The clear egg white turns opaque as the albumin denatures and coagulates.

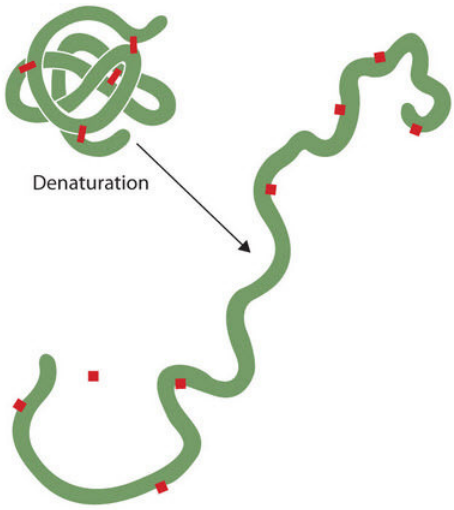


Figure **21.1.7**: Denaturation of a protein.

The primary structures of proteins are quite sturdy. In general, fairly vigorous conditions are needed to hydrolyze peptide bonds. At the secondary through quaternary levels, however, proteins are quite vulnerable to attack, though they vary in their vulnerability to denaturation. The delicately folded globular proteins are much easier to denature than are the tough, fibrous proteins of hair and skin.

There are a variety of ways to denature proteins including those below.

- Heat above $50°C$
- Strong acids
- Strong bases
- Ionic compounds (i.e. $NaCl$)
- Reducing agents
- Detergents
- Heavy metal ions
- Agitation

If you have ever had a hair permanent or chemically straightened your hair, the process involved the denaturation of proteins. The reducing agent (usually an ammonium compound) breaks the disulfide bonds in the hair. The hair is then curled or straightened which aligns the amino acids in a different pattern. An oxidizing agent is applied and the disulfide bonds reform between different amino acids. The change is permanent for the hair that you have at the time but new hair growing in will have the structure of the original proteins and your hair is back to its normal state.

Contributors and Attributions

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21.02: Enzymes

The first enzyme to be isolated was discovered in 1926 by American chemist James Sumner, who crystallized the protein. The enzyme was urease, which catalyzes the hydrolytic decomposition of urea, a component of urine, into ammonia and carbon dioxide.

$$\mathrm{H_2NCONH_2}\,(aq) + \mathrm{H_2O}\,(l) \overset{\text{urease}}{\rightarrow} 2\mathrm{NH_3}\,(g) + \mathrm{CO_2}\,(g)$$

His discovery was ridiculed at first, because nobody believed that enzymes would behave the same way that other chemicals did. Sumner was eventually proven right and won the Nobel Prize in Chemistry in 1946.

Enzymes

An **enzyme** is a protein that acts as a biological catalyst. Recall that a catalyst is a substance that increases the rate of a chemical reaction without itself being consumed in the reaction. Cellular processes consist of many chemical reactions that must occur quickly in order for the cell to function properly. Enzymes catalyze most of the chemical reactions that occur in a cell. A **substrate** is the molecule or molecules on which the enzyme acts. In the urease catalyzed reaction above, urea is the substrate. The figure below diagrams a typical enzymatic reaction.

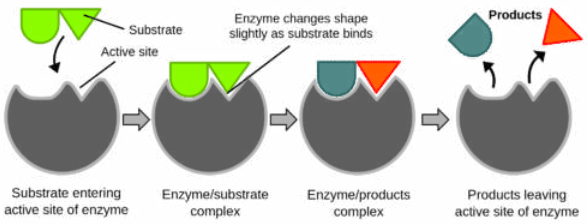


Figure **21.2.1**: The sequence of steps for a substrate binding to an enzyme in its active site, reacting, then being released as products.

The first step in the reaction is that the substrate binds to a specific part of the enzyme molecule. The binding of the substrate is dictated by the shape of each molecule. Side chains on the enzyme interact with the substrate in a specific way, resulting in the making and breaking of bonds. The **active site** is the place on an enzyme where the substrate binds. An enzyme binds in such a way that it typically has one active site, usually a pocket or crevice formed by the folding pattern of the protein. Because the active site of an enzyme has such a unique shape, only one particular substrate is capable of binding to that enzyme. In other words, each enzyme catalyzes only one chemical reaction with only one substrate. Once the enzyme/substrate complex is formed, the reaction occurs, and the substrate is transformed into products. Finally, the product molecule or molecules are released from the active site. Note that the enzyme is left unaffected by the reaction and is now capable of catalyzing the reaction of another substrate molecule.

Inhibitors

An **inhibitor** is a molecule which interferes with the function of an enzyme, either by slowing or stopping the chemical reaction. Inhibitors can work in a variety of ways, but one of the most common is illustrated in the figure below.

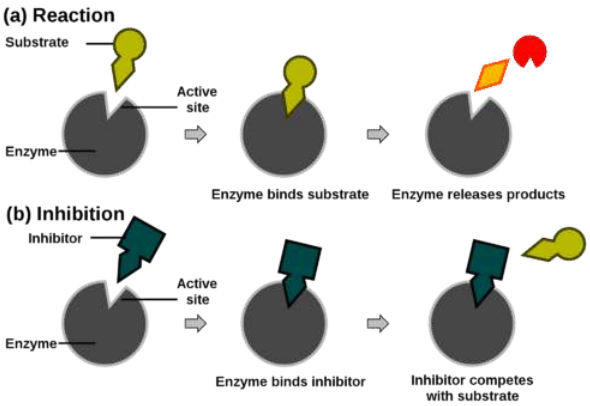


Figure **21.2.2**: A competitive inhibitor is a molecule that binds to the active site of an enzyme without reacting, thus preventing the substrate from binding.

The competitive inhibitor binds competitively at the active site and blocks the substrate from binding. Since no reaction occurs with the inhibitor, the enzyme is prevented from catalyzing the reaction. Cyanide is a potent poison which acts as a competitive inhibitor. It binds to the active site of the enzyme *cytochrome c oxidase* and interrupts cellular respiration. The binding of the cyanide to the enzyme is irreversible and the affected organism dies quickly.

Non-competitive Inhibition

A non-competitive inhibitor does not bind at the active site. It attaches at some other site on the enzyme, and changes the shape of the protein. This shift in three-dimensional structure alters the shape of the active site so that the substrate will no longer fit in the site properly (see figure below).

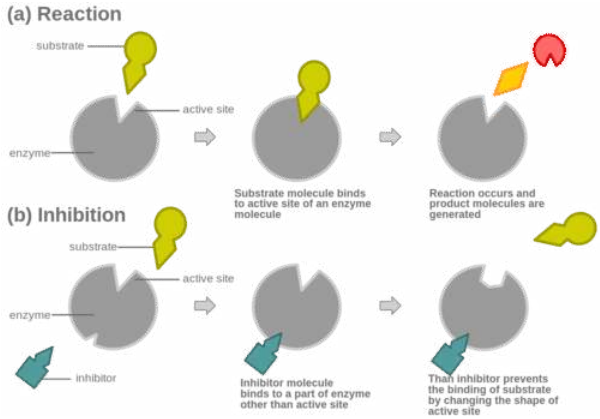


Figure **21.2.3**: Non-competitive inhibitors.

Cofactors

Some enzymes require the presence of a non-protein molecule called a cofactor on order to function properly. Cofactors can be inorganic metal ions or small organic molecules. Many vitamins, such as B vitamins, act as cofactors. Some metal ions which function as cofactors for various enzymes include zinc, magnesium, potassium, and iron.

Summary

- An enzyme is a protein that acts as a biological catalyst.
- A substrate is the molecule or molecules on which the enzyme acts.
- The active site is the place on an enzyme where the substrate binds.
- Each enzyme catalyzes only one chemical reaction with only one substrate.
- An inhibitor is a molecule which interferes with the function of an enzyme, either by slowing or stopping the chemical reaction.
- A competitive inhibitor is a molecule that binds to the active site of an enzyme without reacting, thus preventing the substrate from binding.
- A non-competitive inhibitor does not bind at the active site; it attaches at some other site on the enzyme.
- Some enzymes require the presence of a non-protein molecule called a cofactor on order to function properly.

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21.03: Monosaccharides

The brain is a marvelous organ. And it's a hungry one, too. The major fuel for the brain is glucose—a carbohydrate. The average adult brain represents about 2% of our body's weight, but uses 25% of the glucose in the body. Moreover, specific areas of the brain use glucose at different rates. If you are concentrating hard (taking a test, for example), certain parts of the brain need a lot of extra glucose, while other parts of the brain only use their normal amount.

Monosaccharides

Some foods that are high in carbohydrates include bread, pasta, and potatoes. Because carbohydrates are easily digested, athletes often rely on carbohydrate-rich foods to enable a high level of performance.



Figure 21.3.1: Foods that serve as carbohydrate sources.

The term carbohydrate comes from the fact that the majority contain carbon, hydrogen, and oxygen in a ratio of 1:2:1, making for an empirical formula of CH_2O. This is somewhat misleading, because the molecules are not actually hydrates of carbon at all. **Carbohydrates** are monomers and polymers of aldehydes and ketones that have multiple hydroxyl groups attached.

Carbohydrates are the most abundant source of energy found in most foods. The simplest carbohydrates, also called simple sugars, are plentiful in fruits. A **monosaccharide** is a carbohydrate consisting of one sugar unit. Common examples of simple sugars or monosaccharides are glucose and fructose. Both of these monosaccharides are referred to as hexoses, since they have six carbons. Glucose is abundant in many plant sources, and makes up sweeteners such as corn sugar and grape sugar. Fructose is found in many fruits, as well as in honey. These sugars are structural isomers of one another, with the difference being that glucose contains an aldehyde functional group, whereas fructose contains a ketone functional group.

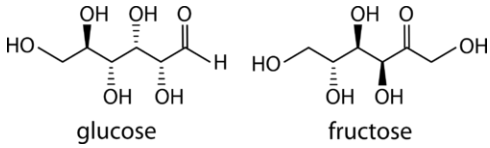


Figure 21.3.2: Glucose and fructose are monosaccharides, or simple sugars.

Glucose and fructose are both very soluble in water. In aqueous solution, the predominant forms are not the straight-chain structure shown above. Rather, they adopt a cyclic structure (see figure below). Glucose is six membered ring, while fructose is a five-membered ring. Both rings contain an oxygen atom.

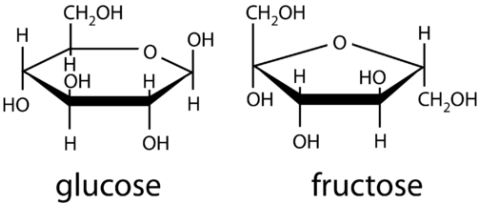


Figure 21.3.3: The cyclic form of sugars is the favored form in aqueous solution.

Another important group of monosaccharides are the pentoses, containing five carbons in the chain. Ribose and deoxyribose are two pentoses that are components of the structures of DNA and RNA.

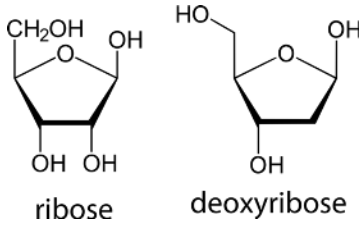


Figure **21.3.4**: Ribose and deoxyribose.

Summary

- Carbohydrates are monomers and polymers of aldehydes and ketones that have multiple hydroxyl groups attached.
- A monosaccharide is a carbohydrate consisting of one sugar unit.
- Common examples of simple sugars or monosaccharides are glucose and fructose.
- Another important group of monosaccharides are the pentoses, containing five carbons in the chain; DNA and RNA are partly comprised of pentoses.

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21.04: Disaccharides

Milk is one of the basic foods needed for good nutrition, especially for growing children. It contains vitamins and minerals necessary for healthy development. Unfortunately, milk and other dairy products also contain lactose, a carbohydrate that can make some people very ill. Lactose intolerance is a condition in which the lactose in milk cannot be digested well in the small intestine. The undigested lactose then moves into the large intestine where bacteria attack it, forming large amounts of gas. Symptoms of lactose intolerance include bloating, cramps, nausea, and vomiting. Often, in the case of children, the individual will outgrow this problem. Avoidance of foods containing lactose is recommended for people who show signs of lactose intolerance. Since dairy products can provide many vital nutrients, tablets can be taken that provide the needed digestive materials in the small intestine. Lactose-free milk is also readily available.

Disaccharides

The simple sugars form the foundation of more complex carbohydrates. The cyclic forms of two sugars can be linked together by means of a condensation reaction. The figure below shows how a glucose molecule and a fructose molecule combine to form a sucrose molecule. A hydrogen atom from one molecule and a hydroxyl group from the other molecule are eliminated as water, with a resulting covalent bond linking the two sugars together at that point.

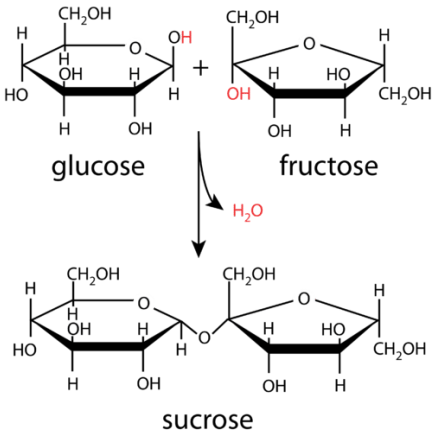


Figure **21.4.1**: Glucose and fructose combine to produce the disaccharide sucrose in a condensation reaction.

Sucrose, commonly known as table sugar, is an example of a disaccharide. A **disaccharide** is a carbohydrate formed by the joining of two monosaccharides. Other common disaccharides include lactose and maltose. Lactose, a component of milk, is formed from glucose and galactose, while maltose is formed from two glucose molecules.

During digestion, these disaccharides are hydrolyzed in the small intestine to form the component monosaccharides, which are then absorbed across the intestinal wall and into the bloodstream to be transported to the cells.

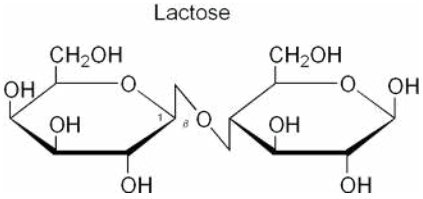


Figure **21.4.2**: Lactose.

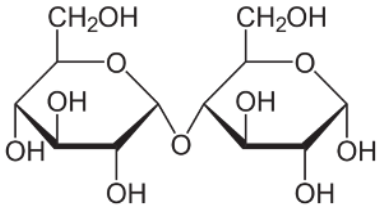


Figure **21.4.3**: Maltose.

Summary

- A **disaccharide** is a carbohydrate formed by the joining of two monosaccharides.
- Common disaccharides include sucrose, lactose, and maltose.

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21.05: Polysaccharides

As the weather warms up, the runners come out. Not just the casual joggers, but also the really serious runners who actually enjoy running all 26.2 miles of a marathon. Prior to these races (and a lot of shorter ones), you hear a lot about carbo-loading. This practice involves eating a lot of starch in the days prior to the race. The starch is converted to glucose, which is normally used for biochemical energy. Excess glucose is stored as glycogen in liver and muscle tissue to be used when needed. If there is a lot of glycogen available, the muscles will have more biochemical energy to draw on when needed for the long run. Meanwhile, the rest of us will sit at the sidewalk restaurant, eating our spaghetti, and enjoying watching other people work hard.

Polysaccharides

Many simple sugars can combine by repeated condensation reactions until a very large molecule is formed. A **polysaccharide** is a complex carbohydrate polymer formed from the linkage of many monosaccharide monomers. One of the best known polysaccharides is starch, the main form of energy storage in plants. Starch is a staple in most human diets. Foods such as corn, potatoes, rice, and wheat have high starch contents. Starch is made of glucose monomers and occurs in both straight-chain and branched forms. Amylose is the straight-chain form, and consists of hundreds of linked glucose molecules. The branched form of starch is called amylopectin. In the small intestine, starch is hydrolyzed to form glucose. The glucose can then be converted to biochemical energy or stored for later use.

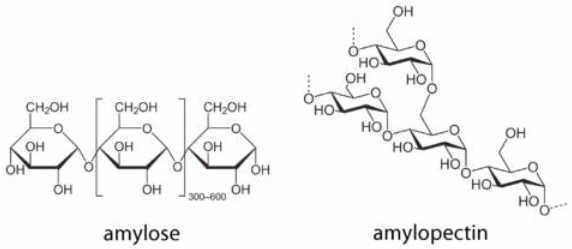


Figure **21.5.1**: Amylose and amylopectin are the two most common components of naturally occurring starch. Both consist of many glucose monomers connected into a polymer. Starch serves as energy storage in plants.

Glycogen is an even more highly branched polysaccharide of glucose monomers that serves the function of energy storage in animals. Glycogen is made and stored primarily in the cells of the liver and muscles.

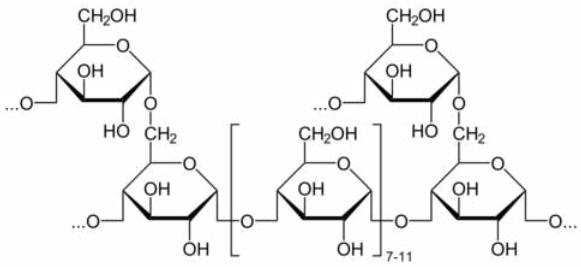


Figure **21.5.2**: Glycogen is a branched polymer of glucose and serves as energy storage in animals.

Cellulose is another polymer of glucose, consisting of anywhere from hundreds to over ten thousand monomers. It is the structural component of the cell walls of green plants and is the single most common organic molecule on Earth. Roughly **33%** of all plant matter is cellulose. The linkage structure in cellulose is different than that of starch, and cellulose is indigestible except by a few microorganisms that live in the digestive tracts of cattle and termites. The figure below shows a triple strand of cellulose. There is no branching and the fibers adopt a very stiff rod-like structure with numerous hydrogen bonds between the fibers adding to its strength. Cellulose is the main component of paper, cardboard, and textiles made from cotton, linen, and other plant fibers.

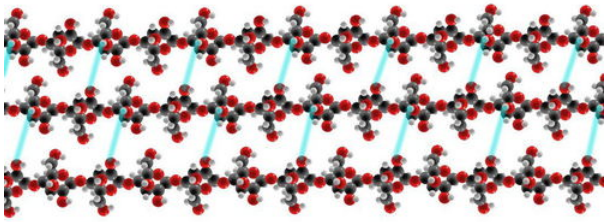


Figure **21.5.3**: Cellulose is composed of very long strands of glucose monomers that are hydrogen bonded to one another. Cellulose is largely indigestible and comprises the cell walls of plants.

Summary

- A polysaccharide is a complex carbohydrate polymer formed from the linkage of many monosaccharide monomers.
- One of the best known polysaccharides is starch, the main form of energy storage in plants.
- Glycogen is an even more highly branched polysaccharide of glucose monomers that serves the function of storing energy in animals.
- Cellulose is another polymer of glucose; it is the structural component of the cell walls of green plants.

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21.06: Nucleic Acids

Cancer treatment is a complex and challenging effort. Cancer cells grow without the usual controls that act on normal cells. One approach to treating cancer is to alter the structure of the DNA in order to slow down or stop the growth of the abnormal cells. Compounds that structurally resemble the normal building blocks of DNA have been shown to be very effective in stopping some forms of cancer from spreading throughout the body.

Nucleic Acids

The Swiss biochemist Friedrich Miescher first discovered nitrogen-containing compounds in the nuclei of cells in 1869. The term nucleic acid was used to describe these molecules because of their discovery within the cell nucleus, and because of the presence of phosphate groups and their relationship to phosphoric acid. A **nucleic acid** is a large biopolymer consisting of many nucleotides. The two primary nucleic acids which are found in cells are deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). DNA is the carrier of genetic information and is ultimately responsible for how cells produce proteins in order to carry out all the functions necessary for life. RNA is a related molecule that is involved in the mechanism by which the information stored in DNA is eventually converted into protein molecules.

The basic components of nucleic acids are nucleotides. A **nucleotide** is a molecule that contains a five-carbon sugar, a phosphate group, and a nitrogen-containing base. The five-carbon sugar is either ribose, in the case of RNA, or deoxyribose, in the case of DNA. The only difference between the two molecule is the presence of a hydroxyl group attached to one member of the carbon ring in RNA. In DNA, that same carbon atom is attached only to a hydrogen atom (see figure below). Note that in drawing the structure of organic molecules, the single hydrogen atoms are not shown in the structure, but are understood to be attached at each carbon point unless another molecule is shown.

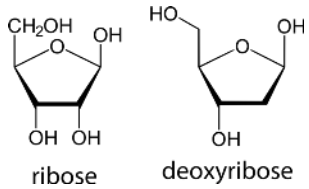


Figure **21.6.1**: The sugars ribose and deoxyribose are components of RNA and DNA respectively.

The nucleotides form the backbone of RNA and DNA. Each nucleotide consists of a base, a pentose (either ribose or deoxyribose) and phosphate groups (see figure below). Three of the bases in RNA and DNA are identical (adenine, cytosine, and guanine). Thymine is found in DNA, while uracil is found in RNA.

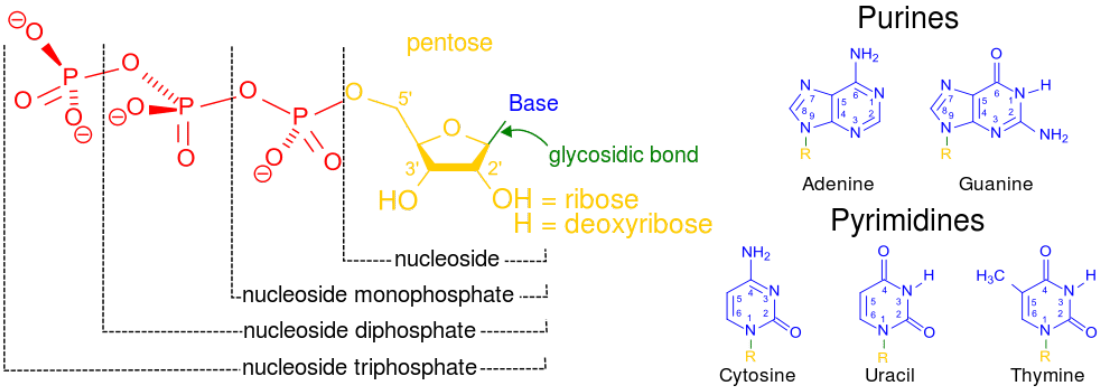


Figure **21.6.2**: Nucleotides.

Summary

- A nucleic acid is a large biopolymer consisting of many nucleotides.
- The two primary nucleic acids which are found in cells are deoxyribonucleic acid (DNA) and ribonucleic acid (RNA).
- A nucleotide is a molecule that contains a five-carbon sugar, a phosphate group, and a nitrogenous base.

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21.07: DNA and RNA

Linus Pauling was one of the greatest scientists of the twentieth century. Pauling was a two-time Nobel Prize winner (in chemistry in 1954, and the peace prize in 1962). However, he didn't always come in first. In the 1950s, there was a great deal of interest in the structure of DNA. Pauling spent some time on this puzzle, although he was primarily interested in proteins. He proposed a DNA structure where the bases were on the outside and the phosphate groups were on the inside. This idea turned out to be incorrect, but it certainly did not take away from his outstanding scientific reputation.

