CHEMISTRY OF NATURE AND CULTURE: FOOD, FITNESS, AND DRUGS

ATTRIBUTION

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PREFACE

In 1977, chemists Theodore L. Brown and H. Eugene LeMay (joined in subsequent editions by Bruce Bursten and Julia Burdge) published a general chemistry textbook titled Chemistry: The Central Science. Since that time, the label the central science has become more and more associated with chemistry above all other sciences.

Why? Follow along, if you will. Science is grounded, first and foremost, in mathematics. Math is the language of science. Any study of true science must use math as an inescapable tool. The most fundamental science is physics, the study of matter and energy. (For the sake of argument, I include astronomy as part of physics.) Then we progress to the study of the description of matter and how that description can change—that's chemistry.

As this point, however, several directions are possible. Do you want to study the chemistry of living things? That's biology. The chemistry of the earth? That's geology. The chemistry of how compounds work in our body? That's pharmacology. The application of chemistry to better our lives? That's engineering (chemical engineering, to be more specific, but we've just opened the door to the applied sciences). Granted, there are connections between more fundamental sciences and others—geophysics, astrobiology, and so forth—but a map of the sciences and their interconnections shows the most obvious branches after chemistry. This is why we consider chemistry the central science.

This concept is reinforced by the fact that many science majors require a course or two of chemistry as part of their curriculum (indeed, perhaps this is the reason you are using this textbook). Do you want to study biology? You'll need some chemistry courses. Are you a geology major? You'll need to know some chemistry. Many engineering disciplines, not just chemical engineering, require some background in chemistry as well. The reason that chemistry is required by so many other disciplines is that it is, to overuse the word, central.

Chemistry is not just central; it's all around you. You participate in chemistry every day. This idea is one of the major themes in this book—Introductory Chemistry. Chemistry is all around you, and you practice it every day whether you know it or not. Throughout these chapters, I will attempt to convince you that you play with chemicals every day, perform chemistry every day, and depend on chemistry every day. This is what makes chemistry an integral part, and what should make chemistry an integral part, of the modern literate adult.

The goal of this textbook is not to make you an expert. True expertise in any field is a years-long endeavor. Here I will survey some of the basic topics of chemistry. This survey should give you enough knowledge to appreciate the impact of chemistry in everyday life and, if necessary, prepare you for additional instruction in chemistry.

The text starts with an introduction to chemistry. Some users might find this a throwaway chapter, but I urge you to look it over. Many people—even scientists—do not know what science really is, and we all can benefit if we learn what science is and, importantly, what science is not. Chemistry, like all sciences, is inherently quantitative, so Chapter 2 "Measurements" discusses measurements and the conventions for expressing them. Yes, chemistry has conventions and arbitrarily adopted, agreed-on standards against which everything is expressed. Students are sometimes dismayed to learn that a hard science like chemistry has arbitrary standards. But then, all fields have their arbitrary standards that experts in that field must master if they are to be considered "experts." Chemistry, like other sciences, is no different.

Chemistry is based on atoms, so that concept comes next. Atoms make molecules, another important topic in chemistry. But atoms and molecules can change—a fundamental concept in chemistry. Therefore, unlike some other competing texts, I introduce chemical change early. Chemistry is little without the concept of chemical change, so I deem it important to introduce the concept as early as possible.

Quantity is also important in chemistry—I'm being repetitious. After chemical change comes a discussion of the unit of chemical change, the mole, and how it is used to relate chemicals to each other (a process known as stoichiometry). A discussion of the gas phase comes next—again earlier than in other texts. It is important for students to understand that we can model the physical properties of a phase of matter. Models are a crucial part of science, so reinforcing that idea earlier rather than later gives students a general understanding that they can apply to later material.

Energy is also an important topic in chemistry, so now that atoms and molecules, chemical reactions, and stoichiometry have been introduced, I include energy as a quantitative property. With this, the basic topics of chemistry are introduced; the remaining chapters discuss either more applied topics or topics less crucial to their survey of knowledge even if they are fundamental to our understanding: electronic structure, bonding, phases, solutions, acids and bases, chemical equilibrium, oxidation and reduction, and nuclear chemistry. I finish the text with a quick introduction to organic chemistry, if only to whet the appetites of those who thirst to know more.

Throughout each chapter, I present two features that reinforce the theme of the textbook—that chemistry is all around you. The first is a feature titled, appropriately, "Chemistry Is Everywhere." These features examine a topic of the chapter and demonstrate how this topic shows up in everyday life. In Chapter 1 "What Is Chemistry?", "Chemistry Is Everywhere" focuses on the personal hygiene products that you may use every morning: toothpaste, soap, and shampoo, among others. These products are chemicals, aren't they? Ever wonder about the chemical reactions that they undergo to give you clean and healthy teeth or shiny hair? I will explore some of these chemical reactions in future chapters. But this feature makes it clear that chemistry is, indeed, everywhere.

The other feature focuses on chemistry that you likely indulge in every day: eating and drinking. In the "Food and Drink App," I discuss how the chemistry of the chapter applies to things that you eat and drink every day. Carbonated beverages depend on the behavior of gases, foods contain acids and bases, and we actually eat certain rocks. (Can you guess which rocks without looking ahead?) Cooking, eating, drinking, and metabolism—we are involved with all these chemical processes all the time. These two features allow us to see the things we interact with every day in a new light—as chemistry.