DNA and RNA

The three parts of a DNA nucleotide are assembled as shown in the figure below.

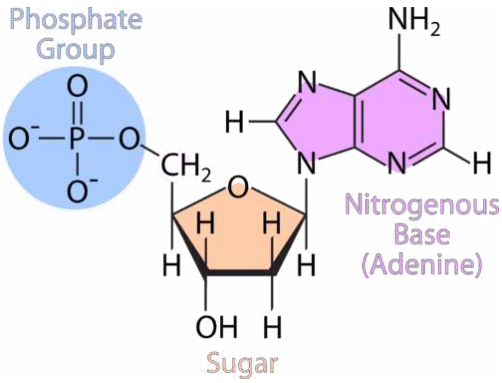


Figure **21.7.1**: Nucleotides are composed of a phosphate group, a sugar, and one of five different nitrogenous bases.

Every DNA and RNA polymer consists of multiple nucleotides strung together into extremely long chains. The only variation in each nucleotide is the identity of the nitrogenous base. The figure above shows one example of a nitrogenous base, called adenine. There are only five different nitrogenous bases found in all nucleic acids. The four bases of DNA are adenine, thymine, cytosine, and guanine, abbreviated A, T, C, and G respectively. In RNA, the base thymine is not found and is instead replaced by a different base called uracil, abbreviated U. The other three bases are present in both DNA and RNA.

The specific structure of DNA proved elusive to scientists for many years. In 1953, James Watson and Francis Crick proposed that the structure of DNA consists of two side-by-side polynucleotide chains wrapped into the shape of a **double helix**. One aspect of this structure is that each nitrogenous base on one of the DNA strands must be paired up with another base on the opposite strand. The figure below illustrates the base pairing. Each adenine base is always paired with a thymine, while each cytosine is paired with a guanine. The bases fit together perfectly from one strand to the other and are also held together by hydrogen bonds. The A-T pairing contains two hydrogen bonds, while the C-G pairing contains three hydrogen bonds. The ends of each strand are labeled either with 3' or 5', based on a numbering of the deoxyribose sugar ring.

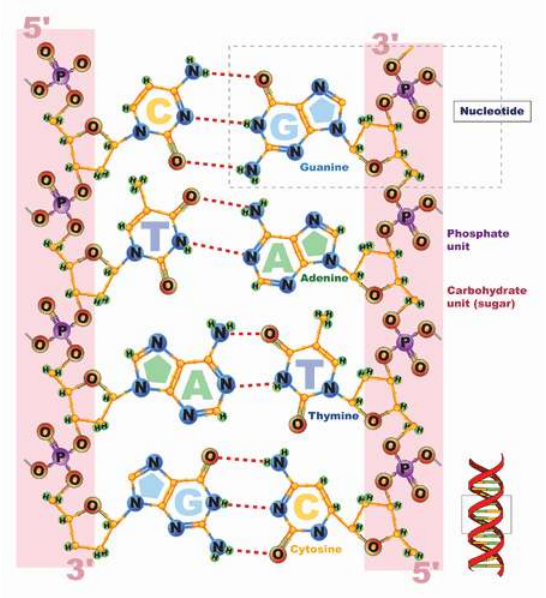


Figure **21.7.2**: Base pairing in DNA.

The double helical structure of DNA is shown in the figure below.

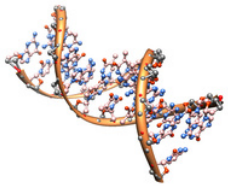


Figure **21.7.3**: The DNA double helix.

Summary

- Every DNA and RNA polymer consists of multiple nucleotides strung together into extremely long chains.
- The only variation in each nucleotide is the identity of the nitrogenous base.
- The four bases of DNA are adenine, thymine, cytosine, and guanine, abbreviated A, T, C, and G respectively. In RNA, the base thymine is not found and is instead replaced by a different base called uracil, abbreviated U; the other three bases are present in both DNA and RNA.
- James Watson and Francis Crick proposed that the structure of DNA consists of two side-by-side polynucleotide chains wrapped into the shape of a double helix.

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21.08: Genetic Code

The Human Genome Project started in 1990 with the lofty goal of sequencing the complete set of human DNA. This project was completed in April 2003, ahead of schedule and under the budget set for it (a rare occurrence for a government project). With this knowledge, we can now identify genetic disorders quickly and personalize treatment for many diseases. However, much work still remains to fully understand the connections between specific DNA sequences and specific diseases.

The Genetic Code

Each particular organism contains many protein molecules that are specific to that organism. The particular base sequence of DNA is responsible for the production of all of the different proteins that are present in each and every living thing that has ever inhabited the Earth. How does that work? Cells use the unique sequence of DNA bases to decide which proteins to synthesize. A **gene** is a segment of DNA that carries a code for making a specific polypeptide chain. The cell essentially decodes the DNA in order to make whatever peptides and proteins are needed by that organism.

The **genetic code** works as a series of three-letter codes. Each sequence of three letters, called a triplet, corresponds to one of the twenty common amino acids. The triplets are read by the cell, one after the other, in the process of protein synthesis. The table below shows all of the possible triplets and the amino acids that result from each three-letter code.

Table **21.8.1**: DNA Triplet Codes for Amino Acids

AAA	Lys	GAA	Glu	TAA	Stop	CAA	Gln
AAG	Lys	GAG	Glu	TAG	Stop	CAG	Gln
AAT	Asn	GAT	Asp	TAT	Tyr	CAT	His
AAC	Asn	GAC	Asp	TAC	Tyr	CAC	His
AGA	Arg	GGA	Gly	TGA	Stop	CGA	Arg
AGG	Arg	GGG	Gly	TGG	Trp	CGG	Arg
AGT	Ser	GGT	Gly	TGT	Cys	CGT	Arg
AGC	Ser	GGC	Gly	TGC	Cys	CGC	Arg
ATA	Ile	GTA	Val	TTA	Leu	CTA	Leu
ATG	Met	GTG	Val	TTG	Leu	CTG	Leu
ATT	Ile	GTT	Val	TTT	Phe	CTT	Leu
ATC	Ile	GTC	Val	TTC	Phe	CTC	Leu
ACA	Thr	GCA	Ala	TCA	Ser	CCA	Pro
ACG	Thr	GCG	Ala	TCG	Ser	CCG	Pro
ACT	Thr	GCT	Ala	TCT	Ser	CCT	Pro
ACC	Thr	GCC	Ala	TCC	Ser	CCC	Pro

The DNA code word GCA corresponds to the amino acid arginine, while the DNA code word TCG corresponds to the amino acid serine. Most amino acids are represented by more than one possible triplet code, but each triplet code yields only one particular amino acid. Three of the DNA code words (TAA, TAG, and TGA) are stop or termination code words. The translation of a DNA base sequence begins with a start code word and runs until a stop code word is reached.

Even with only four different bases, the number of possible nucleotide sequences in a DNA chain is virtually limitless. The particular DNA sequence of an organism constitutes the genetic blueprint for that organism. This genetic blueprint is found in the

nucleus of each cell of the organism, and is passed on from parents to offspring. The incredible diversity of life on Earth stems from the differences in the genetic code of every living thing.

Summary

- The particular base sequence of DNA is responsible for the production of all of the different proteins that are present in each and every living thing that has ever inhabited the Earth.
- A gene is a segment of DNA that carries a code for making a specific polypeptide chain.
- The genetic code works as a series of three-letter codes.

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21.09: Protein Synthesis

The assembly line is an American invention that was developed around 1901 to mass-produce cars. Prior to that time, teams of workers would build a car together. With the advent of the assembly line, cars could be produced much more quickly, and at lower cost. The assembly line idea quickly spread to other products. Being able to line up parts in order, and have a smooth process for putting those parts together, means that an item can be produced quickly and reproducibly, coming out the same way every time.

Protein Synthesis

The process of protein synthesis is summarized in the diagram below. DNA produces an RNA template, which then directs the amino acids to be introduced into the growing protein chain in the proper sequence. A specific transfer-RNA (tRNA) attaches to each specific amino acid and brings the amino acid to the RNA for incorporation.

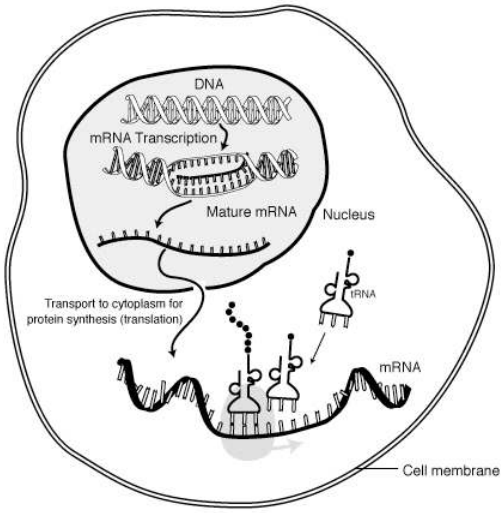


Figure **21.9.1**: Overview of protein synthesis.

The first step in the process is **transcription**—the unfolding of DNA and the production of a messenger-RNA (mRNA) strand. This step takes place in the nucleus of the cell.

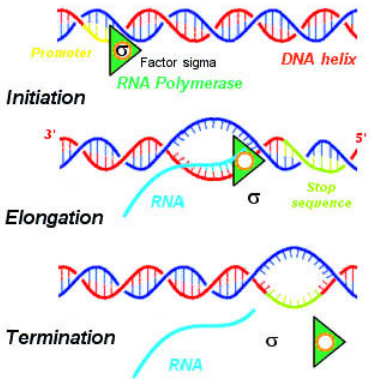


Figure **21.9.2**: Formation of RNA from DNA.

The DNA uncoils and provides the pattern for the formation of a single strand of mRNA. After production of the RNA, the DNA refolds into the original double helix. The mRNA is exported to the cytoplasm (outside the nucleus) for further processing.

Amino acids will link with specific tRNA molecules for proper placement in the protein chain. The tRNA is a small coiled molecule that accepts an amino acid on one end and matches up to a specific three-base portion of the mRNA on the other end. The tRNA interacts with the mRNA so as to put the amino acid in the proper sequence for the developing protein. After adding the amino acid to the sequence, the tRNA is then cleaved from the amino acid and recycled for further use in the process.

The process of amino acid assembly takes place in the ribosome. This structure consists of two subunits containing ribosomal RNA that enclose the mRNA, and catalyze the formation of the amide linkages in the growing protein in a process known as **translation**. When protein synthesis is complete, the two subunits dissociate and release the completed protein chain.

The process of protein synthesis is fairly fast. Amino acids are added to the growing peptide chain at a rate of about 3-5 amino acids per second. A small protein (100-200 amino acids) can be produced in a minute or less.

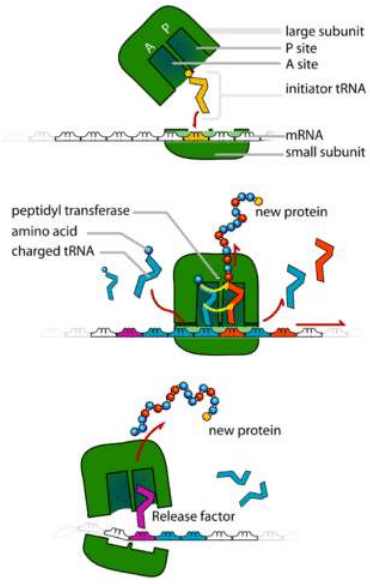


Figure **21.9.3**: Role of ribosome in protein synthesis.

Summary

- The first step of protein synthesis is transcription—the unfolding of DNA and the production of a messenger-RNA (mRNA) strand.
- In the second step of protein synthesis—translation—tRNA and mRNA interact to code amino acids into growing polypeptide chains.

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21.10: Lipids

There is a lot of interest these days in healthy diets, as well as concerns about heart problems. There is also a strong market for the sales of omega-3 fatty acids, which are said to help lower triglyceride (fat) levels in blood. But too many people rely on the supplements to help their hearts and don't understand the chemistry behind it all. Yes, taking omega-3 fatty acids will give you some of the fatty acids your body requires. No, this is not a substitute for eating a healthy diet and exercising. You can't sit in front of the TV set, eat a large pizza, and expect these pills to keep you healthy. It's important to eat healthfully and get exercise.

Triglycerides

A **lipid** is a member of a class of water-insoluble compounds that includes oils, fats, and waxes. Oils and fats are based on the same general structure, but fats are solids at room temperature, while oils are liquids. Butter is an example of a fat and is derived from animals. Some oils include olive oil and canola oil, which are obtained from plants. Lipids are an essential part of a healthy diet, though excess dietary fat can be harmful. Lipids store energy in the body and are also needed to keep cell membranes healthy.

One type of lipid is called a **triglyceride**, an ester derived from glycerol combined with three fatty acid molecules.

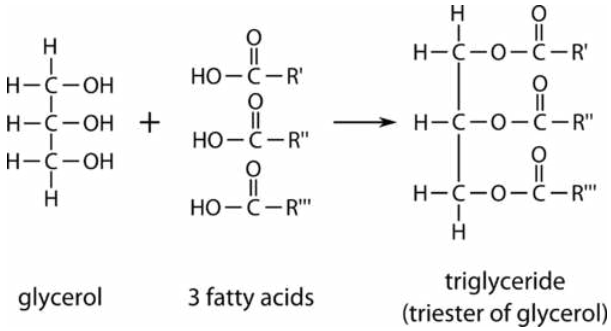


Figure **21.10.1**: Triglyceride components.

Glycerol is a triol, an alcohol which contains three hydroxyl functional groups. A fatty acid is a long carbon chain, generally 12 to 24 carbons in length, with an attached carboxyl group. Each of the three fatty acid molecules undergoes an esterification with one of the hydroxyl groups of the glycerol molecule. The result is a large triester molecule referred to as a triglyceride.

Triglycerides function as a long-term storage form of energy in the human body. Because of the long carbon chains, triglycerides are nearly nonpolar molecules and thus do not dissolve readily in polar solvents such as water. Instead, oils and fats are soluble in nonpolar organic solvents such as hexane and ethers.

Fats may be either saturated or unsaturated. A **saturated fat** is a fat that consists of triglycerides whose carbon chains consist entirely of carbon-carbon single bonds. Therefore, the carbon chains are saturated with the maximum number of hydrogen atoms possible. An **unsaturated fat** is a fat that consists of triglycerides whose carbon chains contain one or more carbon-carbon double bonds. A fat with one double bond is called monounsaturated, while a fat with multiple double bonds is called polyunsaturated (see figure below).

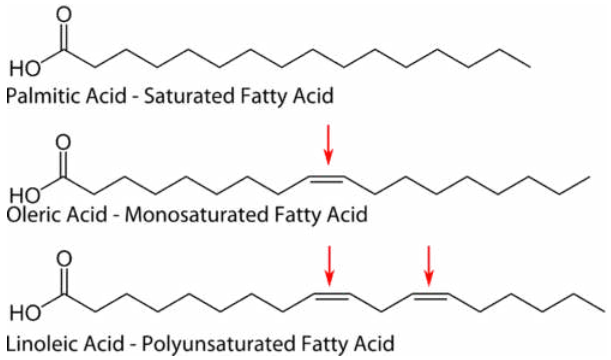


Figure **21.10.2**: Saturated and unsaturated fatty acids.

High consumption of saturated fats is linked to an increased risk of cardiovascular disease. Some examples of foods with high concentrations of saturated fats include butter, cheese, lard, and some fatty meats. Foods with higher concentrations of unsaturated fats include nuts, avocado, and vegetable oils such as canola oil and olive oil. The figure below shows the percentages of fat types in some common foods.

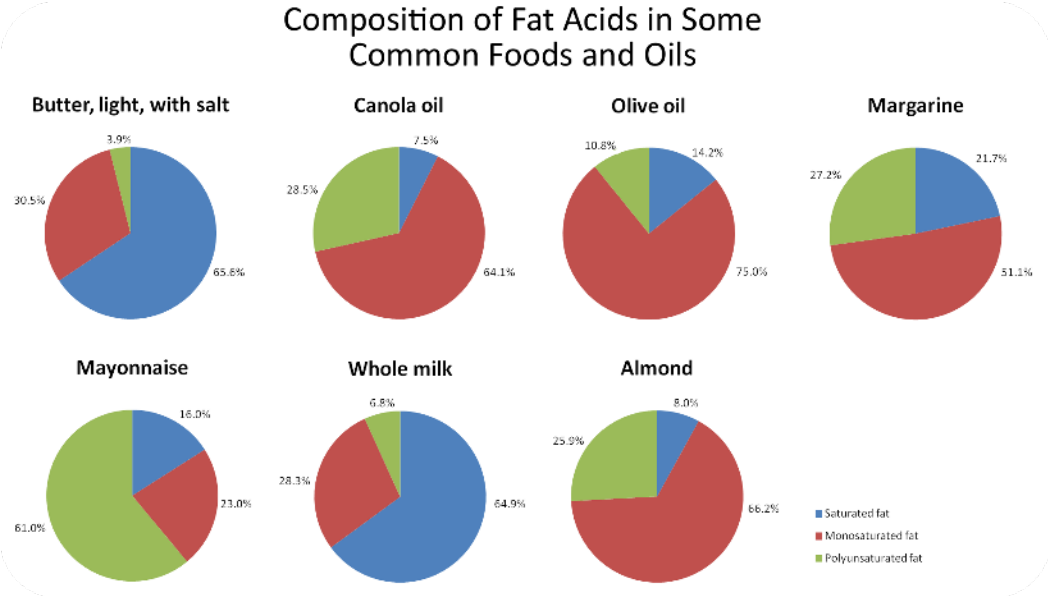


Figure **21.10.3**: Some common foods and oils along with their percentages of saturated, monounsaturated, and polyunsaturated fats.

Summary

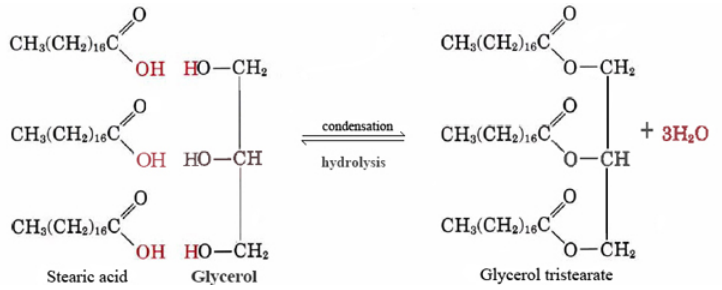
- A lipid is a member of a class of water-insoluble compounds that includes oils, fats, and waxes.
- One type of lipid is called a **t**riglyceride, an ester derived from glycerol combined with three fatty acid molecules.
- A saturated fat is a fat that consists of triglycerides whose carbon chains consist entirely of carbon-carbon single bonds.
- An unsaturated fat is a fat that consists of triglycerides whose carbon chains contain one or more carbon-carbon double bonds.

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21.11: Nonpolar Lipids

A good example of a nonpolar lipid is the neutral fat glycerol tristearate. This most-common form of animal fat serves as a storehouse for energy and as insulation against heat loss. On a molecular level it is constructed from three molecules of stearic acid and one of glycerol:



(1)

A great many nonpolar lipids can be made by combining different long- chain acids with glycerol. Because these acids were originally derived from fats, they are collectively referred to as **fatty acids**.

Notice that for each stearic or other fatty acid molecule that combines with one of the —OH groups of glycerol, a molecule of water is given off, and so the reaction is a condensation. It turns out that a great many important biological molecules are put together by condensation reactions during which water is given off. The reverse of Eq. (1), in which water reacts with a large molecule and splits it into smaller pieces, is called *hydrolysis*. By carrying out hydrolysis living organisms can break down molecules manufactured by other species. The simple building blocks obtained this way can then be recombined by condensation reactions to form structures appropriate to their new host.

By contrast with the glycerol tristearate found in animals, vegetable fats contain numerous double bonds in their long hydrocarbon chains. This polyunsaturation introduces “kinks” in the hydrocarbon chains because of the barrier to rotation and the 120° angles associated with the double bonds. Consequently it is more difficult to align the chains side by side (see Figure **21.11.1**), and the unsaturated fats do not pack together as easily in a crystal lattice. As was true with alkanes, chain length also determines whether a fat is liquid or solid, and where the melting point occurs.

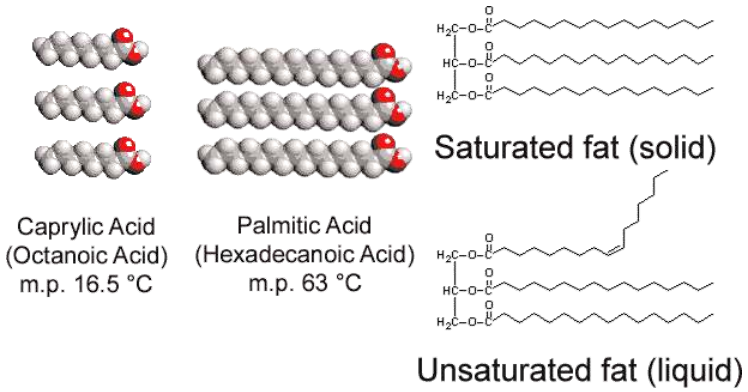


Figure **21.11.1**: Caprylic Acid has a shorter carbon chain than palmitic acid and thus melts at a lower temperature. When a double bond leaves part of a fatty acid chain unsaturated, the molecules can not pack in a crystal lattice as tightly, and this lowers the melting point.

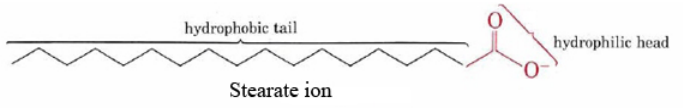
Most unsaturated fats (like corn oil) are liquids at ordinary temperatures, while saturated fats (like butter) are solids. Vegetable oils can be converted by hydrogenation to compounds that are solids. This process involves adding H_2 catalytically to the double bonds:



Hydrolysis of fats [the reverse of Eq. (1)] is important in the manufacture of soaps. It can be speeded up by the addition of a strong base like NaOH or KOH, in which case the reaction is called **saponification**. Since saponification requires that the pH of the

reaction mixture be high, the fatty acid that is produced will dissociate to its anion. When glycerol tristearate is saponified with NaOH for example, sodium stearate, a relatively water-soluble substance and a common soap, is formed.

The ability of soaps to clean grease and oil from soiled surfaces is a result of the dual hydrophobic-hydrophilic structures of their molecules. The stearate ion, for example, consists of a long nonpolar hydrocarbon chain with a highly polar —COO^- group at one end.



The hydrophobic hydrocarbon chain tries to avoid contact with aqueous media, while the anionic group readily accommodates the dipole attractions and hydrogen bonds of water molecules.

The two main ways that the hydrophobic portions of stearate ions can avoid water are to cluster together on the surface or to dissolve in a small quantity of oil or grease (see Figure **21.11.2**).

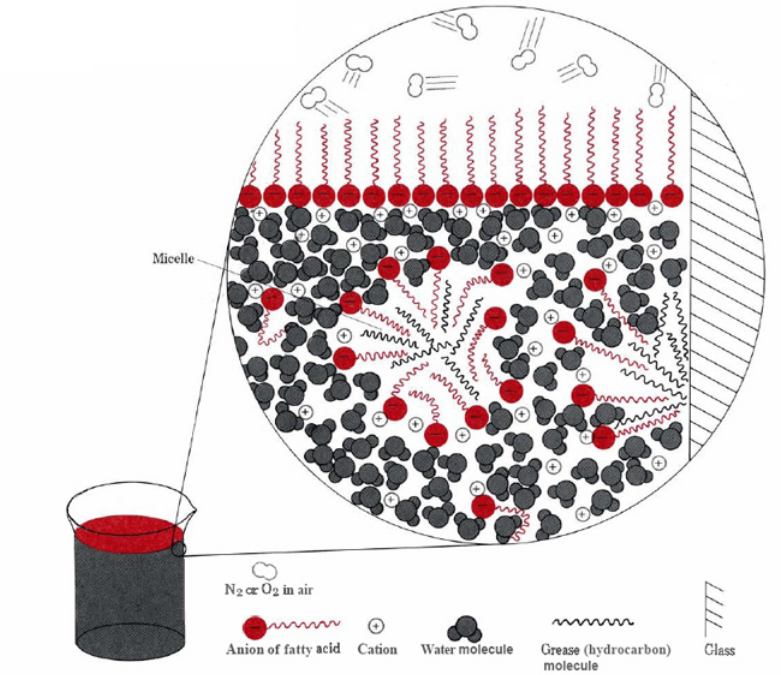
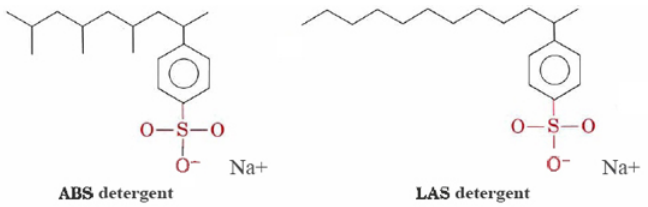


Figure **21.11.2**: Behavior of soap molecules in aqueous solution. Micelles containing grease molecules are made more soluble by the polar ends of soap molecules.

In the latter case the hydrophilic heads of the soap molecules contact the water outside the grease, forming a structure known as a **micelle**. Since the outsides of the micelles are negatively charged, they repel one another and prevent the grease droplets from recombining. The grease is therefore suspended (emulsified) in the water and can be washed away easily.

Natural soaps, such as sodium stearate, were originally made in the home by heating animal fat with wood ashes, which contained potash, K_2CO_3. Large quantities are still produced industrially, but to a considerable extent soaps have been replaced by detergents. This is a consequence of the undesirable behavior of soaps in hard water. Calcium, magnesium, and other hard-water cations form insoluble compounds when combined with the anions of fatty acids. This produces scummy precipitates and prevents the soap molecules from emulsifying grease unless a large excess is used.

Detergents such as alkylbenzenesulfonates (ABS) and linear alkylbenzenesulfonates (LAS) have structures very similar to sodium stearate except that the charged group in their hydrophilic heads is —SO_3^- attached to a benzene ring. The ABS detergents also have methyl (CH_3) groups branching off their hydrocarbon chains.



Such molecules do not precipitate with hard-water cations and therefore are more suitable for machine washing of clothes. The LAS detergents replaced ABS during the mid-nineteen-sixties when it was discovered that the latter were not biodegradable. They were causing rivers and even tap water to become covered with detergent suds and foam. Apparently the enzymes in microorganisms that had evolved to break down the unbranched hydrocarbon chains in natural fats and fatty acids were incapable of digesting the branched chains of ABS molecules. LAS detergents, though manufactured by humans, mimic the structures of naturally occurring molecules and are biodegradable.

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21.12: Phospholipids

If you were to go to the dentist to get a tooth pulled, you would not want to feel any pain. The dentist would inject an anesthetic into your gum to numb it. One theory as to why anesthetics work deals with the movement of ions across the cell membrane. The anesthetic gets into the membrane structure and causes shifts in how ions move across the membrane. If ion movement is disrupted, nerve impulses will not be transmitted and you will not sense pain—at least, not until the anesthetic wears off.

Phospholipids

A **phospholipid** is a lipid that contains a phosphate group and is a major component of cell membranes. A phospholipid consists of a hydrophilic (water-loving) head and hydrophobic (water-fearing) tail (see figure below). The phospholipid is essentially a triglyceride in which a fatty acid has been replaced by a phosphate group of some sort.

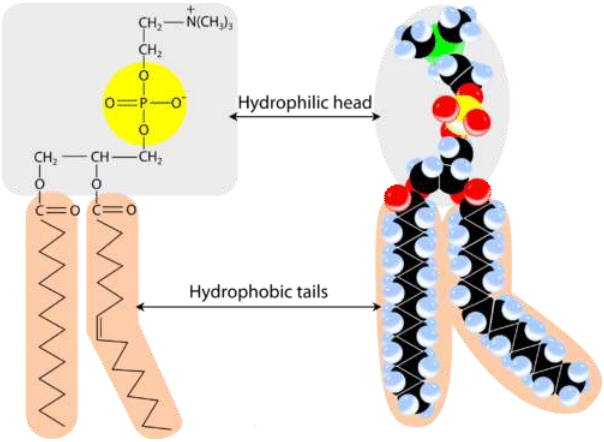


Figure **21.12.1**: A phospholipid consists of a head and a tail. The "head" of the molecule contains the phosphate group and is hydrophilic, meaning that it will dissolve in water. The "tail" of the molecule is made up of two fatty acids, which are hydrophobic and do not dissolve in water.

Following the rule of "like dissolves like", the hydrophilic head of the phospholipid molecule dissolves readily in water. The long fatty acid chains of a phospholipid are nonpolar, and thus avoid water because of their insolubility. In water, phospholipids spontaneously form a double layer called a lipid bilayer, in which the hydrophobic tails of phospholipid molecules are sandwiched between two layers of hydrophilic heads (see figure below). In this way, only the heads of the molecules are exposed to the water, while the hydrophobic tails interact only with each other.

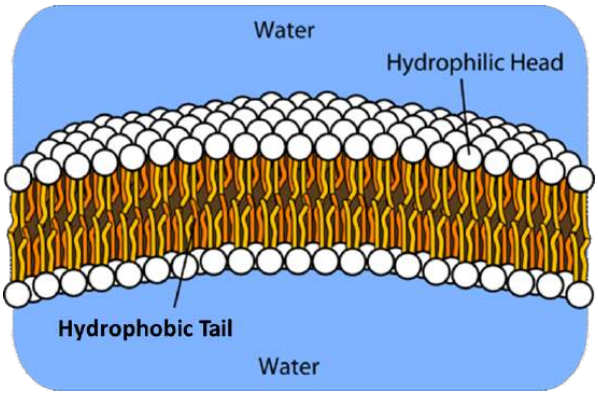


Figure **21.12.2**: In a water solution, phospholipids form a bilayer where the hydrophobic tails point towards each other on the interior and only the hydrophilic heads are exposed to the water.

Phospholipid bilayers are critical components of cell membranes. The lipid bilayer acts as a barrier to the passage of molecules and ions into and out of the cell. However, an important function of the cell membrane is to allow selective passage of certain substances into and out of cells. This is accomplished by the embedding of various protein molecules in and through the lipid bilayer (see figure below). These proteins form channels through which certain specific ions and molecules are able to move. Many

membrane proteins also contain attached carbohydrates on the outside of the lipid bilayer, allowing it to form hydrogen bonds with water.

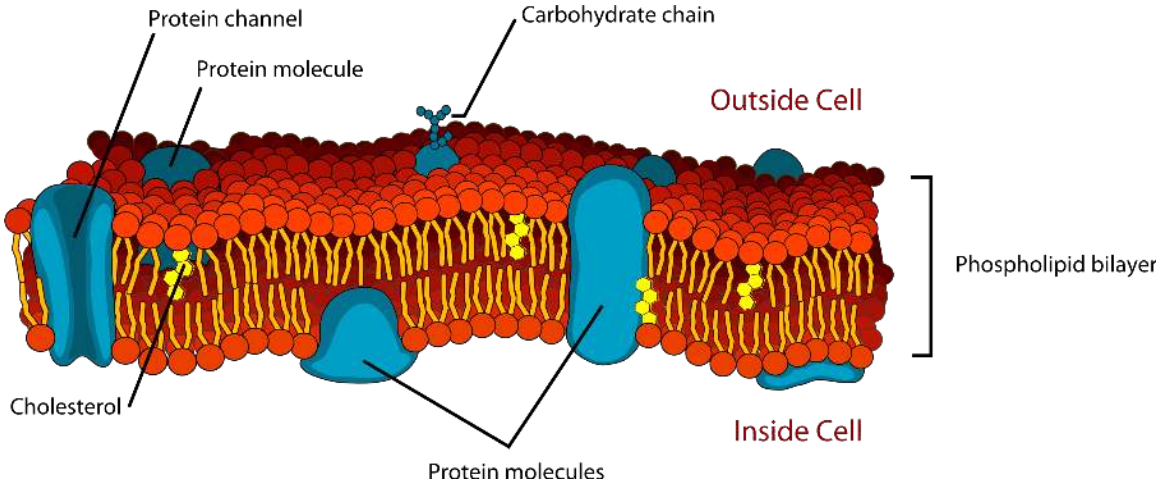


Figure **21.12.3**: The phospholipid bilayer of a cell membrane contains embedded protein molecules, which allow for selective passage of ions and molecules through the membrane.

Summary

- A phospholipid is a lipid that contains a phosphate group.
- A phospholipid consists of a hydrophilic (water-loving) head and hydrophobic (water-fearing) tail.
- In water, phospholipids spontaneously form a double layer called a lipid bilayer, in which the hydrophobic tails of phospholipid molecules are sandwiched between two layers of hydrophilic heads.
- Phospholipid bilayers are critical components of cell membranes.

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21.13: Steroids

Learning Objectives

- To identify the functions of steroids produced in mammals.

All the lipids discussed so far are *saponifiable*, reacting with aqueous alkali to yield simpler components, such as glycerol, fatty acids, amino alcohols, and sugars. Lipid samples extracted from cellular material, however, also contain a small but important fraction that does not react with alkali. The most important nonsaponifiable lipids are the steroids. These compounds include the *bile salts*, *cholesterol* and related compounds, and certain *hormones* (such as cortisone and the sex hormones).

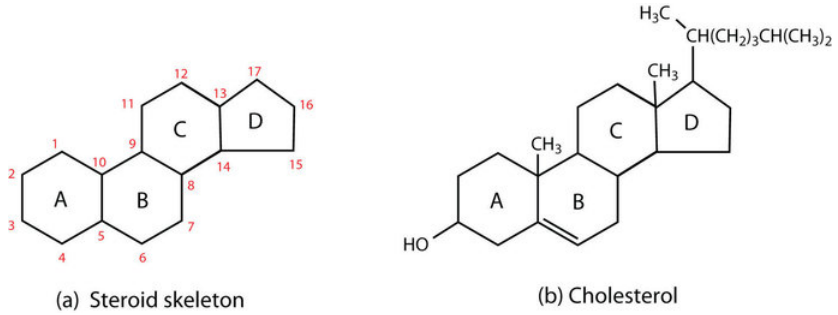


Figure **21.13.1** Steroids. (a) The four-fused-ring steroid skeleton uses letter designations for each ring and the numbering of the carbon atoms. (b) The cholesterol molecule follows this pattern.

Steroids occur in plants, animals, yeasts, and molds but not in bacteria. They may exist in free form or combined with fatty acids or carbohydrates. All steroids have a characteristic structural component consisting of four fused rings. Chemists identify the rings by capital letters and number the carbon atoms as shown in Figure **21.13.1*a***. Slight variations in this structure or in the atoms or groups attached to it produce profound differences in biological activity.

Cholesterol

Cholesterol (Figure **21.13.1*b***) does not occur in plants, but it is the most abundant steroid in the human body (240 g is a typical amount). Excess cholesterol is believed to be a primary factor in the development of atherosclerosis and heart disease, which are major health problems in the United States today. About half of the body's cholesterol is interspersed in the lipid bilayer of cell membranes. Much of the rest is converted to cholic acid, which is used in the formation of bile salts. Cholesterol is also a precursor in the synthesis of sex hormones, adrenal hormones, and vitamin D.

Excess cholesterol not metabolized by the body is released from the liver and transported by the blood to the gallbladder. Normally, it stays in solution there until being secreted into the intestine (as a component of bile) to be eliminated. Sometimes, however, cholesterol in the gallbladder precipitates in the form of gallstones (Figure **21.13.2**). Indeed, the name *cholesterol* is derived from the Greek *chole*, meaning "bile," and *stereos*, meaning "solid."



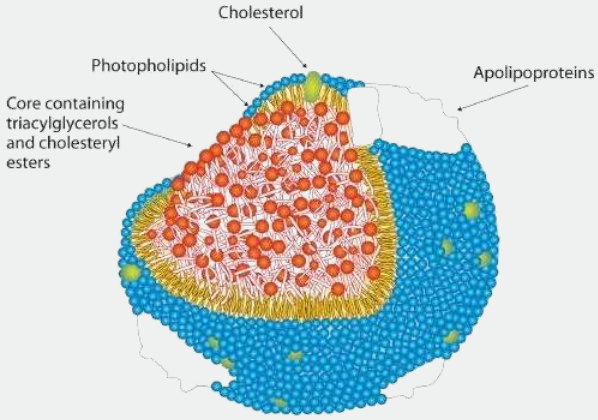
Figure **21.13.2**: Numerous small gallstones made up largely of cholesterol, all removed in one patient. Grid scale 1 mm

To Your Health: Cholesterol and Heart Disease

Heart disease is the leading cause of death in the United States for both men and women. The Centers for Disease Control and Prevention reported that heart disease claimed 631,636 lives in the United States (26% of all reported deaths) in 2006.

Scientists agree that elevated cholesterol levels in the blood, as well as high blood pressure, obesity, diabetes, and cigarette smoking, are associated with an increased risk of heart disease. A long-term investigation by the National Institutes of Health showed that among men ages 30 to 49, the incidence of heart disease was five times greater for those whose cholesterol levels were above 260 mg/100 mL of serum than for those with cholesterol levels of 200 mg/100 mL or less. The cholesterol content of blood varies considerably with age, diet, and sex. Young adults average about 170 mg of cholesterol per 100 mL of blood, whereas males at age 55 may have cholesterol levels at 250 mg/100 mL or higher because the rate of cholesterol breakdown decreases with age. Females tend to have lower blood cholesterol levels than males.

To understand the link between heart disease and cholesterol levels, it is important to understand how cholesterol and other lipids are transported in the body. Lipids, such as cholesterol, are not soluble in water and therefore cannot be transported in the blood (an aqueous medium) unless they are complexed with proteins that are soluble in water, forming assemblages called *lipoproteins*. Lipoproteins are classified according to their density, which is dependent on the relative amounts of protein and lipid they contain. Lipids are less dense than proteins, so lipoproteins containing a greater proportion of lipid are less dense than those containing a greater proportion of protein.



Research on cholesterol and its role in heart disease has focused on serum levels of low-density lipoproteins (LDLs) and high-density lipoproteins (HDLs). One of the most fascinating discoveries is that high levels of HDLs reduce a person's risk of developing heart disease, whereas high levels of LDLs increase that risk. Thus the serum LDL:HDL ratio is a better predictor of heart disease risk than the overall level of serum cholesterol. Persons who, because of hereditary or dietary factors, have high LDL:HDL ratios in their blood have a higher incidence of heart disease.

How do HDLs reduce the risk of developing heart disease? No one knows for sure, but one role of HDLs appears to be the transport of excess cholesterol to the liver, where it can be metabolized. Therefore, HDLs aid in removing cholesterol from blood and from the smooth muscle cells of the arterial wall.

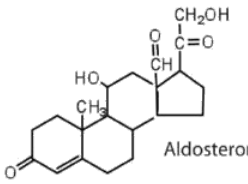
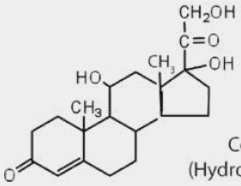
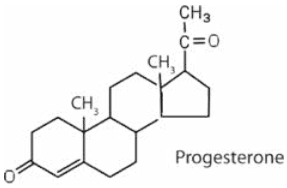
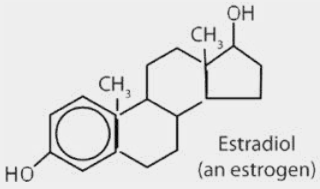
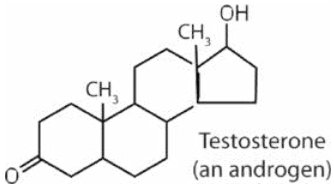
Dietary modifications and increased physical activity can help lower total cholesterol and improve the LDL:HDL ratio. The average American consumes about 600 mg of cholesterol from animal products each day and also synthesizes approximately 1 g of cholesterol each day, mostly in the liver. The amount of cholesterol synthesized is controlled by the cholesterol level in the blood; when the blood cholesterol level exceeds 150 mg/100 mL, the rate of cholesterol biosynthesis is halved. Hence, if cholesterol is present in the diet, a feedback mechanism suppresses its synthesis in the liver. However, the ratio of suppression is not a 1:1 ratio; the reduction in biosynthesis does not equal the amount of cholesterol ingested. Thus, dietary substitutions of unsaturated fat for saturated fat, as well as a reduction in consumption of *trans* fatty acids, is recommended to help lower serum cholesterol and the risk of heart disease.

Steroid Hormones

Hormones are chemical messengers that are released in one tissue and transported through the circulatory system to one or more other tissues. One group of hormones is known as steroid hormones because these hormones are synthesized from cholesterol, which is also a steroid. There are two main groups of steroid hormones: adrenocortical hormones and sex hormones.

The adrenocortical hormones, such as aldosterone and cortisol (Table **21.13.1**), are produced by the adrenal gland, which is located adjacent to each kidney. Aldosterone acts on most cells in the body, but it is particularly effective at enhancing the rate of reabsorption of sodium ions in the kidney tubules and increasing the secretion of potassium ions and/or hydrogen ions by the tubules. Because the concentration of sodium ions is the major factor influencing water retention in tissues, aldosterone promotes water retention and reduces urine output. Cortisol regulates several key metabolic reactions (for example, increasing glucose production and mobilizing fatty acids and amino acids). It also inhibits the inflammatory response of tissue to injury or stress. Cortisol and its analogs are therefore used pharmacologically as immunosuppressants after transplant operations and in the treatment of severe skin allergies and autoimmune diseases, such as rheumatoid arthritis.

Table **21.13.1**: Representative Steroid Hormones and Their Physiological Effects

Hormone	Effect
 Aldosterone	regulates salt metabolism; stimulates kidneys to retain sodium and excrete potassium
 Cortisol (Hydrocortisone)	stimulates the conversion of proteins to carbohydrates
 Progesterone	regulates the menstrual cycle; maintains pregnancy
 Estradiol (an estrogen)	stimulates female sex characteristics; regulates changes during the menstrual cycle
 Testosterone (an androgen)	stimulates and maintains male sex characteristics

The sex hormones are a class of steroid hormones secreted by the gonads (ovaries or testes), the placenta, and the adrenal glands. Testosterone and androstenedione are the primary male sex hormones, or *androgens*, controlling the primary sexual characteristics of males, or the development of the male genital organs and the continuous production of sperm. Androgens are also responsible for the development of secondary male characteristics, such as facial hair, deep voice, and muscle strength. Two kinds of sex

hormones are of particular importance in females: progesterone, which prepares the uterus for pregnancy and prevents the further release of eggs from the ovaries during pregnancy, and the estrogens, which are mainly responsible for the development of female secondary sexual characteristics, such as breast development and increased deposition of fat tissue in the breasts, the buttocks, and the thighs. Both males and females produce androgens and estrogens, differing in the amounts of secreted hormones rather than in the presence or absence of one or the other.

Sex hormones, both natural and synthetic, are sometimes used therapeutically. For example, a woman who has had her ovaries removed may be given female hormones to compensate. Some of the earliest chemical compounds employed in cancer chemotherapy were sex hormones. For example, estrogens are one treatment option for prostate cancer because they block the release and activity of testosterone. Testosterone enhances prostate cancer growth. Sex hormones are also administered in preparation for sex-change operations, to promote the development of the proper secondary sexual characteristics. Oral contraceptives are synthetic derivatives of the female sex hormones; they work by preventing ovulation.

Bile Salts

Bile is a yellowish green liquid (pH 7.8–8.6) produced in the liver. The most important constituents of bile are bile salts, which are sodium salts of amidelike combinations of bile acids, such as cholic acid (part (a) of Figure **21.13.3**) and an amine such as the amino acid glycine (part (b) of Figure **21.13.3**). They are synthesized from cholesterol in the liver, stored in the gallbladder, and then secreted in bile into the small intestine. In the gallbladder, the composition of bile gradually changes as water is absorbed and the other components become more concentrated.

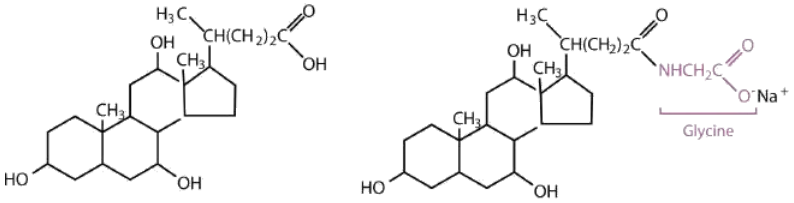


Figure **21.13.3** Bile Acids. (a) Cholic acid is an example of a bile acid. (b) Sodium glycocholate is a bile salt synthesized from cholic acid and glycine.

Because they contain both hydrophobic and hydrophilic groups, bile salts are highly effective detergents and emulsifying agents; they break down large fat globules into smaller ones and keep those smaller globules suspended in the aqueous digestive environment. Enzymes can then hydrolyze fat molecules more efficiently. Thus, the major function of bile salts is to aid in the digestion of dietary lipids.

> Surgical removal is often advised for a gallbladder that becomes infected, inflamed, or perforated. This surgery does not seriously affect digestion because bile is still produced by the liver, but the liver's bile is more dilute and its secretion into the small intestine is not as closely tied to the arrival of food.

Summary

Steroids have a four-fused-ring structure and have a variety of functions. Cholesterol is a steroid found in mammals that is needed for the formation of cell membranes, bile acids, and several hormones. Bile salts are secreted into the small intestine to aid in the digestion of fats.

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CHAPTER OVERVIEW

3: Matter

3.1: Matter
3.2: Physical and Chemical Properties
3.3: Physical and Chemical Changes
3.4: Elements and Compounds
3.5: Pure Substances and Mixtures
3.6: Separation of Mixtures

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3.1: Matter

Learning Objective

- Learn the basic terms used to describe matter
- To describe the solid, liquid and gas phases.

The definition of chemistry—the study of the interactions of matter with other matter and with energy—uses some terms that should also be defined. We start the study of chemistry by defining some basic terms.