Each section starts with one or more Learning Objectives, which are the main points of the section. Key Takeaways, which review the main points, end each section. Each chapter is full of examples to illustrate the key points, and each example is followed by a similar Test Yourself exercise to see if a student understands the concept. Each section ends with its own set of paired exercises to practice the material from that section, and each chapter ends with Additional Exercises that are more challenging or require multiple steps or skills to answer.

The mathematical problems in this text have been treated in one of two ways: either as a conversion-factor problem or as a formula problem. It is generally recognized that consistency in problem solving is a positive pedagogical tool. Students and instructors may have different ways to work problems mathematically, and if it is mathematically consistent, the same answer will result. However, I have found it better to approach mathematical exercises in a consistent fashion, without (horrors!) cutesy shortcuts. Such shortcuts may be useful for one type of problem, but if students do not do a problem correctly, they are clueless as to why they went wrong. Having two basic mathematical approaches (converting and formulas) allows the text to focus on the logic of the approach, not the tricks of a shortcut.

Inundations of unnecessary data, such as the densities of materials, are minimized for two reasons. First, they contribute nothing to understanding the concepts. Second, as an introductory textbook, this book focuses on the concepts and does not serve as a reference of data. There are other well-known sources of endless data should students need them.

Good luck, and good chemistry, to you all!

CHAPTER 1: WHAT IS CHEMISTRY?

Opening Essay

If you are reading these words, you are likely starting a chemistry course. Get ready for a fantastic journey through a world of wonder, delight, and knowledge. One of the themes of this book is "chemistry is everywhere," and indeed it is; you would not be alive if it weren't for chemistry because your body is a big chemical machine. If you don't believe it, don't worry. Every chapter in this book contains examples that will show you how chemistry is, in fact, everywhere. So enjoy the ride—and enjoy chemistry.

LEARNING OBJECTIVE

1. Learn the basic terms used to describe matter.

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. SOME BASIC DEFINITIONS

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 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 1

Which of the following is matter and not matter?
  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.

To understand matter and how it changes, we need to be able to describe matter. There are two basic ways to describe matter: **physical properties** and **chemical properties**. Physical properties are characteristics that describe matter as it exists. Some of many physical characteristics of matter are shape, color, size, and temperature. An important physical property is the **phase** (or **state**) of matter. The three fundamental states of matter are solid, liquid, and gas (see Figure 1.1 "The Phases of Matter").

Chemical properties are characteristics of matter that describe how matter changes form in the presence of other matter. Does a sample of matter burn? Burning is a chemical property. Does it behave violently when put in water? This reaction is a chemical property as well (Figure 1.2 "Chemical Properties"). In the following chapters, we will see how descriptions of physical and chemical properties are important aspects of chemistry.

If matter always stayed the same, chemistry would be rather boring. Fortunately, a major part of chemistry involves change. A physical change occurs when a sample of matter changes one or more of its physical properties. For example, a solid may melt (Figure 1.3 "Physical Changes"), or alcohol in a thermometer may change volume as the temperature changes. A physical change does not affect the chemical composition of matter.

Figure 1.2: *Chemical Properties. The fact that this match burns is a chemical property of the match. Image used with permission (Sebastian Ritter (Rise0011))*

A chemical change is the process of demonstrating a chemical property, such as the burning match in Figure 1.2 "Chemical Properties". As the matter in the match burns, its chemical composition changes, and new forms of matter with new physical properties are created. Note that chemical changes are frequently accompanied by physical changes, as the new matter will likely have different physical properties from the original matter.

Solid
Has fixed shape and volume

Liquid
Takes shape of container
Forms horizontal surface
Has fixed volume
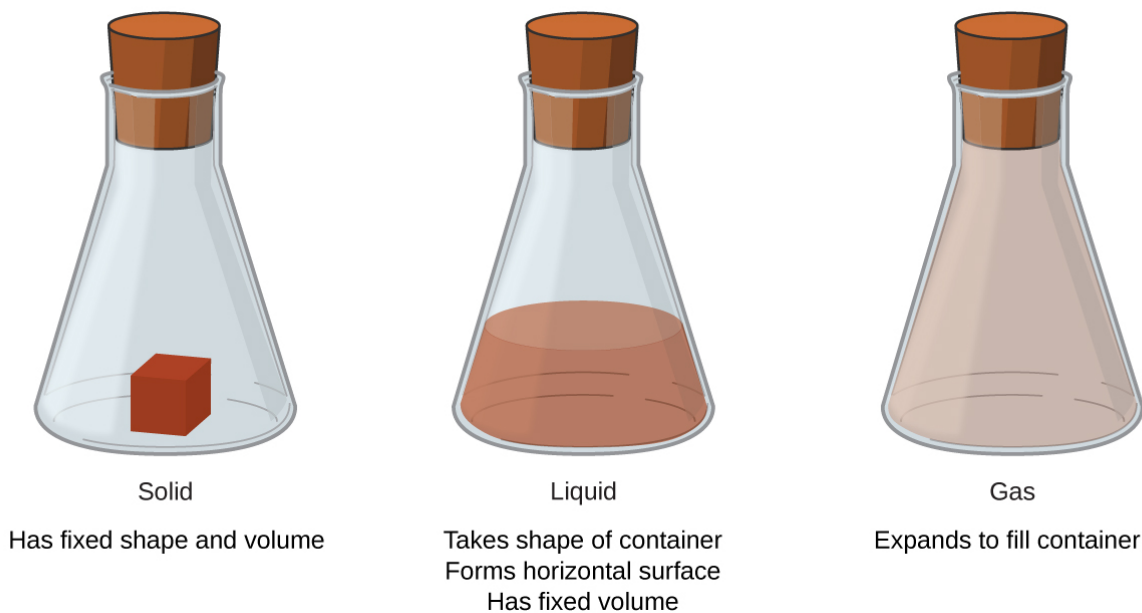
Gas
Expands to fill container

Figure 1.1: *The three fundamental states of matter - solid, liquid, and gas.*

A sample of matter that has the same physical and chemical properties throughout is called a **substance**. Sometimes the phrase *pure substance* is used, but the word *pure* isn't needed. The definition of the term *substance* is an example of

how chemistry has a specific definition for a word that is used in everyday language with a different, vaguer definition. Here, we will use the term *substance* with its strict chemical definition.