Matter

Matter is anything that has mass and takes up space. A book is matter, a computer is matter, food is matter, and dirt in the ground is matter. Sometimes matter may be difficult to identify. For example, air is matter, but because it is so thin compared to other matter (e.g., a book, a computer, food, and dirt), we sometimes forget that air has mass and takes up space. Things that are not matter include thoughts, ideas, emotions, and hopes.

Example 3.1.1

Which of the following is matter and not matter?

a. a hot dog
b. love
c. a tree

Solution

a. A hot dog has mass and takes up space, so it is matter.
b. Love is an emotion, and emotions are not matter.
c. A tree has mass and takes up space, so it is matter.

Exercise 3.1.1

Which of the following is matter and not matter?

a. the moon
b. an idea for a new invention

Answer

a. The moon is matter.
b. The invention itself may be matter, but the idea for it is not.

States of Matter

Water can take many forms. At low temperatures (below 0°C), it is a solid. When at "normal" temperatures (between 0°C and 100°C), it is a liquid. While at temperatures above 100°C, water is a gas (steam). The state the water is in depends upon the temperature. Each state (solid, liquid, and gas) has its own unique set of physical properties. Matter typically exists in one of three states: **solid**, **liquid**, or **gas**.





Figure **3.1.1**: Matter is usually classified into three classical states, with plasma sometimes added as a fourth state. From left to right: quartz (solid), water (liquid), nitrogen dioxide (gas).

The state a given substance exhibits is also a physical property. Some substances exist as gases at room temperature (oxygen and carbon dioxide), while others, like water and mercury metal, exist as liquids. Most metals exist as solids at room temperature. All substances can exist in any of these three states. Figure **3.1.2** shows the differences among solids, liquids, and gases at the molecular level. 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.

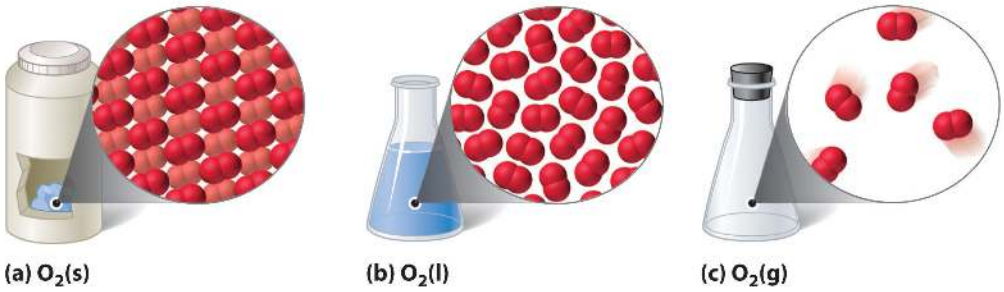
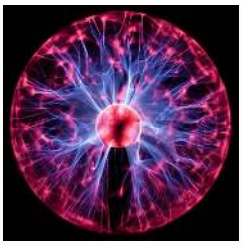


Figure **3.1.2**: A Representation of the Solid, Liquid, and Gas States. (a) Solid O_2 has a fixed volume and shape, and the molecules are packed tightly together. (b) Liquid O_2 conforms to the shape of its container but has a fixed volume; it contains relatively densely packed molecules. (c) Gaseous O_2 fills its container completely—regardless of the container's size or shape—and consists of widely separated molecules.

Plasma: A Fourth State of Matter

Technically speaking a fourth state of matter called plasma exists, but it does not naturally occur on earth, so we will omit it from our study here.



A plasma globe operating in a darkened room. Image used with permission (CC BY-SA 3.0; Chocolateoak).

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.

Solids are defined by the following characteristics:

- Definite shape (rigid)
- Definite volume
- Particles vibrate around fixed axes

If we were to cool liquid mercury to its freezing point of $-39°C$, and under the right pressure conditions, we would notice all of the liquid particles would go into the solid state. Mercury can be solidified when its temperature is brought to its freezing point. However, when returned to room temperature conditions, mercury does not exist in solid state for long, and returns back to its more common liquid form.

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 3.1.3. 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.

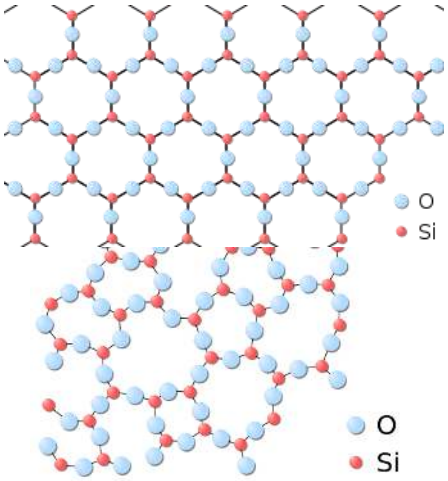


Figure 3.1.3: (left) The periodic crystalline lattice structure of quartz SiO_2 in two-dimensions. (right) The random network structure of glassy SiO_2 in two-dimensions. Note that, as in the crystal, each Silicon atom is bonded to 4 oxygen atoms, where the fourth oxygen atom is obscured from view in this plane. Images used with permission (public domain)

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.

Liquids have the following characteristics:

- No definite shape (takes the shape of its container)
- Has definite volume
- Particles are free to move over each other, but are still attracted to each other

A familiar liquid is mercury metal. Mercury is an anomaly. It is the only metal we know of that is liquid at room temperature. Mercury also has an ability to stick to itself (surface tension) - a property all liquids exhibit. Mercury has a relatively high surface tension, which makes it very unique. Here you see mercury in its common liquid form.



Video* 3.1.1: Mercury boiling to become a gas.*

If we heat liquid mercury to its boiling point of **357°C**, and under the right pressure conditions, we would notice all particles in the liquid state go into the gas state.

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. This describes the gas state, which we will consider in more detail elsewhere. Like liquids, gases have no definite shape, but unlike solids and liquids, gases have no definite volume either. 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. Gases have the following characteristics:

- No definite shape (takes the shape of its container)
- No definite volume
- Particles move in random motion with little or no attraction to each other
- Highly compressible

Table* 3.1.1: Characteristics of the Three States of Matter*

Characteristics	Solids	Liquids	Gases
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 3.1.1

What state or states of matter does each statement, describe?

a. This state has a definite volume, but no definite shape.

b. This state has no definite volume.
c. This state allows the individual particles to move about while remaining in contact.

SOLUTION

a. This statement describes the liquid state.
b. This statement describes the gas state.
c. This statement describes the liquid state.

Exercise 3.1.1

What state or states of matter does each statement 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.

Answer a:

solid

Answer b:

gas

Answer c:

solid

Key Takeaways

- Chemistry is the study of matter and its interactions with other matter and energy.
- Matter is anything that has mass and takes up space.
- Three states of matter exist - solid, liquid, and gas.
- Solids have a definite shape and volume.
- Liquids have a definite volume, but take the shape of the container.
- Gases have no definite shape or volume.

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3.2: Physical and Chemical Properties

Learning Objectives

To separate physical from chemical properties.

All matter has physical and chemical properties. Physical properties are characteristics that scientists can measure without changing the composition of the sample under study, such as mass, color, and volume (the amount of space occupied by a sample). Chemical properties describe the characteristic ability of a substance to react to form new substances; they include its flammability and susceptibility to corrosion. All samples of a pure substance have the same chemical and physical properties. For example, pure copper is always a reddish-brown solid (a physical property) and always dissolves in dilute nitric acid to produce a blue solution and a brown gas (a chemical property).

Physical Property

A *physical property* is a characteristic of a substance that can be observed or measured without changing the identity of the substance. Silver is a shiny metal that conducts electricity very well.It can be molded into thin sheets, a property called malleability. Salt is dull and brittle and conducts electricity when it has been dissolved into water, which it does quite easily. Physical properties of matter include color, hardness, malleability, solubility, electrical conductivity, density, melting points, and boiling points.

For the elements, color does not vary much from one element to the next. The vast majority of elements are colorless, silver, or gray. Some elements do have distinctive colors: sulfur and chlorine are yellow, copper is (of course) copper-colored, and elemental bromine is red. However, density can be a very useful parameter for identifying an element. Of the materials that exist as solids at room temperature, iodine has a very low density compared to zinc, chromium, and tin. Gold has a very high density, as does platinum. Pure water, for example, has a density of 0.998 g/cm^3 at 25°C. The average densities of some common substances are in Table 3.2.1. Notice that corn oil has a lower mass to volume ratio than water. This means that when added to water, corn oil will "float."

Table 3.2.1: Densities of Common Substances

Substance	Density at 25°C (g/cm3)
blood	1.035
body fat	0.918
whole milk	1.030
corn oil	0.922
mayonnaise	0.910
honey	1.420

- Hardness helps determine how an element (especially a metal) might be used. Many elements are fairly soft (silver and gold, for example) while others (such as titanium, tungsten, and chromium) are much harder. Carbon is an interesting example of hardness. In graphite, (the "lead" found in pencils) the carbon is very soft, while the carbon in a diamond is roughly seven times as hard.



Figure **3.2.1**: Pencil (left) and Diamond ring (right). Both are a form of carbon, but exhibit very different physical properties.

Melting and boiling points are somewhat unique identifiers, especially of compounds. In addition to giving some idea as to the identity of the compound, important information can be obtained about the purity of the material.

Chemical Properties

Chemical properties of matter describes its "potential" to undergo some chemical change or reaction by virtue of its composition. What elements, electrons, and bonding are present to give the potential for chemical change. It is quite difficult to define a chemical property without using the word "change". Eventually you should be able to look at the formula of a compound and state some chemical property. At this time this is very difficult to do and you are not expected to be able to do it. For example hydrogen has the potential to ignite and explode given the right conditions - this is a chemical property. Metals in general have they chemical property of reacting with an acid. Zinc reacts with hydrochloric acid to produce hydrogen gas - this is a chemical property.



Figure **3.2.2**: Heavy rust on the links of a chain near the Golden Gate Bridge in San Francisco; it was continuously exposed to moisture and salt spray, causing surface breakdown, cracking, and flaking of the metal. Image used with permission (CC BY-SA 3.0; Marlith).

A chemical property of iron is that it is capable of combining with oxygen to form iron oxide, the chemical name of rust (Figure **3.2.2**). The more general term for rusting and other similar processes is corrosion. Other terms that are commonly used in descriptions of chemical changes are burn, rot, explode, decompose, and ferment. Chemical properties are very useful in identifying substances. However, unlike physical properties, chemical properties can only be observed as the substance is in the process of being changed into a different substance.

***Table* 3.2.2:** *Contrasting Physical and Chemistry Properties*

Physical Property	Chemical Property
Gallium metal melts at 30 ^{o}C	Iron metal rusts.
Mercury is a very dense liquid.	A green banana turns yellow when it ripens.
Gold is shiny.	A dry piece of paper burns.

Example 3.2.1

Which of the following is a chemical property of iron?

a. Iron corrodes in moist air
b. Density = 7.874 g/cm^3
c. Iron is soft when pure.
d. Iron melts at 1808 K.

SOLUTION

Iron corrodes in air is the only chemical property of iron from the list.

Exercise 3.2.1*A*

Which of the following is a physical property of matter?

a. corrosiveness
b. pH (acidity)
c. density
d. flammability

Answer:

c

Exercise 3.2.1*B*

Which of the following is a chemical property?

a. flammability
b. melting point
c. boiling point
d. density

Answer:

a

Summary

A physical property is a characteristic of a substance that can be observed or measured without changing the identity of the substance. Physical properties include color, density, hardness, and melting and boiling points. A chemical property describes the ability of a substance to undergo a specific chemical change. To identify a chemical property, we look for a chemical change. A chemical change always produces one or more types of matter that differ from the matter present before the change. The formation of rust is a chemical change because rust is a different kind of matter than the iron, oxygen, and water present before the rust formed.

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3.3: Physical and Chemical Changes

Learning Objectives

- Label a change as chemical or physical.
- List evidence that can indicate a chemical change occurred.

Change is happening all around us all of the time. Just as chemists have classified elements and compounds, they have also classified types of changes. Changes are either classified as physical or chemical changes. Chemists learn a lot about the nature of matter by studying the changes that matter can undergo. Chemists make a distinction between two different types of changes that they study - physical changes and chemical changes.

Physical Change

Physical changes are changes in which no bonds are broken or formed. This means that the same types of compounds or elements that were there at the beginning of the change are there at the end of the change. Because the ending materials are the same as the beginning materials, the properties (such as color, boiling point, etc) will also be the same. Physical changes involve moving molecules around, but not changing them. Some types of physical changes include:

- Changes of state (changes from a solid to a liquid or a gas and vice versa)
- Separation of a mixture
- Physical deformation (cutting, denting, stretching)
- Making solutions (special kinds of mixtures)

As an ice cube melts, its shape changes as it acquires the ability to flow. However, its composition does not change. Melting is an example of a physical change. A physical change is a change to a sample of matter in which some properties of the material change, but the identity of the matter does not. When we heat the liquid water, it changes to water vapor. But even though the physical properties have changed, the molecules are exactly the same as before. We still have each water molecule containing two hydrogen atoms and one oxygen atom covalently bonded. When you have a jar containing a mixture of pennies and nickels and you sort the mixture so that you have one pile of pennies and another pile of nickels, you have not altered the identity of either the pennies or the nickels - you've merely separated them into two groups. This would be an example of a physical change. Similarly, if you have a piece of paper, you don't change it into something other than a piece of paper by ripping it up. What was paper before you started tearing is still paper when you're done. Again, this is an example of a physical change.



Figure* 3.3.1: Ice Melting is a physical change. When liquid water (**H_2O**) freezes into a solid state (ice), it appears changed; However, this change is only physical as the the composition of the constituent molecules is the same: 11.19% hydrogen and 88.81% oxygen by mass. Image used with permission (Public Domain;* Moussa).

Physical changes can further be classified as reversible or irreversible. The melted ice cube may be refrozen, so melting is a reversible physical change. Physical changes that involve a change of state are all reversible. Other changes of state include **vaporization** (liquid to gas), **freezing** (liquid to solid), and **condensation** (gas to liquid). Dissolving is also a reversible physical

change. When salt is dissolved into water, the salt is said to have entered the aqueous state. The salt may be regained by boiling off the water, leaving the salt behind.

Chemical Change

Chemical changes occur when bonds are broken and/or formed between molecules or atoms. This means that one substance with a certain set of properties (such as melting point, color, taste, etc) is turned into a different substance with different properties. Chemical changes are frequently harder to reverse than physical changes.

One good example of a chemical change is burning a candle. The act of burning paper actually results in the formation of new chemicals (carbon dioxide and water, to be exact) from the burning of the wax. Another example of a chemical change is what occurs when natural gas is burned in your furnace. This time, on the left we have a molecule of methane, CH_4, and two molecules of oxygen, O_2, while on the right we have two molecules of water, H_2O, and one molecule of carbon dioxide, CO_2. In this case, not only has the appearance changed, but the structure of the molecules has also changed. The new substances do not have the same chemical properties as the original ones. Therefore, this is a chemical change.



Figure **3.3.2**: Burning of wax to generate water and carbon dioxide is a chemical reaction. Image used with permission (CC-SA-BY-3.0; Andrikkos)

We can't actually see molecules breaking and forming bonds, although that's what defines chemical changes. We have to make other observations to indicate that a chemical change has happened. Some of the evidence for chemical change will involve the energy changes that occur in chemical changes, but some evidence involves the fact that new substances with different properties are formed in a chemical change.

Observations that help to indicate chemical change include:

- Temperature changes (either the temperature increases or decreases)
- Light is given off
- Unexpected color changes (a substance with a different color is made, rather than just mixing the original colors together)
- Bubbles are formed (but the substance is not boiling - you made a substance that is a gas at the temperature of the beginning materials, instead of a liquid)
- Different smell or taste (do not taste your chemistry experiments, though!)
- A solid forms if two clear liquids are mixed (look for *floaties* - technically called a precipitate)

Example 3.3.1

Label each of the following changes as a physical or chemical change. Give evidence to support your answer.

a. Boiling water
b. A nail rusting
c. A green solution and colorless solution are mixed. The resulting mixture is a solution with a pale green color.
d. Two colorless solutions are mixed. The resulting mixture has a yellow precipitate.

Solution:

a. Physical: boiling and melting are physical changes. When water boils no bonds are broken or formed. The change could be written: $H_2O\,(l) \rightarrow H_2O\,(g)$
b. Chemical: The dark grey nail changes color to form an orange flaky substance (the rust); this must be a chemical change. Color changes indicate chemical change. The following reaction occurs: $Fe + O_2 \rightarrow Fe_2O_3$
c. Physical: because none of the properties changed, this is a physical change. The green mixture is still green and the colorless solution is still colorless. They have just been spread together. No color *change* occurred or other evidence of chemical change.
d. Chemical: the formation of a precipitate and the color change from colorless to yellow indicate a chemical change.

Exercise 3.3.1

Label each of the following changes as a physical or chemical change.

a. A mirror is broken.
b. An iron nail corroded in moist air
c. Copper metal is melted.
d. A catalytic converter changes nitrogen dioxide to nitrogen gas and oxygen gas.

Answer a:

physical change

Answer b:

chemical change

Answer c:

physical change

Answer d:

chemical change

Summary

- Chemists make a distinction between two different types of changes that they study - physical changes and chemical changes.
- Physical changes are changes that do not alter the identity of a substance.
- Chemical changes are changes that occur when one substance is turned into another substance.
- Chemical changes are frequently harder to reverse than physical changes. Observations that indicate a chemical change occurred include color change, temperature change, light given off, formation of bubbles, formation of a precipitate, etc.

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3.4: Elements and Compounds

Introduction

The famous fictional British detective Sherlock Holmes was often said to make the statement "elementary, my dear Watson". In reality, the closest he ever came to that line was an exchange with Watson in the short story "The Crooked Man". Holmes shows shrewd insight into Watson's activities of the day. When asked how he knew what Watson was doing, Holmes simply replies "Elementary". Regardless of exactly how he put it, Sherlock was simply referring to what the Free Dictionary defines as "relating to, or constituting the basic, essential, or fundamental part".

Elements

An **element** is the simplest form of matter that has a unique set of properties. Examples of well-known elements include oxygen, iron, and gold (see below). Elements cannot be broken down into a simpler substance. Likewise, one element cannot be chemically converted into a different element.



Chemical elements are the simplest of substances. (A) An oxygen tank like this is used by people with a need for breathing assistance. (B) A simple skillet can be made from cast iron. (C) Gold bars are formed and used for monetary purposes.

Some elements have been known for centuries (gold, silver, iron, and copper among others) while others have been created in the lab only within the last several years. Most elements do not exist as such in nature. They are so reactive that they can be found only in combination with other materials.

Several of the elements are very valuable while others are quite inexpensive. Gold is currently worth almost $1700 per ounce. Aluminum, on the other hand, only sells for about 90 cents per pound, considerably lower than gold. Copper is worth somewhat more, selling for approximately $3.50 per pound. Platinum is very valuable at about $1650 an ounce, not quite as expensive as gold.

Explore More

Select five elements from this interactive Periodic Table

- http://www.chemicalelements.com

Answer the following questions:

1. What is the name of the element?

2. When was it discovered?

3. Who discovered it?

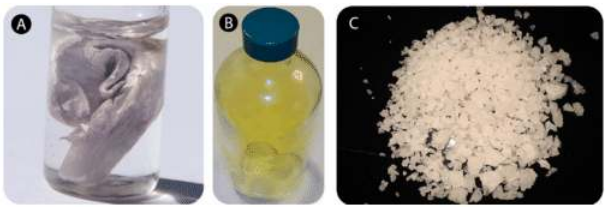
4. What is one use for this element?

Compounds

A **compound** is a substance that contains two or more elements chemically combined in a fixed proportion. The elements carbon and hydrogen combine to form many different compounds. One of the simplest is called methane, in which there are always four times as many hydrogen particles as carbon particles. Methane is a pure substance because it always has the same composition. However, it is not an element because it can be broken down into simpler substances - carbon and hydrogen.

Recall that the components of a mixture can be separated from one another by physical means. This is not true for a compound. Table salt is a compound consisting of equal parts of the elements sodium and chlorine. Salt cannot be separated into its two elements by filtering, distillation, or any other physical process. Salt and other compounds can only be decomposed into their elements by a chemical process. A **chemical change** is a change that produces matter with a different composition. Many compounds can be decomposed into their elements by heating. When sugar is heated, it decomposes into carbon and water. Water is still a compound, but one which cannot be broken down into hydrogen and oxygen by heating. Instead, the passage of an electrical current through water will produce hydrogen and oxygen gases.

The properties of compounds are generally very different than the properties of the elements from which the compound is formed. Sodium is an extremely reactive soft metal that cannot be exposed to air or water. Chlorine is a deadly gas. The compound sodium chloride is a white solid which is essential for all living things (see below).



(A) Sodium is so reactive that it must be stored under oil. (B) Chlorine is a poisonous yellow-green gas. (C) Salt crystals, a compound of sodium and chlorine.

Summary

- An element is the simplest form of matter that has a unique set of properties.
- One element cannot be chemically converted to another element.
- A compound is a substance that contains two or more elements chemically combined in a fixed proportion.

Contributors

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3.5: Pure Substances and Mixtures

Learning Objective

- Distinguish between pure substances and mixtures
- Identify mixtures as homogeneous or heterogeneous

Pure Substances

When we speak of a **pure substance**, we are speaking of something that contains only one kind of matter. This can either be one single element or one single compound, but every sample of this substance that you examine must contain exactly the same thing with a fixed, definite set of properties.

Pure Substance	Element or Compound?	Consists of:
Lead (Pb)	element	lead atoms
Oxygen gas (O_2)	element	oxygen molecules*
Water (H_2O)	compound	water molecules
Ammonia (NH_3)	compound	ammonia molecules

*Note: pure oxygen gas consists of molecules but it is still considered an element, rather than a compound, as the molecules are made up of a single type of element. Compounds are made up of one or more element.

Mixtures

If we take two or more pure substances and mix them together, we refer to this as a **mixture.** Mixtures can always be separated again into component pure substances, because *bonding* among the atoms of the constituent substances does not occur in a mixture. Whereas a compound may have very different properties from the elements that compose it, in mixtures the substances keep their individual properties. For example sodium is a soft shiny metal and chlorine is a pungent green gas. These two elements can combine to form the compound, sodium chloride (table salt) which is a white, crystalline solid having *none* of the properties of either sodium or chlorine. If, however, you *mixed* table salt with ground pepper, you would still be able to see the individual grains of each of them and, if you were patient, you could take tweezers and carefully separate them back into pure salt and pure pepper.

Heterogeneous mixture

A **heterogeneous mixture** is a mixture in which the composition is not uniform throughout the mixture. Vegetable soup is a heterogeneous mixture. Any given spoonful of soup will contain varying amounts of the different vegetables and other components of the soup.

Homogeneous mixture/ Solution

A **homogeneous mixture** is combination of two or more substances that are so intimately mixed that the mixture behaves as a single substance. Another word for a homogeneous mixture is solution. Thus, a combination of salt and steel wool is a heterogeneous mixture because it is easy to see which particles of the matter are salt crystals and which are steel wool. On the other hand, if you take salt crystals and dissolve them in water, it is very difficult to tell that you have more than one substance present just by looking—even if you use a powerful microscope. The salt dissolved in water is a homogeneous mixture, or a solution (Figure **3.5.3**).



Figure* 3.5.3*: *Types of Mixtures © Thinkstock On the left, the combination of two substances is a heterogeneous mixture because the particles of the two components look different. On the right, the salt crystals have dissolved in the water so finely that you cannot tell that salt is present. The homogeneous mixture appears like a single substance.*

Example 3.5.3

Identify the following combinations as heterogeneous mixtures or homogenous mixtures.

a. soda water (Carbon dioxide is dissolved in water.)
b. a mixture of iron metal filings and sulfur powder (Both iron and sulfur are elements.)

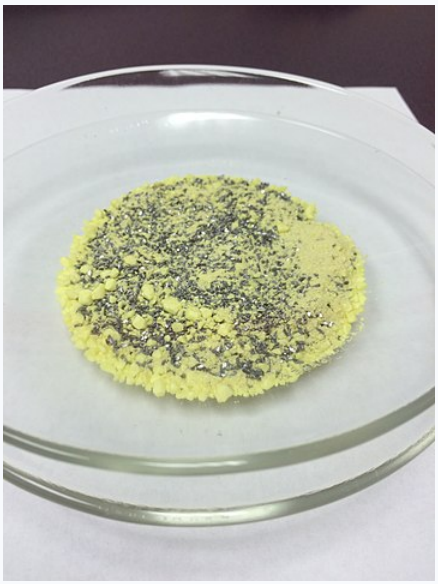


Figure* 3.5.4*: *A mixture of iron filings and sulfur powder* (Asoult, Fe-S mixture 03, CC BY 4.0)

Solution

a. Because carbon dioxide is dissolved in water, we can infer from the behavior of salt crystals dissolved in water that carbon dioxide dissolved in water is (also) a homogeneous mixture.
b. Assuming that the iron and sulfur are simply mixed together, it should be easy to see what is iron and what is sulfur, so this is a heterogeneous mixture.

Exercise 3.5.3

Are the following combinations homogeneous mixtures or heterogeneous mixtures?

a. the human body
b. an amalgam, a combination of some other metals dissolved in a small amount of mercury

Answers

a. heterogeneous mixture
b. homogeneous mixture

Categorizing Matter

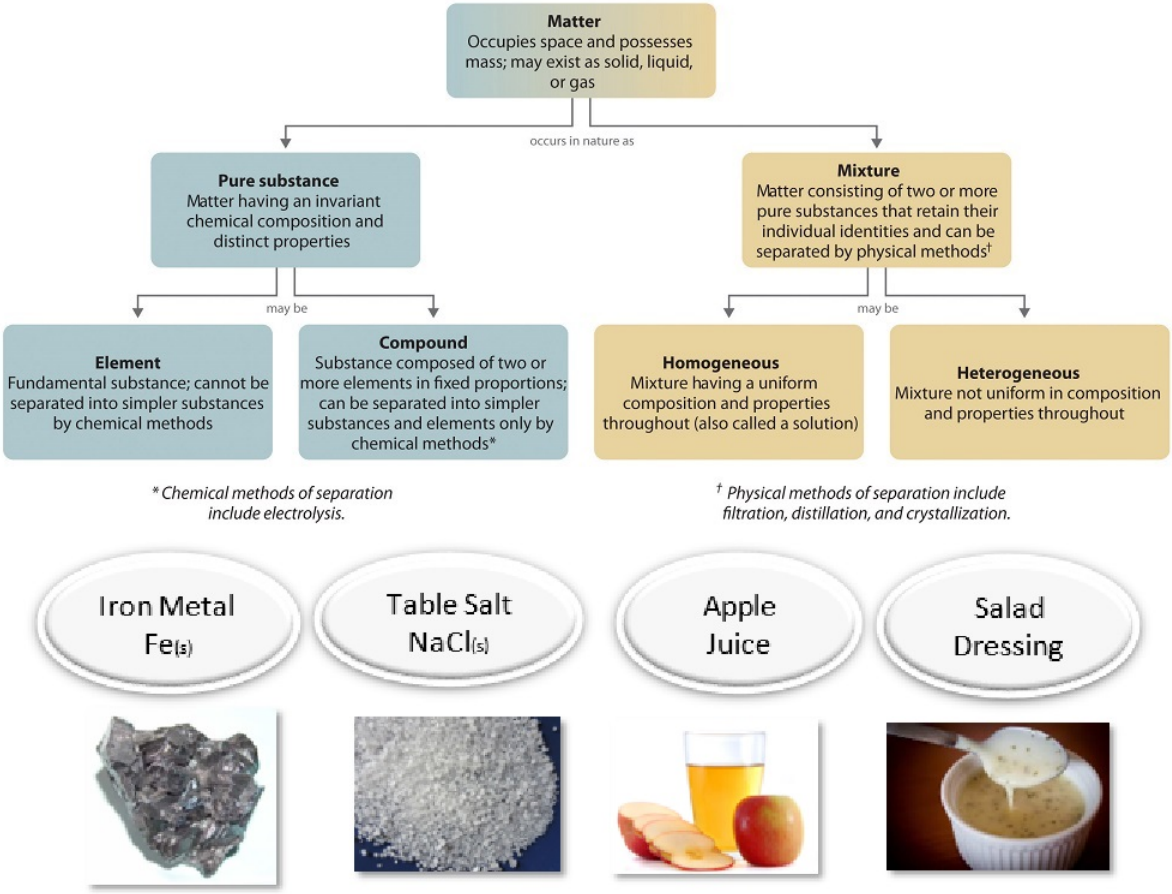


Figure **3.5.1**: *Relationships between the Types of Matter and the Methods Used to Separate Mixtures*

Ordinary table salt is called sodium chloride. It is considered a **substance** because it has a uniform and definite composition. All samples of sodium chloride are chemically identical. Water is also a pure substance. Salt easily dissolves in water, but salt water cannot be classified as a substance because its composition can vary. You may dissolve a small amount of salt or a large amount into a given amount of water. A mixture is a physical blend of two or more components, each of which retains its own identity and properties in the **mixture**. Only the form of the salt is changed when it is dissolved into water. It retains its composition and properties.

Phase

A phase is any part of a sample that has a uniform composition and properties. By definition, a pure substance or a homogeneous mixture consists of a single phase. A heterogeneous mixture consists of two or more phases. When oil and water are combined, they do not mix evenly, but instead form two separate layers. Each of the layers is called a phase.

Example 3.5.1

Identify each substance as a compound, an element, a heterogeneous mixture, or a homogeneous mixture (solution).

a. filtered tea
b. freshly squeezed orange juice
c. a compact disc
d. aluminum oxide, a white powder that contains a 2:3 ratio of aluminum and oxygen atoms
e. selenium

Given: a chemical substance

Asked for: its classification

Strategy:

A. Decide whether a substance is chemically pure. If it is pure, the substance is either an element or a compound. If a substance can be separated into its elements, it is a compound.
B. If a substance is not chemically pure, it is either a heterogeneous mixture or a homogeneous mixture. If its composition is uniform throughout, it is a homogeneous mixture.

Solution:

a. **A)** Tea is a solution of compounds in water, so it is not chemically pure. It is usually separated from tea leaves by filtration.
B) Because the composition of the solution is uniform throughout, it is ***a homogeneous mixture***.
b. **A)** Orange juice contains particles of solid (pulp) as well as liquid; it is not chemically pure.
B) Because its composition is not uniform throughout, orange juice is ***a heterogeneous mixture***.
c. **A)** A compact disc is a solid material that contains more than one element, with regions of different compositions visible along its edge. Hence a compact disc is not chemically pure.
B) The regions of different composition indicate that a compact disc is ***a heterogeneous mixture.***
d. **A)** Aluminum oxide is a single, chemically ***pure compound***.
e. **A)** Selenium is one of the known ***elements***.

Exercise 3.5.1

Identify each substance as a compound, an element, a heterogeneous mixture, or a homogeneous mixture (solution).

a. white wine
b. mercury
c. ranch-style salad dressing
d. table sugar (sucrose)

Answer a:

homogeneous mixture (solution)

Answer b:

element

Answer c:

heterogeneous mixture

Answer d:

compound

Example 3.5.2

How would a chemist categorize each example of matter?

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

SOLUTION

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.
b. Soil is composed of small pieces of a variety of materials, so it is a heterogeneous mixture.
c. Water is a substance; more specifically, because water is composed of hydrogen and oxygen, it is a compound.
d. Oxygen, a substance, is an element.

Exercise 3.5.2

How would a chemist categorize each example of matter?

a. coffee
b. hydrogen
c. an egg

Answer a:

a homogeneous mixture (solution), assume it's filtered coffee

Answer b:

element

Answer c:

heterogeneous mixture.

Summary

Matter can be classified into two broad categories: pure substances and mixtures. A pure substance is a form of matter that has a constant composition and properties that are constant throughout the sample. Mixtures are physical combinations of two or more elements and/or compounds. Mixtures can be classified as homogeneous or heterogeneous. Elements and compounds are both examples of pure substances. Compounds are substances that are made up of more than one type of atom. Elements are the simplest substances made up of only one type of atom.

Key Takeaways

- Pure substances are composed of a single element or compounds.
- Combinations of different substances are called mixtures.
- Homogeneous mixtures are mixtures of two or more compounds (or elements) that are **not** visually distinguishable from each other.
- Heterogeneous mixtures are mixtures of two or more compounds (or elements) that **are** visually distinguishable from one another.

Contributors

-
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3.6: Separation of Mixtures

Beginning in the late 1840's, thousands of prospectors rushed to California to search for gold. One of the approaches taken to isolate the gold from the soil was called "panning". Dirt would be placed in the pan and covered with water. After thorough mixing, the pan is gently swirled to remove dissolved material while the heavier gold settles to the bottom of the pan. The gold is then separated from the mixture of soil and water.

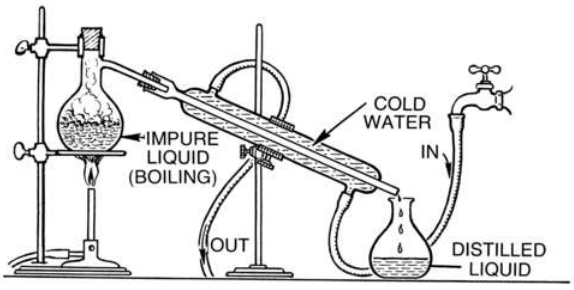
Not everyone is out searching for gold (and not many of those searches is going to get much gold, either). In a chemical reaction, it is important to isolate the component(s) of interest from all the other materials so they can be further characterized. Studies of biochemical systems, environmental analysis, pharmaceutical research - these and many other areas of research require reliable separation methods. Here are a number of common separation techniques:

Chromatography

Chromatography is the separation of a mixture by passing it in solution or suspension or as a vapor (as in gas chromatography) through a medium in which the components move at different rates. Thin-layer chromatography is a special type of chromatography used for separating and identifying mixtures that are or can be colored, especially pigments.

Distillation

Distillation is an effective method to separate mixtures comprised of two or more pure liquids. Distillation is a purification process where the components of a liquid mixture are vaporized and then condensed and isolated. In simple distillation, a mixture is heated and the most volatile component vaporizes at the lowest temperature. The vapor passes through a cooled tube (a condenser), where it condenses back into its liquid state. The condensate that is collected is called distillate.



Distillation apparatus.

In the figure above, we see several important pieces of equipment. There is a heat source, a test tube with a one-hole stopper attached to a glass elbow and rubber tubing. The rubber tubing is placed into a collection tube which is submerged in cold water. There are other more complicated assemblies for distillation that can also be used, especially to separate mixtures which are comprised of pure liquids with boiling points that are close to one another.

Evaporation

Evaporation is a technique used to separate out homogeneous mixtures where there is one or more dissolved salts. The method drives off the liquid components from the solid components. The process typically involves heating the mixture until no more liquid remains. Prior to using this method, the mixture should only contain one liquid component, unless it is not important to isolate the liquid components. This is because all liquid components will evaporate over time. This method is suitable to separate a soluble solid from a liquid.

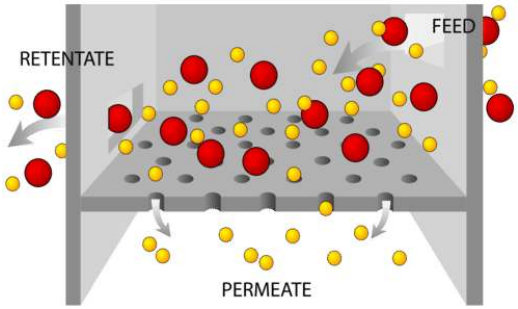
In many parts of the world, table salt is obtained from the evaporation of sea water. The heat for the process comes from the sun.



Once the sea water in these evaporation ponds has evaporated, the salt can be harvested.

Filtration

Filtration is a separation method used to separate out pure substances in mixtures comprised of particles, some of which are large enough in size to be captured with a porous material. Particle size can vary considerably, given the type of mixture.For instance, stream water is a mixture that contains naturally occurring biological organisms like bacteria, viruses, and protozoans. Some water filters can filter out bacteria,the length of which is on the order of 1 micron. Other mixtures, like soil, have relatively large particle sizes, which can be filtered through something like a coffee filter.



Filtration.

Summary

- Mixtures can be separated using a variety of techniques.
- Chromatography involves solvent separation on a solid medium.
- Distillation takes advantage of differences in boiling points.
- Evaporation removes a liquid from a solution to leave a solid material.
- Filtration separates solids of different sizes.

Explore More

Use this resource to answer the following questions:

- **Separating Mixtures** at http://www.bbc.co.uk/bitesize/ks3/sc...es/revision/9/.

1. List three methods of separating mixtures.

2. When is filtration the most efficient method for separation?

3. When is evaporation the most efficient method for separation?

4. Compare simple and fractional distillation.

Contributors

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CHAPTER OVERVIEW

5: Nomenclature

5.1 Naming Binary Ionic Compounds

5.2 Naming Molecular (Covalent) Compounds

5.3 Naming Compounds that contain Polyatomic Ions

5.4 Naming Acids

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5.1 Naming Binary Ionic Compounds

Naming Ionic Compounds

Naming ionic compounds is simple: combine the name of the cation and the name of the anion, in both cases omitting the word *ion*. *Do not use numerical prefixes if there is more than one ion necessary to balance the charges.* NaCl is sodium chloride, a combination of the name of the cation (sodium) and the anion (chloride). MgO is magnesium oxide. $MgCl_2$ is magnesium chloride —*not* magnesium dichloride.

In naming ionic compounds whose cations can have more than one possible charge, we must also include the charge, in parentheses and in roman numerals, as part of the name. Hence FeS is iron(II) sulfide, while Fe_2S_3 is iron(III) sulfide. Again, no numerical prefixes appear in the name. The number of ions in the formula is dictated by the need to balance the positive and negative charges.

Example 3:

Name each ionic compound.

a. $CaCl_2$
b. AlF_3
c. Co_2O_3

Solution

a. Using the names of the ions, this ionic compound is named calcium chloride. *It is not calcium(II) chloride* because calcium forms only one cation when it forms an ion, and it has a characteristic charge of 2+.
b. The name of this ionic compound is aluminum fluoride.
c. We know that cobalt can have more than one possible charge; we just need to determine what it is. Oxide always has a 2− charge, so with three oxide ions, we have a total negative charge of 6−. This means that the two cobalt ions have to contribute 6+, which for two cobalt ions means that each one is 3+. Therefore, the proper name for this ionic compound is cobalt(III) oxide.

Exercise 3

Name each ionic compound.

a. Sc_2O_3
b. AgCl

Answers

a. scandium oxide
b. silver chloride

How do you know whether a formula—and by extension, a name—is for a molecular compound or for an ionic compound? Molecular compounds form between nonmetals and nonmetals, while ionic compounds form between metals and nonmetals. The periodic table can be used to determine which elements are metals and nonmetals.

There also exists a group of ions that contain more than one atom. These are called **polyatomic ions**. Table 2 lists the formulas, charges, and names of some common polyatomic ions. Only one of them, the ammonium ion, is a cation; the rest are anions. Most of them also contain oxygen atoms, so sometimes they are referred to as ***oxyanions***. Some of them, such as nitrate and nitrite, and sulfate and sulfite, have very similar formulas and names, so care must be taken to get the formulas and names correct. Note that the -ite polyatomic ion has one less oxygen atom in its formula than the -ate ion but with the same ionic charge.

Table 2: *Common Polyatomic Ions*

Name	Formula and Charge		Name	Formula and Charge
ammonium	NH_4^+		hydroxide	OH^-
acetate	$C_2H_3O_2^-$, or CH_3COO^-		nitrate	NO_3^-
bicarbonate (hydrogen	HCO_3^-		nitrite	NO_2^-

carbonate)			
bisulfate(hydrogensulfate)	HSO_4^-	peroxide	C_2^{2-}
carbonate	CO_3^{2-}	perchlorate	ClC_4^-
chlora	ClO_3^-	phosphate	PC_4^{3-}

te			
chromate	CrO_4^{2-}	sulfate	SC_4^{2-}
cyanide	CN^-	sulfite	SC_3^{2-}
dichromate	$Cr_2O_7^{2-}$	triiodide	I_3^-

The naming of ionic compounds that contain polyatomic ions follows the same rules as the naming for other ionic compounds: simply combine the name of the cation and the name of the anion. Do not use numerical prefixes in the name if there is more than one polyatomic ion; the only exception to this is if the name of the ion itself contains a numerical prefix, such as dichromate or triiodide.

Writing the formulas of ionic compounds has one important difference. If more than one polyatomic ion is needed to balance the overall charge in the formula, enclose the formula of the polyatomic ion in parentheses and write the proper numerical subscript to the right and *outside* the parentheses. Thus, the formula between calcium ions, Ca^{2+}, and nitrate ions, NO_3^-, is properly written $Ca(NO_3)_2$, not $CaNO_{32}$ or CaN_2O_6. Use parentheses where required. The name of this ionic compound is simply calcium nitrate.

Example 4:

Write the proper formula and give the proper name for each ionic compound formed between the two listed ions.

a. NH_4^+ and S^{2-}
b. Al^{3+} and PO_4^{3-}
c. Fe^{2+} and PO_4^{3-}

Solution

a. Because the ammonium ion has a 1+ charge and the sulfide ion has a 2− charge, we need two ammonium ions to balance the charge on a single sulfide ion. Enclosing the formula for the ammonium ion in parentheses, we have $(NH_4)_2S$. The compound's name is ammonium sulfide.
b. Because the ions have the same magnitude of charge, we need only one of each to balance the charges. The formula is $AlPO_4$, and the name of the compound is aluminum phosphate.

c. Neither charge is an exact multiple of the other, so we have to go to the least common multiple of 6. To get $6+$, we need three iron(II) ions, and to get $6-$, we need two phosphate ions. The proper formula is $Fe_3(PO_4)_2$, and the compound's name is iron(II) phosphate.

Exercise 4

Write the proper formula and give the proper name for each ionic compound formed between the two listed ions.

a. NH_4^+ and PO_4^{3-}
b. Co^{3+} and NO_2^-

Answers

a. $(NH_4)_3PO_4$, ammonium phosphate
b. $Co(NO_2)_3$, cobalt(III) nitrite

Food and Drink App: Sodium in Your Food

The element sodium, at least in its ionic form as Na^+, is a necessary nutrient for humans to live. In fact, the human body is approximately 0.15% sodium, with the average person having one-twentieth to one-tenth of a kilogram in their body at any given time, mostly in fluids outside cells and in other bodily fluids.

Sodium is also present in our diet. The common table salt we use on our foods is an ionic sodium compound. Many processed foods also contain significant amounts of sodium added to them as a variety of ionic compounds. Why are sodium compounds used so much? Usually sodium compounds are inexpensive, but, more importantly, most ionic sodium compounds dissolve easily. This allows processed food manufacturers to add sodium-containing substances to food mixtures and know that the compound will dissolve and distribute evenly throughout the food. Simple ionic compounds such as sodium nitrite ($NaNO_2$) are added to cured meats, such as bacon and deli-style meats, while a compound called sodium benzoate is added to many packaged foods as a preservative. Table **3** is a partial list of some sodium additives used in food. Some of them you may recognize after reading this chapter. Others you may not recognize, but they are all ionic sodium compounds with some negatively charged ion also present.

Table 3: *Some Sodium Compounds Added to Food*

Sodium Compound	Use in Food
Sodium acetate	preservative, acidity regulator
Sodium adipate	food acid
Sodium alginate	thickener, vegetable gum, stabilizer, gelling agent, emulsifier
Sodium aluminum phosphate	acidity regulator, emulsifier
Sodium aluminosilicate	anticaking agent
Sodium ascorbate	antioxidant
Sodium benzoate	preservative
Sodium bicarbonate	mineral salt
Sodium bisulfite	preservative, antioxidant
Sodium carbonate	mineral salt
Sodium carboxymethylcellulose	emulsifier
Sodium citrates	food acid
Sodium dehydroacetate	preservative
Sodium erythorbate	antioxidant
Sodium erythorbin	antioxidant
Sodium ethyl para-hydroxybenzoate	preservative
Sodium ferrocyanide	anticaking agent
Sodium formate	preservative
Sodium fumarate	food acid
Sodium gluconate	stabilizer
Sodium hydrogen acetate	preservative, acidity regulator
Sodium hydroxide	mineral salt
Sodium lactate	food acid
Sodium malate	food acid
Sodium metabisulfite	preservative, antioxidant, bleaching agent
Sodium methyl para-hydroxybenzoate	preservative
Sodium nitrate	preservative, color fixative
Sodium nitrite	preservative, color fixative
Sodium orthophenyl phenol	preservative
Sodium propionate	preservative
Sodium propyl para-hydroxybenzoate	preservative
Sodium sorbate	preservative
Sodium stearoyl lactylate	emulsifier

Sodium Compound	Use in Food
Sodium succinates	acidity regulator, flavor enhancer
Sodium salts of fatty acids	emulsifier, stabilizer, anticaking agent
Sodium sulfite	mineral salt, preservative, antioxidant
Sodium sulfite	preservative, antioxidant
Sodium tartrate	food acid
Sodium tetraborate	preservative

The use of so many sodium compounds in prepared and processed foods has alarmed some physicians and nutritionists. They argue that the average person consumes too much sodium from his or her diet. The average person needs only about 500 mg of sodium every day; most people consume more than this—up to 10 times as much. Some studies have implicated increased sodium intake with high blood pressure; newer studies suggest that the link is questionable. However, there has been a push to reduce the amount of sodium most people ingest every day: avoid processed and manufactured foods, read labels on packaged foods (which include an indication of the sodium content), don't oversalt foods, and use other herbs and spices besides salt in cooking.



Figure 2: *Food labels include the amount of sodium per serving. This particular label shows that there are 75 mg of sodium in one serving of this particular food item.*

Key Takeaways

- Ions form when atoms lose or gain electrons.
- Ionic compounds have positive ions and negative ions.
- Ionic formulas balance the total positive and negative charges.
- Ionic compounds have a simple system of naming.
- Groups of atoms can have an overall charge and make ionic compounds.