Chemistry recognizes two different types of substances: **elements** and compounds. An element is the simplest type of chemical substance; it cannot be broken down into simpler chemical substances by ordinary chemical means. There are about 115 elements known to science, of which 80 are stable (The other elements are radioactive). Each element has its own unique set of physical and chemical properties. Examples of elements include iron, carbon, and gold.

Figure 1.3: *Physical Changes - Ice, water, and water vapor are three different physical states of water, but do not affect its chemical composition*

A **compound** is a combination of more than one element. The physical and chemical properties of a compound are different from the physical and chemical properties of its constituent elements; that is, it behaves as a completely different substance. There are over 50 million compounds known, and more are being discovered daily. Examples of compounds include water, penicillin, and sodium chloride (the chemical name for common table salt).

Elements and compounds are not the only ways in which matter can be present. We frequently encounter objects that are physical combinations of more than one element or compound. Physical combinations of more than one substance are called **mixtures**. There are two types of mixtures. A **heterogeneous mixture** is a mixture composed of two or more substances. It is easy to tell, sometimes by the naked eye, that more than one

Figure 1.4: *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.*

substance is present. A **homogeneous mixture** is a combination of two or more substances that is 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 1.4 "Types of Mixtures").

There are other descriptors that we can use to describe matter, especially elements. We can usually divide elements into metals and nonmetals, and each set shares certain (but not always all) properties. A **metal** is an element that is solid at room temperature (although mercury is a well-known exception), is shiny and silvery, conducts electricity and heat well, can be pounded into thin sheets (a property called *malleability*), and can be drawn into thin wires (a property called *ductility*). A **nonmetal** is an element that is brittle when solid, does not conduct electricity or heat very well, and cannot be made into thin sheets or wires (Figure 1.5 "Semimetals"). Nonmetals also exist in a variety of phases and colors at room temperature. Some elements have properties of both metals and nonmetals and are called **semimetals (or metalloids)**. We will see later how these descriptions can be assigned rather easily to various elements.

Figure 1.5: *Semimetals - On the left is some elemental mercury, the only metal that exists as a liquid at room temperature. It has all the other expected properties of a metal. On the right, elemental sulfur is a yellow nonmetal that usually is found as a powder.*

Chemistry Is Everywhere: In the Morning

Most people have a morning ritual, a process that they go through every morning to get ready for the day. Chemistry appears in many of these activities.

If you take a shower or bath in the morning, you probably use soap, shampoo, or both. These items contain chemicals that interact with the oil and dirt on your body and hair to remove them and wash them away. Many of these products also contain chemicals that make you smell good; they are called fragrances.

When you brush your teeth in the morning, you usually use toothpaste, a form of soap, to clean your teeth. Toothpastes typically contain tiny, hard particles called abrasives that physically scrub your teeth. Many toothpastes also contain fluoride, a substance that chemically interacts with the surface of the teeth to help prevent cavities.

Perhaps you take vitamins, supplements, or medicines every morning. Vitamins and other supplements contain chemicals your body needs in small amounts to function properly. Medicines are chemicals that help combat diseases and promote health.

Perhaps you make some fried eggs for breakfast. Frying eggs involves heating them enough so that a chemical reaction occurs to cook the eggs.

After you eat, the food in your stomach is chemically reacted so that the body (mostly the intestines) can absorb food, water, and other nutrients.

If you drive or take the bus to school or work, you are using a vehicle that probably burns gasoline, a material that burns fairly easily and provides energy to power the vehicle. Recall that burning is a chemical change.

These are just a few examples of how chemistry impacts your everyday life. And we haven't even made it to lunch yet!

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.
- ❖ Matter can be described in terms of physical properties and chemical properties.
- ❖ Physical properties and chemical properties of matter can change
- ❖ Matter is composed of elements and compounds.
- ❖ Combinations of different substances are called mixtures.
- ❖ Elements can be described as metals, nonmetals, and semimetals.

1. Identify each as either matter or not matter.
   A. a book

   B. hate

   C. light

   D. a car

   E. a fried egg

2. Give an example of matter in each phase: solid, liquid, or gas.

3. Does each statement represent a physical property or a chemical property?

   A. Sulfur is yellow.

   B. Steel wool burns when ignited by a flame.

   C. A gallon of milk weighs over eight pounds.

4. Does each statement represent a physical property or a chemical property?

   A. A pile of leaves slowly rots in the backyard.

   B. In the presence of oxygen, hydrogen can interact to make water.

   C. Gold can be stretched into very thin wires.

5. Does each statement represent a physical change or a chemical change?

   A. Water boils and becomes steam.

   B. Food is converted into usable form by the digestive system.

   C. The alcohol in many thermometers freezes at about –40 degrees Fahrenheit.

6. Does each statement represent a physical change or a chemical change?

   A. Graphite, a form of elemental carbon, can be turned into diamond, another form of carbon, at very high temperatures and pressures.