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5.2 Naming Molecular (Covalent) Compounds

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5.3 Naming Compounds that contain Polyatomic Ions

There also exists a group of ions that contain more than one atom. These are called **polyatomic ions**. Table 2 lists the formulas, charges, and names of some common polyatomic ions. Only one of them, the ammonium ion, is a cation; the rest are anions. Most of them also contain oxygen atoms, so sometimes they are referred to as ***oxyanions***. Some of them, such as nitrate and nitrite, and sulfate and sulfite, have very similar formulas and names, so care must be taken to get the formulas and names correct. Note that the -ite polyatomic ion has one less oxygen atom in its formula than the -ate ion but with the same ionic charge.

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bicarbonate (hydrogen	HCO_3^-	nitrite	NO_2^-

carbonate)			
bisulfate(hydrogensulfate)	HSO_4^-	peroxide	C_2^{2-}
carbonate	CO_3^{2-}	perchlorate	ClC_4^-
chlora	ClO_3^-	phosphate	PC_4^{3-}

te			
chromate	CrO_4^{2-}	sulfate	SC_4^{2-}
cyanide	CN^-	sulfite	SC_3^{2-}
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b. Al^{3+} and PO_4^{3-}
c. Fe^{2+} and PO_4^{3-}

Solution

a. Because the ammonium ion has a 1+ charge and the sulfide ion has a 2− charge, we need two ammonium ions to balance the charge on a single sulfide ion. Enclosing the formula for the ammonium ion in parentheses, we have $(NH_4)_2S$. The compound's name is ammonium sulfide.
b. Because the ions have the same magnitude of charge, we need only one of each to balance the charges. The formula is $AlPO_4$, and the name of the compound is aluminum phosphate.

c. Neither charge is an exact multiple of the other, so we have to go to the least common multiple of 6. To get $6+$, we need three iron(II) ions, and to get $6-$, we need two phosphate ions. The proper formula is $Fe_3(PO_4)_2$, and the compound's name is iron(II) phosphate.

Exercise 4

Write the proper formula and give the proper name for each ionic compound formed between the two listed ions.

a. NH_4^+ and PO_4^{3-}
b. Co^{3+} and NO_2^-

Answers

a. $(NH_4)_3PO_4$, ammonium phosphate
b. $Co(NO_2)_3$, cobalt(III) nitrite

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The element sodium, at least in its ionic form as Na^+, is a necessary nutrient for humans to live. In fact, the human body is approximately 0.15% sodium, with the average person having one-twentieth to one-tenth of a kilogram in their body at any given time, mostly in fluids outside cells and in other bodily fluids.

Sodium is also present in our diet. The common table salt we use on our foods is an ionic sodium compound. Many processed foods also contain significant amounts of sodium added to them as a variety of ionic compounds. Why are sodium compounds used so much? Usually sodium compounds are inexpensive, but, more importantly, most ionic sodium compounds dissolve easily. This allows processed food manufacturers to add sodium-containing substances to food mixtures and know that the compound will dissolve and distribute evenly throughout the food. Simple ionic compounds such as sodium nitrite ($NaNO_2$) are added to cured meats, such as bacon and deli-style meats, while a compound called sodium benzoate is added to many packaged foods as a preservative. Table **3** is a partial list of some sodium additives used in food. Some of them you may recognize after reading this chapter. Others you may not recognize, but they are all ionic sodium compounds with some negatively charged ion also present.

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Sodium bisulfite	preservative, antioxidant
Sodium carbonate	mineral salt
Sodium carboxymethylcellulose	emulsifier
Sodium citrates	food acid
Sodium dehydroacetate	preservative
Sodium erythorbate	antioxidant
Sodium erythorbin	antioxidant
Sodium ethyl para-hydroxybenzoate	preservative
Sodium ferrocyanide	anticaking agent
Sodium formate	preservative
Sodium fumarate	food acid
Sodium gluconate	stabilizer
Sodium hydrogen acetate	preservative, acidity regulator
Sodium hydroxide	mineral salt
Sodium lactate	food acid
Sodium malate	food acid
Sodium metabisulfite	preservative, antioxidant, bleaching agent
Sodium methyl para-hydroxybenzoate	preservative
Sodium nitrate	preservative, color fixative
Sodium nitrite	preservative, color fixative
Sodium orthophenyl phenol	preservative
Sodium propionate	preservative
Sodium propyl para-hydroxybenzoate	preservative
Sodium sorbate	preservative
Sodium stearoyl lactylate	emulsifier

Sodium Compound	Use in Food
Sodium succinates	acidity regulator, flavor enhancer
Sodium salts of fatty acids	emulsifier, stabilizer, anticaking agent
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Sodium sulfite	preservative, antioxidant
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Figure 2: *Food labels include the amount of sodium per serving. This particular label shows that there are 75 mg of sodium in one serving of this particular food item.*

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CHAPTER OVERVIEW

7: Types of Chemical Reactions

7.1: Types of Chemical Reactions - Single and Double Displacement Reactions

7.2: Ionic Equations - A Closer Look

7.3: Neutralization Reactions

7.4: Single Displacement Reactions

7.5: Composition, Decomposition, and Combustion Reactions

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7.1: Types of Chemical Reactions - Single and Double Displacement Reactions

Learning Objectives

- Recognize chemical reactions as single-replacement reactions and double-replacement reactions.
- Use the periodic table, an activity series, or solubility rules to predict whether single-replacement reactions or double-replacement reactions will occur.

Up until now, we have presented chemical reactions as a topic, but we have not discussed how the products of a chemical reaction can be predicted. Here we will begin our study of certain types of chemical reactions that allow us to predict what the products of the reaction will be.

A **single-replacement reaction** is a chemical reaction in which one element is substituted for another element in a compound, generating a new element and a new compound as products. Presented below:

$$2\,HCl\,(aq) + Zn\,(s) \longrightarrow ZnCl_2\,(aq) + H_2\,(g)$$

is an example of a single-replacement reaction. The hydrogen atoms in **HCl** are replaced by **Zn** atoms, and in the process a new element—hydrogen—is formed. Another example of a single-replacement reaction is

$$2\,NaCl\,(aq) + F_2\,(g) \longrightarrow 2\,NaF\,(s) + Cl_2\,(g)$$

Here the negatively charged ion changes from chloride to fluoride. A typical characteristic of a single-replacement reaction is that there is one element as a reactant and another element as a product.

Not all proposed single-replacement reactions will occur between two given reactants. This is most easily demonstrated with fluorine, chlorine, bromine, and iodine. Collectively, these elements are called the *halogens* and are in the next-to-last column on the periodic table (Figure **7.1.1**). The elements on top of the column will replace the elements below them on the periodic table, but not the other way around. Thus, the reaction represented by

$$CaI_2\,(s) + Cl_2\,(g) \longrightarrow CaCl_2\,(s) + I_2\,(s)$$

will occur; but the reaction

$$CaF_2\,(s) + Br_2(\ell) \longrightarrow CaBr_2\,(s) + F_2\,(g)$$

will not, because bromine is below fluorine on the periodic table. This is just one of many ways the periodic table helps us to understand chemistry.

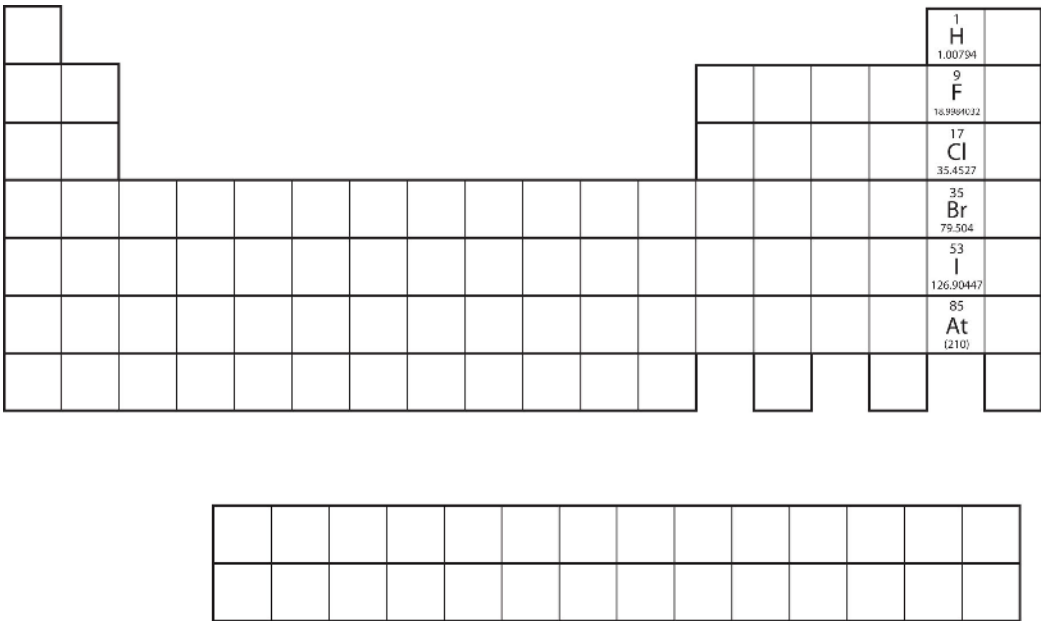


Figure **7.1.1**: Halogens on the Periodic Table. The halogens are the elements in the next-to-last column on the periodic table.

Example 7.1.1

Will a single-replacement reaction occur? If so, identify the products.

a. $MgCl_2 + I_2 \rightarrow ?$
b. $CaBr_2 + F_2 \rightarrow ?$

Solution

a. Because iodine is below chlorine on the periodic table, a single-replacement reaction will not occur.
b. Because fluorine is above bromine on the periodic table, a single-replacement reaction will occur, and the products of the reaction will be CaF_2 and Br_2.

Exercise 7.1.1

Will a single-replacement reaction occur? If so, identify the products.

$$\mathbf{FeI_2 + Cl_2 \longrightarrow}$$

Answer

Yes; $FeCl_2$ and I_2

Chemical reactivity trends are easy to predict when replacing anions in simple ionic compounds—simply use their relative positions on the periodic table. However, when replacing the cations, the trends are not as straightforward. This is partly because there are so many elements that can form cations; an element in one column on the periodic table may replace another element nearby, or it may not. A list called the **activity series** does the same thing the periodic table does for halogens: it lists the elements that will replace elements below them in single-replacement reactions. A simple activity series is shown below.

Activity Series for Cation Replacement in Single-Replacement Reactions

- Li
- K
- Ba
- Sr
- Ca

- Na
- Mg
- Al
- Mn
- Zn
- Cr
- Fe
- Ni
- Sn
- Pb
- H_2
- Cu
- Hg
- Ag
- Pd
- Pt
- Au

Using the activity series is similar to using the positions of the halogens on the periodic table. An element on top will replace an element below it in compounds undergoing a single-replacement reaction. Elements will not replace elements above them in compounds.

Example 7.1.2

Use the activity series to predict the products, if any, of each equation.

1. $FeCl_2 + Zn \rightarrow ?$
2. $HNO_3 + Au \rightarrow ?$

Solution

1. Because zinc is above iron in the activity series, it will replace iron in the compound. The products of this single-replacement reaction are $ZnCl_2$ and Fe.
2. Gold is below hydrogen in the activity series. As such, it will not replace hydrogen in a compound with the nitrate ion. No reaction is predicted.

Exercise 7.1.2

Use the activity series to predict the products, if any, of this equation.

$$\mathrm{AlPO_4 + Mg \longrightarrow}$$

Answer

$Mg_3(PO_4)_2$ and Al

A **double-replacement reaction** occurs when parts of two ionic compounds are exchanged, making two new compounds. A characteristic of a double-replacement equation is that there are two compounds as reactants and two different compounds as products. An example is

$$\mathrm{CuCl_2\,(aq) + 2\,AgNO_3\,(aq) \longrightarrow Cu(NO_3)_2\,(aq) + 2\,AgCl\,(s)}$$

There are two equivalent ways of considering a double-replacement equation: either the cations are swapped, or the anions are swapped. (You cannot swap both; you would end up with the same substances you started with.) Either perspective should allow you to predict the proper products, as long as you pair a cation with an anion, and not a cation with a cation or an anion with an anion.

Example 7.1.3

Predict the products of this double-replacement equation:

$$\mathrm{BaCl_2 + Na_2SO_4 \longrightarrow}$$

Solution

Thinking about the reaction as either switching the cations or switching the anions, we would expect the products to be $BaSO_4$ and NaCl.

Exercise 7.1.3

Predict the products of this double-replacement equation:

$$\mathrm{KBr + AgNO_3 \longrightarrow}$$

Answer

KNO_3 and AgBr

Predicting whether a double-replacement reaction occurs is somewhat more difficult than predicting a single-replacement reaction. However, there is one type of double-replacement reaction that we can predict: the precipitation reaction. A **precipitation reaction** occurs when two ionic compounds are dissolved in water and form a new ionic compound that does not dissolve; this new compound falls out of solution as a solid **precipitate.** The formation of a solid precipitate is the driving force that makes the reaction proceed.

To judge whether double-replacement reactions will occur, we need to know what kinds of ionic compounds form precipitates. For this, we use **solubility rules**, which are general statements that predict which ionic compounds dissolve (are soluble) and which do not (are not soluble, or insoluble). Table **7.1.1** lists some general solubility rules. We need to consider each ionic compound (both the reactants and the possible products) in light of the solubility rules. If a compound is soluble, we use the (aq) label with it, indicating that it dissolves. If a compound is not soluble, we use the (s) label with it and assume that it will precipitate out of solution. If everything is soluble, then no reaction will be expected.

Table **7.1.1**: Some Useful Solubility Rules (soluble)

These compounds generally dissolve in water (are soluble):	Exceptions:
All compounds of Li^+, Na^+, K^+, Rb^+, Cs^+, and NH_4^+	None
All compounds of NO_3^- and $C_2H_3O_2^-$	None
Compounds of Cl^-, Br^-, I^-	Ag^+, Hg_2^{2+}, Pb^{2+}
Compounds of SO_4^{2}	Hg_2^{2+}, Pb^{2+}, Sr^{2+}, Ba^{2+}

Table **7.1.2**: Some Useful Solubility Rules (insoluble)

These compounds generally do not dissolve in water (are insoluble):	Exceptions:
Compounds of CO_3^{2-} and PO_4^{3-}	Compounds of Li^+, Na^+, K^+, Rb^+, Cs^+, and NH_4^+
Compounds of OH^-	Compounds of Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+, Sr^{2+}, and Ba^{2+}

For example, consider the possible double-replacement reaction between Na_2SO_4 and $SrCl_2$. The solubility rules say that all ionic sodium compounds are soluble and all ionic chloride compounds are soluble, except for Ag^+, Hg_2^{2+}, and Pb^{2+}, which are not being considered here. Therefore, Na_2SO_4 and $SrCl_2$ are both soluble. The possible double-replacement reaction products are NaCl and $SrSO_4$. Are these soluble? NaCl is (by the same rule we just quoted), but what about $SrSO_4$? Compounds of the sulfate

ion are generally soluble, but Sr^{2+} is an exception: we expect it to be insoluble—a precipitate. Therefore, we expect a reaction to occur, and the balanced chemical equation would be:

$$Na_2SO_4\,(aq) + SrCl_2\,(aq) \longrightarrow 2\,NaCl\,(aq) + SrSO_4\,(s)$$

You would expect to see a visual change corresponding to $SrSO_4$ precipitating out of solution (Figure 7.1.2).



Figure 7.1.2: Double-Replacement Reactions. Some double-replacement reactions are obvious because you can see a solid precipitate coming out of solution. Source: Photo courtesy of Choij, http://commons.wikimedia.org/wiki/File:Copper_solution.jpg(opens in new window).

Example 7.1.4

Will a double-replacement reaction occur? If so, identify the products.

1. $Ca(NO_3)_2$ + KBr → ?
2. NaOH + $FeCl_2$ → ?

Solution

1. According to the solubility rules, both $Ca(NO_3)_2$ and KBr are soluble. Now we consider what the double-replacement products would be by switching the cations (or the anions)—namely, $CaBr_2$ and KNO_3. However, the solubility rules predict that these two substances would also be soluble, so no precipitate would form. Thus, we predict no reaction in this case.
2. According to the solubility rules, both NaOH and $FeCl_2$ are expected to be soluble. If we assume that a double-replacement reaction may occur, we need to consider the possible products, which would be NaCl and $Fe(OH)_2$. NaCl is soluble, but, according to the solubility rules, $Fe(OH)_2$ is not. Therefore, a reaction would occur, and $Fe(OH)_2$(s) would precipitate out of solution. The balanced chemical equation is

$$2\,NaOH\,(aq) + FeCl_2\,(aq) \longrightarrow 2\,NaCl\,(aq) + Fe(OH)_2\,(s)$$

Exercise 7.1.4

$$Sr(NO_3)_2 + KCl \longrightarrow$$

Answer

No reaction; all possible products are soluble.

Key Takeaways

- A single-replacement reaction replaces one element for another in a compound.
- The periodic table or an activity series can help predict whether single-replacement reactions occur.
- A double-replacement reaction exchanges the cations (or the anions) of two ionic compounds.
- A precipitation reaction is a double-replacement reaction in which one product is a solid precipitate.
- Solubility rules are used to predict whether some double-replacement reactions will occur.

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7.2: Ionic Equations - A Closer Look

Learning Objectives

- Write ionic equations for chemical reactions between ionic compounds.
- Write net ionic equations for chemical reactions between ionic compounds.

For single-replacement and double-replacement reactions, many of the reactions included ionic compounds—compounds between metals and nonmetals, or compounds that contained recognizable polyatomic ions. Now, we take a closer look at reactions that include ionic compounds.

One important aspect about ionic compounds that differs from molecular compounds has to do with dissolution in a liquid, such as water. When molecular compounds, such as sugar, dissolve in water, the individual molecules drift apart from each other. When ionic compounds dissolve, *the ions physically separate from each other*. We can use a chemical equation to represent this process—for example, with NaCl:

$$\mathrm{NaCl\,(s)} \xrightarrow{\mathrm{H_2O}} \mathrm{Na^+\,(aq) + Cl^-\,(aq)}$$

When NaCl dissolves in water, the ions separate and go their own way in solution; the ions are now written with their respective charges, and the (aq) phase label emphasizes that they are dissolved (Figure **7.2.1**). This process is called **dissociation;** we say that the ions *dissociate*.

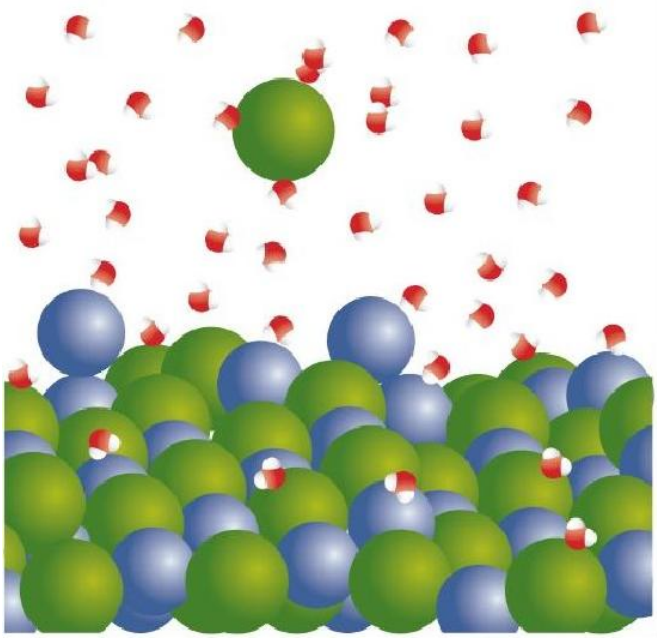


Figure **7.2.1** Ionic Solutions. When an ionic compound dissociates in water, water molecules surround each ion and separate it from the rest of the solid. Each ion goes its own way in solution.

All ionic compounds that dissolve behave this way. This behavior was first suggested by the Swedish chemist Svante August Arrhenius [1859–1927] as part of his PhD dissertation in 1884. Interestingly, his PhD examination team had a hard time believing that ionic compounds would behave like this, so they gave Arrhenius a barely passing grade. Later, this work was cited when Arrhenius was awarded the Nobel Prize in Chemistry. Keep in mind that when the ions separate, *all* the ions separate. Thus, when $CaCl_2$ dissolves, the one Ca^{2+} ion and the two Cl^- ions separate from one another:

$$CaCl_2(s) \overset{H_2O}{\rightarrow} Ca^{2+}(aq) + Cl^-(aq) + Cl^-(aq)$$

$$CaCl_2(s) \overset{H_2O}{\rightarrow} Ca^{2+}(aq) + 2Cl^-(aq)$$

That is, the two chloride ions go off on their own. They do not remain as Cl_2 (that would be elemental chlorine; these are chloride ions), and they do not stick together to make Cl_2^- or Cl_2^{2-}. They become dissociated ions in their own right. Polyatomic ions also retain their overall identity when they are dissolved.

Example 7.2.1

Write the chemical equation that represents the dissociation of each ionic compound.

1. KBr
2. Na_2SO_4

Solution

1. $KBr(s) \rightarrow K^+(aq) + Br^-(aq)$
2. Not only do the two sodium ions go their own way, but the sulfate ion stays together as the sulfate ion. The dissolving equation is $Na_2SO_4(s) \rightarrow 2Na^+(aq) + SO_4^{2-}(aq)$

Exercise 7.2.1

Write the chemical equation that represents the dissociation of $(NH_4)_2S$.

Answer

$(NH_4)_2S(s) \rightarrow 2NH_4^+(aq) + S^{2-}(aq)$

When chemicals in solution react, the proper way of writing the chemical formulas of the dissolved ionic compounds is in terms of the dissociated ions, not the complete ionic formula. A **complete ionic equation** is a chemical equation in which the dissolved ionic compounds are written as separated ions. Solubility rules are very useful in determining which ionic compounds are dissolved and which are not. For example, when NaCl(aq) reacts with $AgNO_3$(aq) in a double-replacement reaction to precipitate AgCl(s) and form $NaNO_3$(aq), the complete ionic equation includes NaCl, $AgNO_3$, and $NaNO_3$ written as separate ions:

$$\mathrm{Na^+(aq) + Cl^-(aq) + Ag^+(aq) + NO_3^-(aq) \longrightarrow AgCl(s) + Na^+(aq) + NO_3^-(aq)}$$

This is more representative of what is occurring in the solution.

Example 7.2.1

Write the complete ionic equation for each chemical reaction.

1. $KBr(aq) + AgC_2H_3O_2(aq) \rightarrow KC_2H_3O_2(aq) + AgBr(s)$
2. $MgSO_4(aq) + Ba(NO_3)_2(aq) \rightarrow Mg(NO_3)_2(aq) + BaSO_4(s)$

Solution

For any ionic compound that is aqueous, we will write the compound as separated ions.