   B. The house across the street has been painted a new color.

   C. The elements sodium and chlorine come together to make a new substance called sodium chloride.

7. Distinguish between an element and a compound. About how many of each are known?

8. What is the difference between a homogeneous mixture and a heterogeneous mixture?

9. Identify each as a heterogeneous mixture or a homogeneous mixture.

   A. Salt is mixed with pepper.

   B. Sugar is dissolved in water.

   C. Pasta is cooked in boiling water.

10. Identify each as a heterogeneous mixture or a homogeneous mixture.

    A. air

    B. dirt

    C. a television set

11. In Exercise 9, which choices are also solutions?

12. In Exercise 10, which choices are also solutions?

13. Why is iron considered a metal?

14. Why is oxygen considered a nonmetal?

15. Distinguish between a metal and a nonmetal.

16. What properties do semimetals have?

17. Elemental carbon is a black, dull-looking solid that conducts heat and electricity well. It is very brittle and cannot be made into thin sheets or long wires. Of these properties, how does carbon behave as a metal? How does carbon behave as a nonmetal?

18. Pure silicon is shiny and silvery but does not conduct electricity or heat well. Of these properties, how does silicon behave as a metal? How does silicon behave as a nonmetal?

ANSWERS

1.
   A. matter

   B. not matter

   C. not matter

   D. matter

   E. matter

3.
   A. physical property

   B. chemical property

   C. physical property

5.
   A. physical change

   B. chemical change

   C. physical change

7. An element is a fundamental chemical part of a substance; there are about 115 known elements. A compound is a combination of elements that acts as a different substance; there are over 50 million known substances.

9.
   A. heterogeneous

   B. homogeneous

   C. heterogeneous

11. Choice b is a solution.

13. Iron is a metal because it is solid, is shiny, and conducts electricity and heat well.

15. Metals are typically shiny, conduct electricity and heat well, and are malleable and ductile; nonmetals are a variety of colors and phases, are brittle in the solid phase, and do not conduct heat or electricity well.

17. Carbon behaves as a metal because it conducts heat and electricity well. It is a nonmetal because it is black and brittle and cannot be made into sheets or wires.

15

2. CHEMISTRY AS A SCIENCE

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."

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.

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.

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?

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 with what occurs naturally.

Figure 1.6: How would you describe this color? Blue or hardnrf? Either way, you're not doing science.

EXAMPLE 2

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 3

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.

Test Yourself

Are these qualitative or quantitative statements?

a. Roses are red, and violets are blue.

b. Four score and seven years ago….

Answers

a. qualitative

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.

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.

EXERCISES

1. Describe the scientific method.

2. What is the scientific definition of a hypothesis? Why is the phrase *a hypothesis is just a guess* an inadequate definition?

3. Why do scientists need to perform experiments?

4. What is the scientific definition of a theory? How is this word misused in general conversation?

5. What is the scientific definition of a law? How does it differ from the everyday definition of a law?

6. Name an example of a field that is not considered a science.

7. Which of the following fields are studies of the natural universe?
   A. biophysics (a mix of biology and physics)

   B. art

   C. business

8. Which of the following fields are studies of the natural universe?
   A. accounting

   B. geochemistry (a mix of geology and chemistry)

   C. astronomy (the study of stars and planets [but not the earth])

9. Which of these statements are qualitative descriptions?
   A. The *Titanic* was the largest passenger ship build at that time.

   B. The population of the United States is about 306,000,000 people.

   C. The peak of Mount Everest is 29,035 feet above sea level.

10. Which of these statements are qualitative descriptions?
    A. A regular movie ticket in Cleveland costs $6.00.

    B. The weather in the Democratic Republic of the Congo is the wettest in all of Africa.

    C. The deepest part of the Pacific Ocean is the Mariana Trench.

11. Of the statements in Exercise 9, which are quantitative?

12. Of the statements in Exercise 10, which are quantitative?

ANSWERS

1. Simply stated, the scientific method includes three steps: (1) stating a hypothesis, (2) testing the hypothesis, and (3) refining the hypothesis.

3. Scientists perform experiments to test their hypotheses because sometimes the nature of natural universe is not obvious.

5. A scientific law is a specific statement that is thought to be never violated by the entire natural universe. Everyday laws are arbitrary limits that society puts on its members.

7.
    A. yes

    B. no

    C. no

9.
    A. qualitative

    B. not qualitative

    C. not qualitative

11. Statements b and c are quantitative.

CHAPTER 2: MEASUREMENTS

Opening Essay

Data suggest that a male child will weigh 50% of his adult weight at about 11 years of age. However, he will reach 50% of his adult height at only 2 years of age. It is obvious, then, that people eventually stop growing up but continue to grow out. Data also suggest that the average human height has been increasing over time. In industrialized countries, the average height of people increased 5.5 inches from 1810 to 1984. Most scientists attribute this simple, basic measurement of the human body to better health and nutrition.

Source: Chart courtesy of Centers for Disease Control and Prevention, http://www.cdc.gov/nchs/ nhanes.htm#Set%201

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.
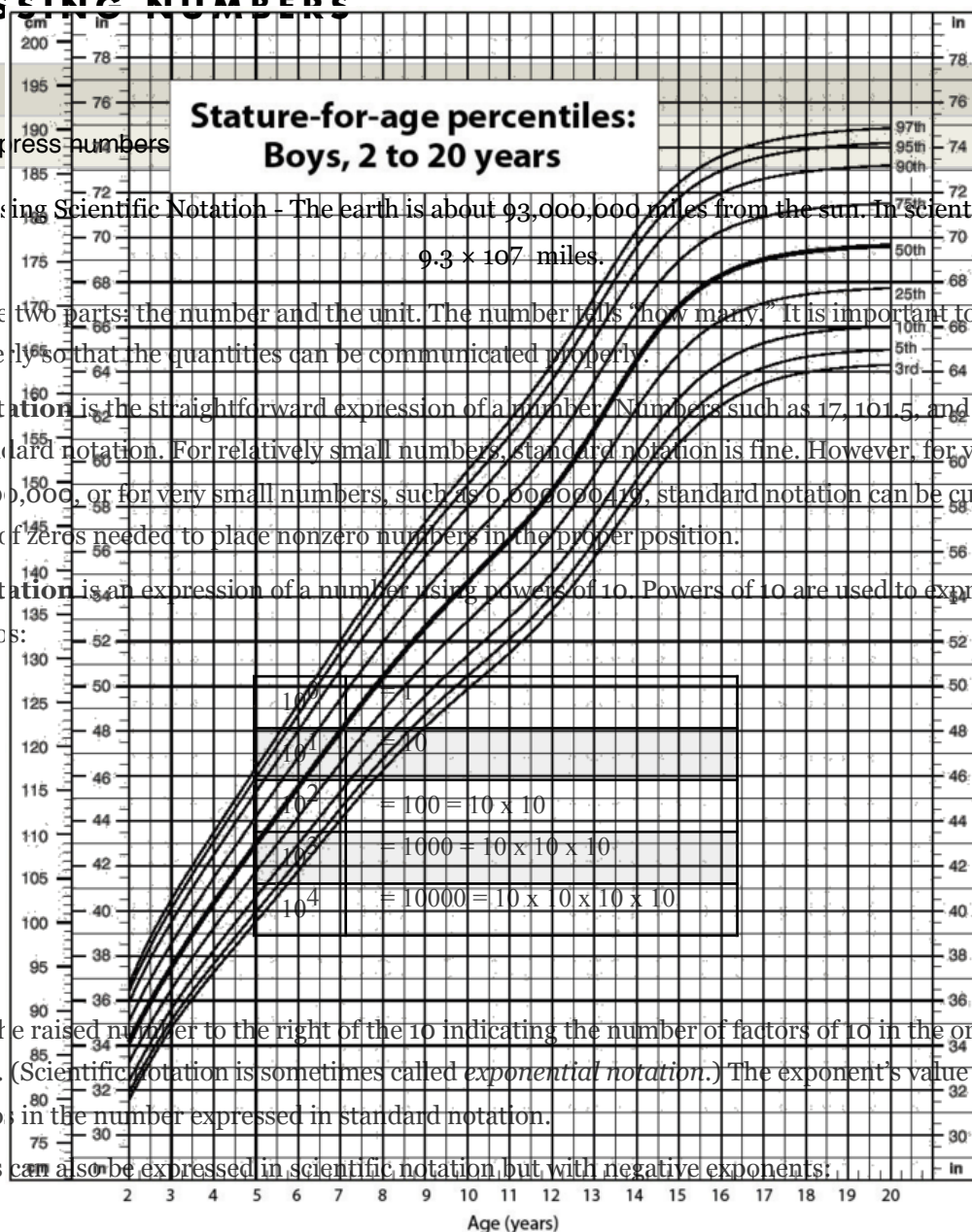
1. EXPRESSING NUMBERS

1. Learn to express numbers

Figure 2.1: Using Scientific Notation - The earth is about 93,000,000 miles from the sun. In scientific notation, this is 9.3×10^7 miles.

Quantities have two parts: the number and the unit. The number tells "how many." It is important to be able to express numbers properly so that the quantities can be communicated properly.

Standard notation is the straightforward expression of a number. Numbers such as 17, 101.5, and 0.00446 are expressed in standard notation. For relatively small numbers, standard notation is fine. However, for very large numbers, such as 306,000,000, or for very small numbers, such as 0.000000419, standard notation can be cumbersome because of the number of zeros needed to place nonzero numbers in the proper position.

Scientific notation is an expression of a number using powers of 10. Powers of 10 are used to express numbers that have many zeros:

$$10^0 = 1$$
$$10^1 = 10$$
$$10^2 = 100 = 10 \times 10$$
$$10^3 = 1000 = 10 \times 10 \times 10$$
$$10^4 = 10000 = 10 \times 10 \times 10 \times 10$$

and so forth. The raised number to the right of the 10 indicating the number of factors of 10 in the original number is the **exponent**. (Scientific notation is sometimes called *exponential notation*.) The exponent's value is equal to the number of zeros in the number expressed in standard notation.

Small numbers can also be expressed in scientific notation but with negative exponents:

$$10^{-2} = .01 = 1/100$$

10^{-3}	= .001 = 1/1000
10^{-4}	= .0001 = 1/10000

and so forth. Again, the value of the exponent is equal to the number of zeros in the denominator of the associated fraction. A negative exponent implies a decimal number less than one.