1. The complete ionic equation is $K^+(aq) + Br^-(aq) + Ag^+(aq) + C_2H_3O_2^-(aq) \rightarrow K^+(aq) + C_2H_3O_2^-(aq) + AgBr(s)$
2. The complete ionic equation is $Mg^{2+}(aq) + SO_4^{2-}(aq) + Ba^{2+}(aq) + 2NO_3^-(aq) \rightarrow Mg^{2+}(aq) + 2NO_3^-(aq) + BaSO_4(s)$

Exercise 7.2.1

Write the complete ionic equation for

$$\mathrm{CaCl_2(aq) + Pb(NO_3)_2(aq) \longrightarrow Ca(NO_3)_2(aq) + PbCl_2(s)}$$

Answer

$Ca^{2+}(aq) + 2Cl^-(aq) + Pb^{2+}(aq) + 2NO_3^-(aq) \rightarrow Ca^{2+}(aq) + 2NO_3^-(aq) + PbCl_2(s)$

You may notice that in a complete ionic equation, some ions do not change their chemical form; they stay exactly the same on the reactant and product sides of the equation. For example, in

$Na^+(aq) + Cl^-(aq) + Ag^+(aq) + NO_3^-(aq) \rightarrow AgCl(s) + Na^+(aq) + NO_3^-(aq)$

the $Ag^+(aq)$ and $Cl^-(aq)$ ions become $AgCl(s)$, but the $Na^+(aq)$ ions and the $NO_3^-(aq)$ ions stay as $Na^+(aq)$ ions and $NO_3^-(aq)$ ions. These two ions are examples of spectator ions—ions that do nothing in the overall course of a chemical reaction. They are present, but they do not participate in the overall chemistry. It is common to cancel spectator ions (something also done with algebraic quantities) on the opposite sides of a chemical equation:

$$\cancel{Na^+(aq)} + Cl^-(aq) + Ag^+(aq) + \cancel{NO_3^-(aq)} \rightarrow AgCl(s) + \cancel{Na^+(aq)} + \cancel{NO_3^-(aq)}$$

What remains when the spectator ions are removed is called the **net ionic equation**, which represents the actual chemical change occurring between the ionic compounds:

$Cl^-(aq) + Ag^+(aq) \rightarrow AgCl(s)$

It is important to reiterate that the spectator ions are still present in solution, but they do not experience any net chemical change, so they are not written in a net ionic equation.

Example 7.2.1

Write the net ionic equation for each chemical reaction.

1. $K^+(aq) + Br^-(aq) + Ag^+(aq) + C_2H_3O_2^-(aq) \rightarrow K^+(aq) + C_2H_3O_2^-(aq) + AgBr(s)$
2. $Mg^{2+}(aq) + SO_4^{2-}(aq) + Ba^{2+}(aq) + 2NO_3^-(aq) \rightarrow Mg^{2+}(aq) + 2NO_3^-(aq) + BaSO_4(s)$

Solution

1. In the first equation, the $K^+(aq)$ and $C_2H_3O_2^-(aq)$ ions are spectator ions, so they are canceled:

$$\cancel{K^+(aq)} + Br^-(aq) + Ag^+(aq) + \cancel{C_2H_3O_2^-(aq)} \rightarrow K^+(aq) + \cancel{C_2H_3O_2^-(aq)} + AgBr(s)$$

The net ionic equation is

$$Br^-(aq) + Ag^+(aq) \rightarrow AgBr(s)$$

2. In the second equation, the $Mg^{2+}(aq)$ and $NO_3^-(aq)$ ions are spectator ions, so they are canceled:

$$\cancel{Mg^{2+}(aq)} + SO_4^{2-}(aq) + Ba^{2+}(aq) + \cancel{2NO_3^-(aq)} \rightarrow Mg^{2+}(aq) + \cancel{2NO_3^-(aq)} + BaSo_4(s)$$

The net ionic equation is

$SO_4^{2-}(aq) + Ba^{2+}(aq) \rightarrow BaSO_4(s)$

Exercise 7.2.1

Write the net ionic equation for

$CaCl_2(aq) + Pb(NO_3)_2(aq) \rightarrow Ca(NO_3)_2(aq) + PbCl_2(s)$

Answer

$Pb^{2+}(aq) + 2Cl^-(aq) \rightarrow PbCl_2(s)$

Chemistry is Everywhere: Soluble and Insoluble Ionic Compounds

The concept of solubility versus insolubility in ionic compounds is a matter of degree. Some ionic compounds are very soluble, some are only moderately soluble, and some are soluble so little that they are considered insoluble. For most ionic compounds, there is also a limit to the amount of compound that can be dissolved in a sample of water. For example, you can dissolve a

maximum of 36.0 g of NaCl in 100 g of water at room temperature, but you can dissolve only 0.00019 g of AgCl in 100 g of water. We consider **NaCl** soluble but **AgCl** insoluble.

One place where solubility is important is in the tank-type water heater found in many homes in the United States. Domestic water frequently contains small amounts of dissolved ionic compounds, including calcium carbonate ($CaCO_3$). However, $CaCO_3$ has the relatively unusual property of being less soluble in hot water than in cold water. So as the water heater operates by heating water, $CaCO_3$ can precipitate if there is enough of it in the water. This precipitate, called *limescale*, can also contain magnesium compounds, hydrogen carbonate compounds, and phosphate compounds. The problem is that too much limescale can impede the function of a water heater, requiring more energy to heat water to a specific temperature or even blocking water pipes into or out of the water heater, causing dysfunction.



Figure **7.2.2** Tank water heater © Thinkstock. Most homes in the United States have a tank-type water heater like this one.

Another place where solubility versus insolubility is an issue is the Grand Canyon. We usually think of rock as insoluble. But it is actually ever so slightly soluble. This means that over a period of about two billion years, the Colorado River carved rock from the surface by slowly dissolving it, eventually generating a spectacular series of gorges and canyons. And all because of solubility!



Figure **7.2.3**: The Grand Canyon was formed by water running through rock for billions of years, very slowly dissolving it. Note the Colorado River is still present in the lower part of the photo. (Sonaal Bangera via unsplash)

Key Takeaways

- Ionic compounds that dissolve separate into individual ions.
- Complete ionic equations show dissolved ionic solids as separated ions.
- Net ionic equations show only the ions and other substances that change in a chemical reaction.

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7.3: Neutralization Reactions

Learning Objectives

- Identify an acid and a base.
- Identify a neutralization reaction and predict its products.

In Chapter 3, we defined an acid as an ionic compound that contains H^+ as the cation. This is slightly incorrect, but until additional concepts were developed, a better definition needed to wait. Now we can redefine an acid: an **acid** is any compound that increases the amount of hydrogen ion (H^+) in an aqueous solution. The chemical opposite of an acid is a base. The equivalent definition of a base is that a **base** is a compound that increases the amount of hydroxide ion (OH^-) in an aqueous solution. These original definitions were proposed by Arrhenius (the same person who proposed ion dissociation) in 1884, so they are referred to as the **Arrhenius definition** of an acid and a base, respectively.

You may recognize that, based on the description of a hydrogen atom, an H^+ ion is a hydrogen atom that has lost its lone electron; that is, H^+ is simply a proton. Do we really have bare protons moving about in aqueous solution? No. What is more likely is that the H^+ ion has attached itself to one (or more) water molecule(s). To represent this chemically, we define the **hydronium ion** as H_3O^+, which represents an additional proton attached to a water molecule. We use the hydronium ion as the more logical way that a hydrogen ion appears in an aqueous solution, although in many chemical reactions H^+ and H_3O^+ are treated equivalently.

The reaction of an acid and a base is called a **neutralization reaction**. Although acids and bases have their own unique chemistries, the acid and base cancel each other's chemistry to produce a rather innocuous substance—water. In fact, the general reaction between an acid and a base is:

$$\text{acid} + \text{base} \longrightarrow \text{water} + \text{salt}$$

where the term **salt** is generally used to define any ionic compound (soluble or insoluble) that is formed from a reaction between an acid and a base. (In chemistry, the word *salt* refers to more than just table salt.) For example, the balanced chemical equation for the reaction between HCl(aq) and KOH(aq) is

$$\mathrm{HCl\,(aq) + KOH\,(aq) \longrightarrow H_2O(\ell) + KCl\,(aq)}$$

where the salt is KCl. By counting the number of atoms of each element, we find that only one water molecule is formed as a product. However, in the reaction between HCl(aq) and $Mg(OH)_2$(aq), additional molecules of HCl and H_2O are required to balance the chemical equation:

$$\mathrm{2\,HCl\,(aq) + Mg(OH)_2\,(aq) \longrightarrow 2\,H_2O(\ell) + MgCl_2\,(aq)}$$

Here, the salt is $MgCl_2$. (This is one of several reactions that take place when a type of antacid—a base—is used to treat stomach acid.)

Example 7.3.1

Write the neutralization reactions between each acid and base.

a. HNO_3(aq) and $Ba(OH)_2$(aq)
b. H_3PO_4(aq) and $Ca(OH)_2$(aq)

Solution

First, we will write the chemical equation with the formulas of the reactants and the expected products; then we will balance the equation.

a. The expected products are water and barium nitrate, so the initial chemical reaction is

$$\mathrm{HNO_3\,(aq) + Ba(OH)_2\,(aq) \longrightarrow H_2O(\ell) + Ba(NO_3)_2\,(aq)}$$

To balance the equation, we need to realize that there will be two H_2O molecules, so two HNO_3 molecules are required:

$$2\,HNO_3\,(aq) + Ba(OH)_2\,(aq) \longrightarrow 2\,H_2O(\ell) + Ba(NO_3)_2\,(aq)$$

This chemical equation is now balanced.

b. The expected products are water and calcium phosphate, so the initial chemical equation is

$$H_3PO_4\,(aq) + Ca(OH)_2\,(aq) \longrightarrow H_2O(\ell) + Ca_3(PO_4)_2\,(s)$$

According to the solubility rules, $Ca_3(PO_4)_2$ is insoluble, so it has an (s) phase label. To balance this equation, we need two phosphate ions and three calcium ions. We end up with six water molecules to balance the equation:

$$2\,H_3PO_4\,(aq) + 3\,Ca(OH)_2\,(aq) \longrightarrow 6\,H_2O(\ell) + Ca_3(PO_4)_2\,(s)$$

This chemical equation is now balanced.

? Exercise 7.3.1

Write the neutralization reaction between H_2SO_4(aq) and $Sr(OH)_2$(aq).

Answer

$$H_2SO_4\,(aq) + Sr(OH)_2\,(aq) \longrightarrow 2\,H_2O(\ell) + SrSO_4\,(aq)$$

Neutralization reactions are one type of chemical reaction that proceeds even if one reactant is not in the aqueous phase. For example, the chemical reaction between HCl(aq) and $Fe(OH)_3$(s) still proceeds according to the equation:

$$3\,HCl\,(aq) + Fe(OH)_3\,(s) \longrightarrow 3\,H_2O(\ell) + FeCl_3\,(aq)$$

even though $Fe(OH)_3$ is not soluble. When one realizes that $Fe(OH)_3$(s) is a component of rust, this explains why some cleaning solutions for rust stains contain acids—the neutralization reaction produces products that are soluble and wash away. (Washing with acids like HCl is one way to remove rust and rust stains, but HCl must be used with caution!)

Complete and net ionic reactions for neutralization reactions will depend on whether the reactants and products are soluble, even if the acid and base react. For example, in the reaction of HCl(aq) and NaOH(aq),

$$HCl\,(aq) + NaOH\,(aq) \longrightarrow H_2O(\ell) + NaCl\,(aq)$$

the complete ionic reaction is

$$H^+\,(aq) + Cl^-\,(aq) + Na^+\,(aq) + OH^-\,(aq) \longrightarrow H_2O(\ell) + Na^+\,(aq) + Cl^-\,(aq)$$

The Na^+(aq) and Cl^-(aq) ions are spectator ions, so we can remove them to have

$$H^+\,(aq) + OH^-\,(aq) \longrightarrow H_2O(\ell)$$

as the net ionic equation. If we wanted to write this in terms of the hydronium ion, H_3O^+(aq), we would write it as

$$H_3O^+\,(aq) + OH^-\,(aq) \longrightarrow 2\,H_2O(\ell)$$

With the exception of the introduction of an extra water molecule, these two net ionic equations are equivalent.

However, for the reaction between HCl(aq) and $Cr(OH)_2$(s), because chromium(II) hydroxide is insoluble, we cannot separate it into ions for the complete ionic equation:

$$2\,H^+\,(aq) + 2\,Cl^-\,(aq) + Cr(OH)_2\,(s) \longrightarrow 2\,H_2O(\ell) + Cr^{2+}\,(aq) + 2\,Cl^-\,(aq)$$

The chloride ions are the only spectator ions here, so the net ionic equation is

$$2\,H^+\,(aq) + Cr(OH)_2\,(s) \longrightarrow 2\,H_2O(\ell) + Cr^{2+}\,(aq)$$

✔ Example 7.3.2

Oxalic acid, $H_2C_2O_4$(s), and $Ca(OH)_2$(s) react very slowly. What is the net ionic equation between these two substances if the salt formed is insoluble? (The anion in oxalic acid is the oxalate ion, $C_2O_4^{2-}$.)

Solution

The products of the neutralization reaction will be water and calcium oxalate:

$H_2C_2O_4(s) + Ca(OH)_2(s) \rightarrow 2H_2O(\ell) + CaC_2O_4(s)$

Because nothing is dissolved, there are no substances to separate into ions, so the net ionic equation is the equation of the three solids and one liquid.

? Exercise 7.3.2

What is the net ionic equation between $HNO_3(aq)$ and $Ti(OH)_4(s)$?

Answer

$4H^+(aq) + Ti(OH)_4(s) \rightarrow 4H_2O(\ell) + Ti^{4+}(aq)$

Key Takeaways

- The Arrhenius definition of an acid is a substance that increases the amount of H^+ in an aqueous solution.
- The Arrhenius definition of a base is a substance that increases the amount of OH^- in an aqueous solution.
- Neutralization is the reaction of an acid and a base, which forms water and a salt.
- Net ionic equations for neutralization reactions may include solid acids, solid bases, solid salts, and water.

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7.4: Single Displacement Reactions

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7.5: Composition, Decomposition, and Combustion Reactions

Learning Objectives

- Recognize composition, decomposition, and combustion reactions.
- Predict the products of a combustion reaction.

Three classifications of chemical reactions will be reviewed in this section. Predicting the products in some of them may be difficult, but the reactions are still easy to recognize.

A **composition reaction** (sometimes also called a *combination reaction* or a *synthesis reaction*) produces a single substance from multiple reactants. A single substance as a product is the key characteristic of the composition reaction. There may be a coefficient other than one for the substance, but if the reaction has only a single substance as a product, it can be called a composition reaction. In the reaction

$$2\,H_2\,(g) + O_2\,(g) \longrightarrow 2\,H_2O(\ell)$$

water is produced from hydrogen and oxygen. Although there are two molecules of water being produced, there is only one substance—water—as a product. So this is a composition reaction.

A **decomposition reaction** starts from a single substance and produces more than one substance; that is, it decomposes. The key characteristics of a decomposition reaction are: one substance as a reactant and more than one substance as the products. For example, in the decomposition of sodium hydrogen carbonate (also known as sodium bicarbonate):

$$2\,NaHCO_3\,(s) \longrightarrow Na_2CO_3\,(s) + CO_2\,(g) + H_2O(\ell)$$

sodium carbonate, carbon dioxide, and water are produced from the single substance sodium hydrogen carbonate.

Composition and decomposition reactions are difficult to predict; however, they should be easy to recognize.

Example 7.5.1: Identifying Reactions

Identify each equation as a composition reaction, a decomposition reaction, or neither.

a. $Fe_2O_3 + 3\,SO_3 \longrightarrow Fe_2(SO_4)_3$
b. $NaCl + AgNO_3 \longrightarrow AgCl + NaNO_3$
c. $(NH_4)_2Cr_2O_7 \longrightarrow Cr_2O_3 + 4\,H_2O + N_2$

Solution

a. In this equation, two substances combine to make a single substance. This is a composition reaction.
b. Two different substances react to make two new substances. This does not fit the definition of either a composition reaction or a decomposition reaction, so it is neither. In fact, you may recognize this as a double-replacement reaction.
c. A single substance reacts to make multiple substances. This is a decomposition reaction.

Exercise 7.5.1

Identify the equation as a composition reaction, a decomposition reaction, or neither.

$$C_3H_8 \longrightarrow C_3H_4 + 2\,H_2$$

Answer

decomposition

A **combustion reaction** occurs when a reactant combines with oxygen, many times from the atmosphere, to produce oxides of all other elements as products; any nitrogen in the reactant is converted to elemental nitrogen, N_2. Many reactants, called *fuels*,

contain mostly carbon and hydrogen atoms, reacting with oxygen to produce CO_2 and H_2O. For example, the balanced chemical equation for the combustion of methane, CH_4, is as follows:

$$\mathrm{CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O}$$

Kerosene can be approximated with the formula $\mathrm{C_{12}H_{26}}$, and its combustion equation is:

$$\mathrm{2\,C_{12}H_{26} + 37\,O_2 \longrightarrow 24\,CO\text{-}2 + 26\,H_2O}$$

Sometimes fuels contain oxygen atoms, which must be counted when balancing the chemical equation. One common fuel is ethanol, $\mathrm{C_2H_5OH}$, whose combustion equation is:

$$\mathrm{C_2H_5OH + 3\,O_2 \longrightarrow 2\,CO_2 + 3\,H_2O}$$

If nitrogen is present in the original fuel, it is converted to $\mathrm{N_2}$, not to a nitrogen-oxygen compound. Thus, for the combustion of the fuel dinitroethylene, whose formula is $\mathrm{C_2H_2N_2O_4}$, we have:

$$\mathrm{2\,C_2H_2N_2O_4 + O_2 \longrightarrow 4\,CO_2 + 2\,H_2O + 2\,N_2}$$

Example 7.5.2: Combustion Reactions

Complete and balance each combustion equation.

1. the combustion of propane ($\mathrm{C_3H_8}$)
2. the combustion of ammonia ($\mathrm{NH_3}$)

Solution

1. The products of the reaction are CO_2 and H_2O, so our unbalanced equation is

   $$\mathrm{C_3H_8 + O_2 \longrightarrow CO_2 + H_2O}$$

   Balancing (and you may have to go back and forth a few times to balance this), we get

   $$\mathrm{C_3H_8 + 5\,O_2 \longrightarrow 3\,CO_2 + 4\,H_2O}$$

2. The nitrogen atoms in ammonia will react to make N_2, while the hydrogen atoms will react with O_2 to make H_2O:

   $$\mathrm{NH_3 + O_2 \longrightarrow N_2 + H_2O}$$

   To balance this equation without fractions (which is the convention), we get

   $$\mathrm{4\,NH_3 + 3\,O_2 \longrightarrow 2\,N_2 + 6\,H_2O}$$

Exercise 7.5.2

Complete and balance the combustion equation for cyclopropanol (\ce{C3H6O}\)).

Answer

$$\mathrm{C_3H_6O + 4\,O_2 \longrightarrow 3\,CO_2 + 3\,H_2O}$$



Figure **7.5.1** A 20 lb (9.1 kg) steel propane cylinder.

Key Takeaways

- A composition reaction produces a single substance from multiple reactants.
- A decomposition reaction produces multiple products from a single reactant.
- Combustion reactions are the combination of some compound with oxygen to make oxides of the other elements as products (although nitrogen atoms react to make N_2).

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CHAPTER OVERVIEW

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9.1: The Mole in Chemical Reactions

Learning Objectives

- Balance a chemical equation in terms of moles.
- Use the balanced equation to construct conversion factors in terms of moles.
- Calculate moles of one substance from moles of another substance using a balanced chemical equation.

Consider this balanced chemical equation:

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$

We interpret this as "two molecules of hydrogen react with one molecule of oxygen to make two molecules of water." The chemical equation is balanced as long as the coefficients are in the ratio 2:1:2. For instance, this chemical equation is also balanced:

$$100\,H_2 + 50\,O_2 \longrightarrow 100\,H_2O$$

This equation is not conventional—because convention says that we use the lowest ratio of coefficients—but it is balanced. So is this chemical equation:

$$5{,}000\,H_2 + 2{,}500\,O_2 \longrightarrow 5{,}000\,H_2O$$

Again, this is not conventional, but it is still balanced. Suppose we use a much larger number:

$$12.044 \times 10^{23} H_2 + 6.022 \times 10^{23} O_2 \rightarrow 12.044 \times 10^{23} H_2O$$

These coefficients are also in the ratio of 2:1:2. But these numbers are related to the number of things in a mole: the first and last numbers are two times Avogadro's number, while the second number is Avogadro's number. That means that the first and last numbers represent 2 mol, while the middle number is just 1 mol. Well, why not just use the number of moles in balancing the chemical equation?

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$

is the same balanced chemical equation we started with! What this means is that chemical equations are not just balanced in terms of molecules; *they are also balanced in terms of moles*. We can just as easily read this chemical equation as "two moles of hydrogen react with one mole of oxygen to make two moles of water." All balanced chemical reactions are balanced in terms of moles.

Example 9.1.1

Interpret this balanced chemical equation in terms of moles.

$$P_4 + 5\,O_2 \longrightarrow P_4O_{10}$$

Solution

The coefficients represent the number of moles that react, not just molecules. We would speak of this equation as "one mole of molecular phosphorus reacts with five moles of elemental oxygen to make one mole of tetraphosphorus decoxide."

Exercise 9.1.1

Interpret this balanced chemical equation in terms of moles.

$$N_2 + 3\,H_2 \longrightarrow 2\,NH_3$$

Answer

One mole of elemental nitrogen reacts with three moles of elemental hydrogen to produce two moles of ammonia.

In Section 4.1, we stated that a chemical equation is simply a recipe for a chemical reaction. As such, chemical equations also give us equivalents—equivalents between the reactants and the products. However, now we understand that *these equivalents are expressed in terms of moles*. Consider the chemical equation

$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$

This chemical reaction gives us the following equivalents:

$$2 \text{ mol } H_2 \Leftrightarrow 1 \text{ mol } O_2 \Leftrightarrow 2 \text{ mol } H_2O$$

Any two of these quantities can be used to construct a conversion factor that lets us relate the number of moles of one substance to an equivalent number of moles of another substance. If, for example, we want to know how many moles of oxygen will react with 17.6 mol of hydrogen, we construct a conversion factor between 2 mol of H_2 and 1 mol of O_2 and use it to convert from moles of one substance to moles of another:

$$17.6\,\cancel{mol\,H_2} \times \frac{1\,mol\,O_2}{2\,\cancel{mol\,H_2}} = 8.80\,mol\,O_2$$

Note how the mol H_2 unit cancels, and mol O_2 is the new unit introduced. This is an example of a **mole-mole calculation,** when you start with moles of one substance and convert to moles of another substance by using the balanced chemical equation. The example may seem simple because the numbers are small, but numbers won't always be so simple!

Example 9.1.2

For the balanced chemical equation

$$2\,C_4H_{10}\,(g) + 13\,O_2 \longrightarrow 8\,CO_2\,(g) + 10\,H_2O(\ell)$$

if 154 mol of O_2 are reacted, how many moles of CO_2 are produced?