A number is expressed in scientific notation by writing the first nonzero digit, then a decimal point, and then the rest of the digits. The part of a number in scientific notation that is multiplied by a power of 10 is called the **coefficient**. Then determine the power of 10 needed to make that number into the original number and multiply the written number by the proper power of 10. For example, to write 79,345 in scientific notation,

$$79{,}345 \; = \; 7.9345 \times 10{,}000 \; = \; 7.9345 \times 10^{4}$$

Thus, the number in scientific notation is 7.9345×10^{4} For small numbers, the same process is used, but the exponent for the power of 10 is negative:
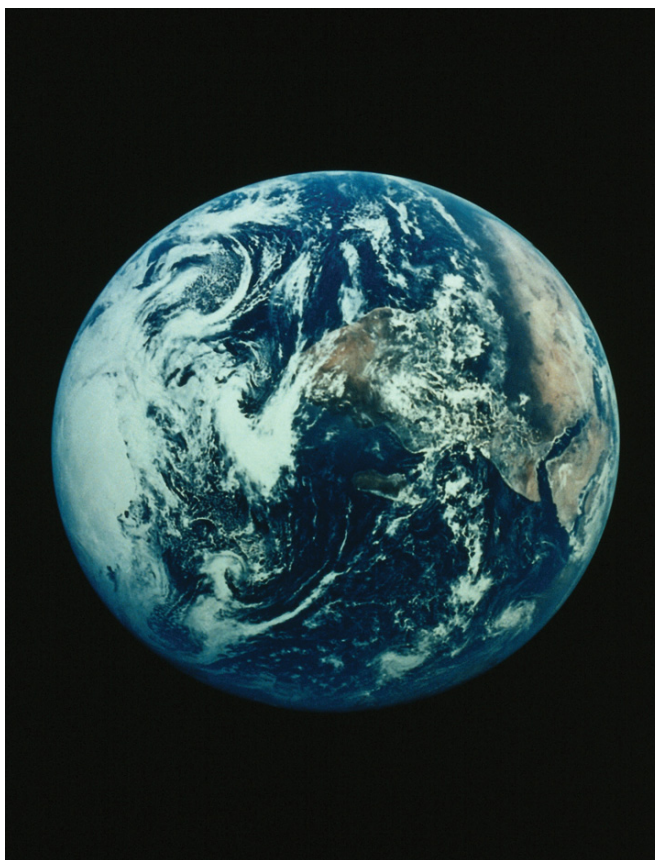
$$0.000411 = 4.11 \times 1/10{,}000 = 4.11 \times 10^{-4}$$

Typically, the extra zero digits at the end or the beginning of a number are not included. (See **Figure 2.1** "Using Scientific Notation".)

EXAMPLE 1

Express these numbers in scientific notation.
- a. 306,000
- b. 0.00884
- c. 2,760,000
- d. 0.000000559

Solution

- a. The number 306,000 is 3.06 times 100,000, or 3.06 times 10^5. In scientific notation, the number is 3.06 × 10^5.

- b. The number 0.00884 is 8.84 times 1/1,000, which is 8.84 times 10^{-3}. In scientific notation, the number is 8.84 × 10^{-3}.

- c. The number 2,760,000 is 2.76 times 1,000,000, which is the same as 2.76 times 10^6. In scientific notation, the number is written as 2.76 × 10^6. Note that we omit the zeros at the end of the original number.

- d. The number 0.000000559 is 5.59 times 1/10,000,000, which is 5.59 times 10^{-7}. In scientific notation, the number is written as 5.59 × 10^{-7}.

Test Yourself

Express these numbers in scientific notation.
- a. 23,070
- b. 0.0009706

Answers
- a. 2.307 × 10^4
- b. 9.706 × 10^{-4}

Another way to determine the power of 10 in scientific notation is to count the number of places you need to move the decimal point to get a numerical value between 1 and 10. The number of places equals the power of 10. This number is positive if you move the decimal point to the right and negative if you move the decimal point to the left:

$$56{,}900 = 5.69 \times 10^4 \qquad 0.000028 = 2.8 \times 10^{-5}$$
$$4 \quad 3\ 2\ 1 \qquad\qquad 1\ 2\ 3\ 4\ 5$$

Many quantities in chemistry are expressed in scientific notation. When performing calculations, you may have to enter a number in scientific notation into a calculator. Be sure you know how to correctly enter a number in scientific notation into your calculator. Different models of calculators require different actions for properly entering scientific notation. If in doubt, consult your instructor immediately.

KEY TAKEAWAYS

❖ Standard notation expresses a number normally.

❖ Scientific notation expresses a number as a coefficient times a power of 10.

❖ The power of 10 is positive for numbers greater than 1 and negative for numbers between 0 and 1.

1. Express these numbers in scientific notation.
    A. 56.9
    B. 563,100
    C. 0.0804
    D. 0.00000667

2. Express these numbers in scientific notation.
    A. −890,000
    B. 602,000,000,000
    C. 0.0000004099
    D. 0.000000000000011

3. Express these numbers in scientific notation.
    A. 0.00656
    B. 65,600
    C. 4,567,000
    D. 0.000005507

4. Express these numbers in scientific notation.
    A. 65
    B. −321.09
    C. 0.000077099
    D. 0.000000000218

5. Express these numbers in standard notation.
    A. 1.381×10^5
    B. 5.22×10^{-7}
    C. 9.998×10^4

6. Express these numbers in standard notation.
    A. 7.11×10^{-2}
    B. 9.18×10^2
    C. 3.09×10^{-10}

7. Express these numbers in standard notation.
    A. 8.09×10^0
    B. 3.088×10^{-5}
    C. -4.239×10^2

8. Express these numbers in standard notation.
    A. 2.87×10^{-8}
    B. 1.78×10^{11}
    C. 1.381×10^{-23}

9. These numbers are not written in proper scientific notation. Rewrite them so that they are in proper scientific notation.

    A. 72.44×10^3
    B. $9,943 \times 10^{-5}$
    C. $588,399 \times 10^2$

10. These numbers are not written in proper scientific notation. Rewrite them so that they are in proper scientific notation.

    A. 0.000077×10^{-7}
    B. 0.000111×10^8
    C. $602,000 \times 10^{18}$

11. These numbers are not written in proper scientific notation. Rewrite them so that they are in proper scientific notation.

    A. 345.1×10^2

    B. 0.234×10^{-3}

    C. $1{,}800 \times 10^{-2}$

12. These numbers are not written in proper scientific notation. Rewrite them so that they are in proper scientific notation.

    A. $8{,}099 \times 10^{-8}$

    B. 34.5×10^0

    C. 0.000332×10^4

13. Write these numbers in scientific notation by counting the number of places the decimal point is moved

    A. $123{,}456.78$

    B. $98{,}490$

    C. 0.000000445

14. Write these numbers in scientific notation by counting the number of places the decimal point is moved

    A. 0.000552

    B. $1{,}987$

    C. 0.00000000887

15. Use your calculator to evaluate these expressions. Express the final answer in proper scientific notation.

    A. $456 \times (7.4 \times 10^8) = ?$

    B. $(3.02 \times 10^5) \div (9.04 \times 10^{15}) = ?$

    C. $0.0044 \times 0.000833 = ?$

16. Use your calculator to evaluate these expressions. Express the final answer in proper scientific notation.

    A. $98{,}000 \times 23{,}000 = ?$

    B. $98{,}000 \div 23{,}000 = ?$

    C. $(4.6 \times 10^{-5}) \times (2.09 \times 10^3) = ?$

17. Use your calculator to evaluate these expressions. Express the final answer in proper scientific notation.

    A. $45 \times 132 \div 882 = ?$

    B. $[(6.37 \times 10^4) \times (8.44 \times 10^{-4})] \div (3.2209 \times 10^{15}) = ?$

18. Use your calculator to evaluate these expressions. Express the final answer in proper scientific notation.

    A. $(9.09 \times 10^8) \div [(6.33 \times 10^9) \times (4.066 \times 10^{-7})] = ?$

    B. $9{,}345 \times 34.866 \div 0.00665 = ?$

ANSWERS

1.

    A. 5.69×10^1

    B. 5.631×10^5

    C. 8.04×10^{-2}

    D. 6.67×10^{-6}

3.

    A. 6.56×10^{-3}

    B. b. 6.56×10^4

    C. c. 4.567×10^6

    D. 5.507×10^{-6}

5.

    A. 138,100

    B. 0.000000522

    C. 99,980

7.

    A. 8.09

    B. 0.00003088

    C. −423.9

9.

    A. 7.244×10^4

    B. 9.943×10^{-2}

    C. 5.88399×10^7

11.

    A. 3.451×10^4

    B. 2.34×10^{-4}

    C. 1.8×10^1

13.

    A. 1.2345678×10^5

    B. 9.849×10^4

    C. 4.45×10^{-7}

15.

    A. 3.3744×10^{11}

    B. 3.3407×10^{-11}

    C. 3.665×10^{-6}

17.

    A. 6.7346×10^0

    B. 1.6691×10^{-14}

2. EXPRESSING UNITS

LEARNING OBJECTIVES
1. Learn the units that go with various quantities.
2. Express units using their abbreviations.
3. Make new units by combining numerical prefixes with units.

A number indicates "how much," but the unit indicates "of what." The "of what" is important when communicating a quantity. For example, if you were to ask a friend how close you are to Lake Erie and your friend says "six," then your friend isn't giving you complete information. Six *what*? Six miles? Six inches? Six city blocks? The actual distance to the lake depends on what units you use.

Chemistry, like most sciences, uses the International System of Units, or SI for short. (The letters *SI* stand for the French "le Système International d'unités.") SI specifies certain units for various types of quantities, based on seven **fundamental units** for various quantities. We will use most of the fundamental units in chemistry. Initially, we will deal with three fundamental units. The meter (m) is the SI unit of length. It is a little longer than a yard. The SI unit of mass is the kilogram (kg), which is about 2.2 pounds (lb). The SI unit of time is the second (s).
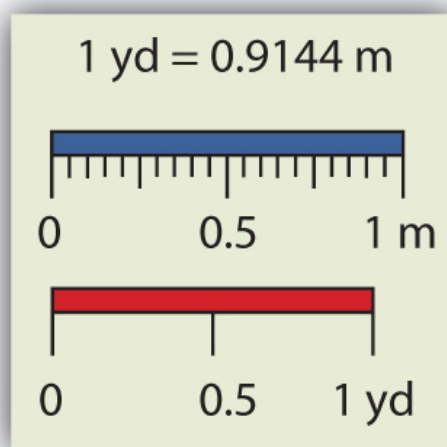

Figure 2.3: *The Meter - The SI standard unit of length, the meter, is a little longer than a yard.*

To express a quantity, you need to combine a number with a unit. If you have a length that is 2.4 m, then you express that length as simply 2.4 m. A time of 15,000 s can be expressed as 1.5×10^4 s in scientific notation.