Solution

We are relating an amount of oxygen to an amount of carbon dioxide, so we need the equivalence between these two substances. According to the balanced chemical equation, the equivalence is

$$13 \text{ mol } O_2 \Leftrightarrow 8 \text{ mol } CO_2$$

We can use this equivalence to construct the proper conversion factor. We start with what we are given and apply the conversion factor:

$$154\,\cancel{mol\,O_2} \times \frac{8\,mol\,CO_2}{13\,\cancel{mol\,O_2}} = 94.8\,mol\,CO_2$$

The mol O_2 unit is in the denominator of the conversion factor so it cancels. Both the 8 and the 13 are exact numbers, so they do not contribute to the number of significant figures in the final answer.

Exercise 9.1.2

Using the above equation, how many moles of H_2O are produced when 154 mol of O_2 react?

Answer

118 mol

It is important to reiterate that balanced chemical equations are balanced in terms of *moles*. Not grams, kilograms, or liters—but moles. Any stoichiometry problem will likely need to work through the mole unit at some point, especially if you are working with a balanced chemical reaction.

Summary

Balanced chemical reactions are balanced in terms of moles. A balanced chemical reaction gives equivalents in moles that allow stoichiometry calculations to be performed.

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9.2: Mole-Mass and Mass-Mass Calculations

Learning Objectives

- From a given number of moles of a substance, calculate the mass of another substance involved using the balanced chemical equation.
- From a given mass of a substance, calculate the moles of another substance involved using the balanced chemical equation.
- From a given mass of a substance, calculate the mass of another substance involved using the balanced chemical equation.

Mole-mole calculations are not the only type of calculations that can be performed using balanced chemical equations. Recall that the molar mass can be determined from a chemical formula and used as a conversion factor. We can add that conversion factor as another step in a calculation to make a **mole-mass calculation**, where we start with a given number of moles of a substance and calculate the mass of another substance involved in the chemical equation, or vice versa.

For example, suppose we have the balanced chemical equation

$$2Al + 3Cl_2 \rightarrow 2AlCl_3$$

Suppose we know we have 123.2 g of Cl_2. How can we determine how many moles of $AlCl_3$ we will get when the reaction is complete? First and foremost, *chemical equations are not balanced in terms of grams; they are balanced in terms of moles*. So to use the balanced chemical equation to relate an amount of Cl_2 to an amount of $AlCl_3$, we need to convert the given amount of Cl_2 into moles. We know how to do this by simply using the molar mass of Cl_2 as a conversion factor. The molar mass of Cl_2 (which we get from the atomic mass of Cl from the periodic table) is 70.90 g/mol. We must invert this fraction so that the units cancel properly:

$$123.2\ \cancel{g\,Cl_2} \times \frac{1\,mol\,Cl_2}{70.90\ \cancel{g\,Cl_2}} = 1.738\ mol\,Cl_2$$

Now that we have the quantity in moles, we can use the balanced chemical equation to construct a conversion factor that relates the number of moles of Cl_2 to the number of moles of $AlCl_3$. The numbers in the conversion factor come from the coefficients in the balanced chemical equation:

$$\frac{2\,mol\,AlCl_3}{3\,mol\,Cl_2}$$

Using this conversion factor with the molar quantity we calculated above, we get

$$1.738\ \cancel{mol\,Cl_2} \times \frac{2\,mol\,AlCl_3}{3\ \cancel{mol\,Cl_2}} = 1.159\,mol\,AlCl_3$$

So, we will get 1.159 mol of $AlCl_3$ if we react 123.2 g of Cl_2.

In this last example, we did the calculation in two steps. However, it is mathematically equivalent to perform the two calculations sequentially on one line:

$$123.2\ \cancel{g\,Cl_2} \times \frac{1\,mol\,Cl_2}{70.90\ \cancel{g\,Cl_2}} \times \frac{2\,mol\,AlCl_3}{3\ \cancel{mol\,Cl_2}} = 1.159\,mol\,AlCl_3$$

The units still cancel appropriately, and we get the same numerical answer in the end. Sometimes the answer may be slightly different from doing it one step at a time because of rounding of the intermediate answers, but the final answers should be effectively the same.

Example 9.2.1

How many moles of HCl will be produced when 249 g of $AlCl_3$ are reacted according to this chemical equation?

$$2AlCl_3 + 3H_2O(\ell) \rightarrow Al_2O_3 + 6HCl(g)$$

Solution

We will do this in two steps: convert the mass of $AlCl_3$ to moles and then use the balanced chemical equation to find the number of moles of HCl formed. The molar mass of $AlCl_3$ is 133.33 g/mol, which we have to invert to get the appropriate conversion factor:

$$249\ \cancel{g\ AlCl_3} \times \frac{1\ mol\ AlCl_3}{133.33\ \cancel{g\ AlCl_3}} = 1.87\ mol\ AlCl_3$$

Now we can use this quantity to determine the number of moles of HCl that will form. From the balanced chemical equation, we construct a conversion factor between the number of moles of $AlCl_3$ and the number of moles of HCl:

$$frac6\ mol\ HCl2\ \cancel{mol\ AlCl_3}$$

Applying this conversion factor to the quantity of $AlCl_3$, we get

$$1.87\ \cancel{mol\ AlCl_3} \times \frac{6\ mol\ HCl}{2\ \cancel{mol\ AlCl_3}} = 5.61\ mol\ HCl$$

Alternatively, we could have done this in one line:

$$249\ \cancel{g\ AlCl_3} \times \frac{1\ \cancel{mol\ AlCl_3}}{133.33\ \cancel{g\ AlCl_3}} \times \frac{6\ mol\ HCl}{2\ \cancel{mol\ AlCl_3}} = 5.60\ mol\ HCl$$

The last digit in our final answer is slightly different because of rounding differences, but the answer is essentially the same.

Exercise 9.2.1

How many moles of Al_2O_3 will be produced when 23.9 g of H_2O are reacted according to this chemical equation?

$$2AlCl_3 + 3H_2O(\ell) \rightarrow Al_2O_3 + 6HCl(g)$$

Answer

0.442 mol

A variation of the mole-mass calculation is to start with an amount in moles and then determine an amount of another substance in grams. The steps are the same but are performed in reverse order.

Example 9.2.2

How many grams of NH_3 will be produced when 33.9 mol of H_2 are reacted according to this chemical equation?

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

Solution

The conversions are the same, but they are applied in a different order. Start by using the balanced chemical equation to convert to moles of another substance and then use its molar mass to determine the mass of the final substance. In two steps, we have

$$33.9\ \cancel{mol\ H_2} \times \frac{2\ mol\ NH_3}{3\ \cancel{mol\ H_2}} = 22.6\ mol\ NH_3$$

Now, using the molar mass of NH_3, which is 17.03 g/mol, we get

$$22.6\ \cancel{mol\ NH_3} \times \frac{17.03\ g\ NH_3}{1\ \cancel{mol\ NH_3}} = 385\ g\ NH_3$$

? Exercise 9.2.2

How many grams of N_2 are needed to produce 2.17 mol of NH_3 when reacted according to this chemical equation?

$$\mathrm{N_2\,(g) + 3\,H_2\,(g) \longrightarrow 2\,NH_3\,(g)}$$

Answer

30.4 g (Note: here we go from a product to a reactant, showing that mole-mass problems can begin and end with any substance in the chemical equation.)

It should be a trivial task now to extend the calculations to **mass-mass calculations**, in which we start with a mass of some substance and end with the mass of another substance in the chemical reaction. For this type of calculation, the molar masses of two different substances must be used—be sure to keep track of which is which. Again, however, it is important to emphasize that before the balanced chemical reaction is used, the mass quantity must first be converted to moles. Then the coefficients of the balanced chemical reaction can be used to convert to moles of another substance, which can then be converted to a mass.

For example, let us determine the number of grams of SO_3 that can be produced by the reaction of 45.3 g of SO_2 and O_2:

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$$

First, we convert the given amount, 45.3 g of SO_2, to moles of SO_2 using its molar mass (64.06 g/mol):

$$45.3\ g\,SO_2 \times \frac{1\ mol\ SO_2}{64.06\ g\,SO_2} = 0.707\ mol\ SO_2$$

Second, we use the balanced chemical reaction to convert from moles of SO_2 to moles of SO_3:

$$0.707\ mol\,SO_2 \times \frac{2\ mol\ SO_3}{2\ mol\,SO_2} = 0.707\ mol\ SO_3$$

Finally, we use the molar mass of SO_3 (80.06 g/mol) to convert to the mass of SO_3:

$$0.707\ mol\,SO_3 \times \frac{80.06\ g\ SO_3}{1\ mol\,SO_3} = 56.6\ g\ SO_3$$

We can also perform all three steps sequentially, writing them on one line as

$$45.3\ g\,SO_2 \times \frac{1\ mol\ SO_2}{64.06\ g\,SO_2} \times \frac{2\ mol\ SO_3}{2\ mol\,SO_2} \times \frac{80.06\ g\ SO_3}{1\ mol\,SO_3} = 56.6\ g\ SO_3$$

We get the same answer. Note how the initial and all the intermediate units cancel, leaving grams of SO_3, which is what we are looking for, as our final answer.

✓ Example 9.2.3

What mass of Mg will be produced when 86.4 g of K are reacted?

$$\mathrm{MgCl_2\,(s) + 2\,K\,(s) \longrightarrow Mg\,(s) + 2\,KCl\,(s)}$$

Solution

We will simply follow the steps

mass K → mol K → mol Mg → mass Mg

In addition to the balanced chemical equation, we need the molar masses of K (39.09 g/mol) and Mg (24.31 g/mol). In one line,

$$86.4\ g\,K \times \frac{1\ mol\ K}{39.09\ g\,K} \times \frac{1\ mol\,Mg}{2\ mol\,K} \times \frac{24.31\ g\ Mg}{1\ mol\,Mg} = 26.87\ g\ Mg$$

? Exercise 9.2.3

What mass of H_2 will be produced when 122 g of Zn are reacted?

$$\mathrm{Zn\,(s) + 2\,HCl\,(aq) \longrightarrow ZnCl_2\,(aq) + H_2\,(g)}$$

Answer

3.77 g

Summary

- Mole quantities of one substance can be related to mass quantities using a balanced chemical equation.
- Mass quantities of one substance can be related to mass quantities using a balanced chemical equation.
- In all cases, quantities of a substance must be converted to moles before the balanced chemical equation can be used to convert to moles of another substance.

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9.3: Mass to Mass Calculations

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9.4: Limiting Reagents

Learning Objectives

- Identify a limiting reagent from a set of reactants.
- Calculate how much product will be produced from the limiting reagent.
- Calculate how much reactant(s) remains when the reaction is complete.

In addition to the assumption that reactions proceed all the way to completion, one additional assumption we have made about chemical reactions is that all the reactants are present in the proper quantities to react to products; this is not always the case. In Figure **9.4.2** we are taking hydrogen atoms and oxygen atoms (left) to make water molecules (right). However, there are not enough oxygen atoms to use up all the hydrogen atoms. We run out of oxygen atoms and cannot make any more water molecules, so the process stops when we run out of oxygen atoms.

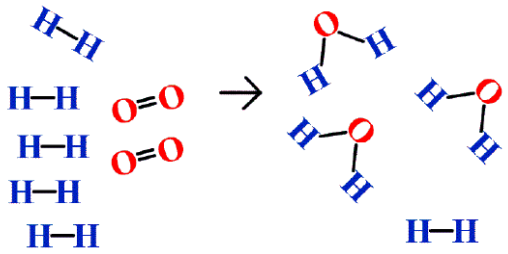


Figure **9.4.2**: Making Water. In this scenario for making water molecules, we run out of O atoms before we use up all the H atoms. Similar situations exist for many chemical reactions when one reactant runs out before the other.

A similar situation exists for many chemical reactions: you usually run out of one reactant before all of the other reactant has reacted. The reactant you run out of is called the limiting reagent; the other reactant or reactants are considered to be *in excess*. A crucial skill in evaluating the conditions of a chemical process is to determine which reactant is the limiting reagent and which is in excess.

The key to recognizing which reactant is the limiting reagent is based on a mole-mass or mass-mass calculation: whichever reactant gives the *lesser* amount of product is the limiting reagent. What we need to do is determine an amount of one product (either moles or mass), assuming all of each reactant reacts. Whichever reactant gives the least amount of that particular product is the limiting reagent. It does not matter which product we use, as long as we use the same one each time. It does not matter whether we determine the number of moles or grams of that product; however, we will see shortly that knowing the final mass of product can be useful.

For example, consider this reaction:

$$4As(s) + 3O_2(g) \rightarrow 2As_2O_3(s)$$

Suppose we start a reaction with 50.0 g of As and 50.0 g of O_2. Which one is the limiting reagent? We need to perform two mole-mass calculations, each assuming that each reactant reacts completely. Then we compare the amount of the product produced by each and determine which is less.

The calculations are as follows:

$$50.0\ \cancel{g\,As} \times \frac{1\ \cancel{mol\,As}}{74.92\ \cancel{g\,As}} \times \frac{2\,mol\,As_2O_3}{4\ \cancel{mol\,As}} = 0.334\,mol\,As_2O_3$$

$$50.0\ \cancel{g\,O_2} \times \frac{1\ \cancel{mol\,O_2}}{32.00\ \cancel{g\,O_2}} \times \frac{2\,mol\,As_2O_3}{3\ \cancel{mol\,O_2}} = 1.04\,mol\,As_2O_3$$

Comparing these two answers, it is clear that 0.334 mol of As_2O_3 is less than 1.04 mol of As_2O_3, so arsenic is the limiting reagent. If this reaction is performed under these initial conditions, the arsenic will run out before the oxygen runs out. We say that the oxygen is "in excess."

Identifying the limiting reagent, then, is straightforward. However, there are usually two associated questions: (1) what mass of product (or products) is then actually formed? and (2) what mass of what reactant is left over? The first question is straightforward to answer: simply perform a conversion from the number of moles of product formed to its mass, using its molar mass. For As_2O_3, the molar mass is 197.84 g/mol; knowing that we will form 0.334 mol of As_2O_3 under the given conditions, we will get

$$0.334\ \cancel{mol\ As_2O_3} \times \frac{197.84\ g\ As_2}{1\ \cancel{mol\ As_2O_3}} = 66.1\ g\ As_2O_3$$

The second question is somewhat more convoluted to answer. First, we must do a mass-mass calculation relating the limiting reagent (here, As) to the other reagent (O_2). Once we determine the mass of O_2 that reacted, we subtract that from the original amount to determine the amount left over. According to the mass-mass calculation,

$$50.0\ \cancel{g\ As} \times \frac{1\ \cancel{mol\ As}}{74.92\ \cancel{g\ As}} \times \frac{3\ \cancel{mol\ O_2}}{4\ \cancel{mol\ As}} \times \frac{32.00\ g\ O_2}{1\ \cancel{mol\ O_2}} = 16.0\ g\ O_2\ reacted$$

Because we reacted 16.0 g of our original O_2, we subtract that from the original amount, 50.0 g, to get the mass of O_2 remaining:

50.0 g O_2 − 16.0 g O_2 reacted = 34.0 g O_2 left over

You must remember to perform this final subtraction to determine the amount remaining; a common error is to report the 16.0 g as the amount remaining.

Example 9.4.1

A 5.00 g quantity of Rb is combined with 3.44 g of $MgCl_2$ according to this chemical reaction:

$$2Rb(s) + MgCl_2(s) \rightarrow Mg(s) + 2RbCl(s)$$

What mass of Mg is formed, and what mass of what reactant is left over?

Solution

Because the question asks what mass of magnesium is formed, we can perform two mass-mass calculations and determine which amount is less.

$$5.00\ \cancel{g\ Rb} \times \frac{1\ \cancel{mol\ Rb}}{85.47\ \cancel{g\ Rb}} \times \frac{1\ \cancel{mol\ Mg}}{2\ \cancel{mol\ Rb}} \times \frac{24.31\ g\ Mg}{1\ \cancel{mol\ Mg}} = 0.711\ g\ Mg$$

$$3.44\ \cancel{g\ MgCl_2} \times \frac{1\ \cancel{mol\ MgCl_2}}{95.21\ \cancel{g\ MgCl_2}} \times \frac{1\ \cancel{mol\ Mg}}{1\ \cancel{mol\ MgCl_2}} \times \frac{24.31\ g\ Mg}{1\ \cancel{mol\ Mg}} = 0.878\ g\ Mg$$

The 0.711 g of Mg is the lesser quantity, so the associated reactant—5.00 g of Rb—is the limiting reagent. To determine how much of the other reactant is left, we have to do one more mass-mass calculation to determine what mass of MgCl2 reacted with the 5.00 g of Rb, and then subtract the amount reacted from the original amount.

$$5.00\ \cancel{g\ Rb} \times \frac{1\ \cancel{mol\ Rb}}{85.47\ \cancel{g\ Rb}} \times \frac{1\ \cancel{mol\ MgCl_2}}{2\ \cancel{mol\ Rb}} \times \frac{95.21\ g\ Mg}{1\ \cancel{mol\ MgCl_2}} = 2.78\ g\ MgCl_2\ reacted$$

Because we started with 3.44 g of MgCl2, we have

3.44 g MgCl2 − 2.78 g MgCl2 reacted = 0.66 g MgCl2 left

Exercise 9.4.1

Given the initial amounts listed, what is the limiting reagent, and what is the mass of the leftover reagent?

$$\underbrace{22.7\ g}_{MgO(s)} + \underbrace{17.9\ g}_{H_2S} \rightarrow MgS(s) + H_2O(l)$$

Answer

H_2S is the limiting reagent; 1.5 g of MgO are left over.

Summary

The limiting reagent is the reactant that produces the least amount of product. Mass-mass calculations can determine how much product is produced and how much of the other reactants remain.

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9.5: Yields

Learning Objective

- Define and determine theoretical yields, actual yields, and percent yields.

In all the previous calculations we have performed involving balanced chemical equations, we made two assumptions:

1. the reaction goes exactly as written, and
2. the reaction proceeds completely.

In reality, such things as side reactions occur that make some chemical reactions rather messy. For example, in the actual combustion of some carbon-containing compounds, such as methane, some CO is produced as well as CO_2. However, we will continue to ignore side reactions, unless otherwise noted. The second assumption, that the reaction proceeds completely, is more troublesome. Many chemical reactions do not proceed to completion as written, for a variety of reasons (some of which we will consider in Chapter 13). When we calculate an amount of product assuming that all the reactant reacts, we calculate the **theoretical yield**, an amount that is theoretically produced as calculated using the balanced chemical reaction.

In many cases, however, this is not what really happens. In many cases, less—sometimes much less—of a product is made during the course of a chemical reaction. The amount that is actually produced in a reaction is called the **actual yield**. By definition, the actual yield is less than or equal to the theoretical yield. If it is not, then an error has been made.

Both theoretical yields and actual yields are expressed in units of moles or grams. It is also common to see something called a percent yield. The **percent yield** is a comparison between the actual yield and the theoretical yield and is defined as

$$\text{percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% \tag{9.5.1}$$

It does not matter whether the actual and theoretical yields are expressed in moles or grams, as long as they are expressed in the same units. However, the percent yield always has units of percent. Proper percent yields are between 0% and 100%—again, if percent yield is greater than 100%, an error has been made.

Example 9.5.1:

A worker reacts 30.5 g of Zn with nitric acid and evaporates the remaining water to obtain 65.2 g of $Zn(NO_3)_2$. What are the theoretical yield, the actual yield, and the percent yield?

$$Zn(s) + 2HNO_3(aq) \rightarrow Zn(NO_3)_2(aq) + H_2(g) \tag{9.5.2}$$

Solution

A mass-mass calculation can be performed to determine the theoretical yield. We need the molar masses of Zn (65.39 g/mol) and $Zn(NO_3)_2$ (189.41 g/mol). In three steps, the mass-mass calculation is

$$30.5\ \cancel{g\ Zn} \times \frac{1\ \cancel{mol\ Zn}}{65.39\ \cancel{g\ Zn}} \times \frac{1\ \cancel{mol\ Zn(NO_3)_2}}{1\ \cancel{mol\ Zn}} \times \frac{189.41\ g\ Zn(NO_3)_2}{1\ \cancel{mol\ Zn(NO_3)_2}} = 88.3\ g\ Zn(NO_3)_2 \tag{9.5.3}$$

Thus, the theoretical yield is 88.3 g of $Zn(NO_3)_2$. The actual yield is the amount that was actually made, which was 65.2 g of $Zn(NO_3)_2$. To calculate the percent yield, we take the actual yield and divide it by the theoretical yield and multiply by 100 (Equation 9.5.1):

$$\frac{65.2\ g\ Zn(NO_3)_2}{88.3\ g\ Zn(NO_3)_2} \times 100\% = 73.8\% \tag{9.5.4}$$

The worker achieved almost three-fourths of the possible yield.

Exercise 9.5.1

A synthesis produced 2.05 g of NH_3 from 16.5 g of N_2. What is the theoretical yield and the percent yield?

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \tag{9.5.5}$$

*Technically, this is a reversible reaction (with double arrows), but for this exercises consider it irreversible (single arrow).

Answer

theoretical yield = 20.1 g; percent yield = 10.2%

Chemistry Is Everywhere: Actual Yields in Drug Synthesis and Purification

Many drugs are the product of several steps of chemical synthesis. Each step typically occurs with less than 100% yield, so the overall percent yield might be very small. The general rule is that the overall percent yield is the product of the percent yields of the individual synthesis steps. For a drug synthesis that has many steps, the overall percent yield can be very tiny, which is one factor in the huge cost of some drugs. For example, if a 10-step synthesis has a percent yield of 90% for each step, the overall yield for the entire synthesis is only 35%. Many scientists work every day trying to improve percent yields of the steps in the synthesis to decrease costs, improve profits, and minimize waste.

Even purifications of complex molecules into drug-quality purity are subject to percent yields. Consider the purification of impure albuterol. Albuterol ($C_{13}H_{21}NO_2$; accompanying figure) is an inhaled drug used to treat asthma, bronchitis, and other obstructive pulmonary diseases. It is synthesized from norepinephrine, a naturally occurring hormone and neurotransmitter. Its initial synthesis makes very impure albuterol that is purified in five chemical steps. The details of the steps do not concern us; only the percent yields do:

impure albuterol → intermediate A	percent yield = 70%
intermediate A → intermediate B	percent yield = 100%
intermediate B → intermediate C	percent yield = 40%
intermediate C → intermediate D	percent yield = 72%
intermediate D → purified albuterol	percent yield = 35%
overall percent yield = 70% × 100% × 40% × 72% × 35% = 7.5%	

That is, only about *one-fourteenth* of the original material was turned into the purified drug. This gives you one reason why some drugs are so expensive; a lot of material is lost in making a high-purity pharmaceutical.



Fig. 5.6.1 A child using an albuterol inhaler, the container of albuterol medication, and a molecular model of the albuterol molecule. Source: Photo on far left © Thinkstock. Photo in center courtesy of Intropin, http://commons.wikimedia.org/wiki/Fi...te_%281%29.JPG.

Summary

Theoretical yield is what you calculate the yield will be using the balanced chemical reaction. Actual yield is what you actually get in a chemical reaction. Percent yield is a comparison of the actual yield with the theoretical yield.

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