Sometimes, a given unit is not an appropriate size to easily express a quantity. For example, the width of a human hair is very small, and it doesn't make much sense to express it in meters. SI also defines a series of **numerical prefixes** that refer to multiples or fractions of a fundamental unit to make a unit more conveniently sized for a specific quantity. The chart lists the prefixes, their abbreviations, and their multiplicative factors. Some of the prefixes, such as kilo-, mega-, and giga-, represent more than one of the fundamental unit, while other prefixes, such as centi-, milli-, and micro-, represent fractions of the original unit. Note, too, that once again we are using powers of 10. Each prefix is a multiple of or fraction of a power of 10.
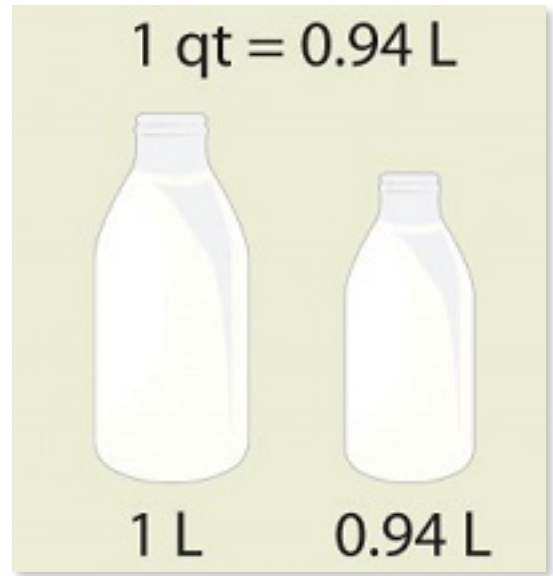
Figure 2.4: *The Liter -The SI unit of volume, the liter, is slightly larger than 1 quart.*
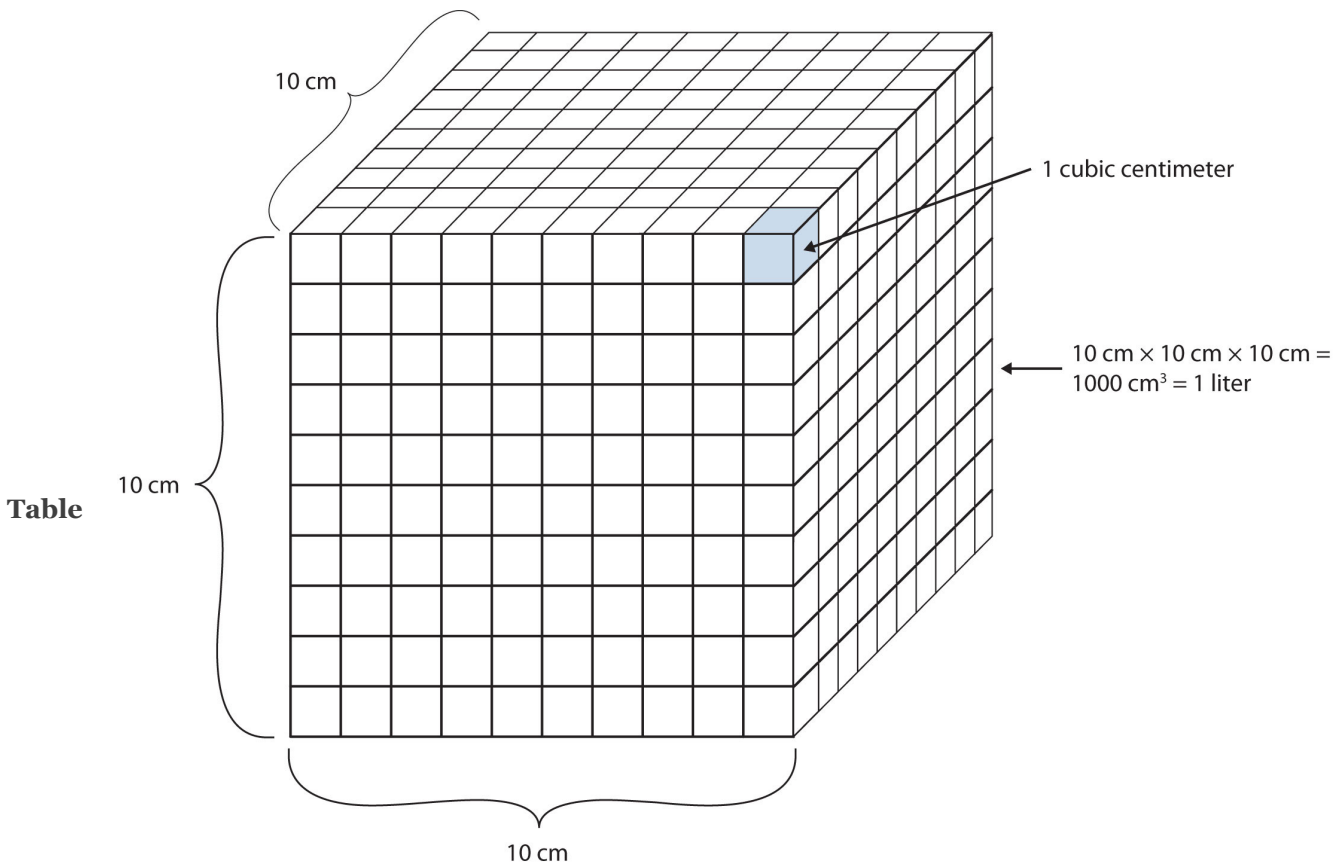

Figure 2.5: *The Size of 1 Liter - One liter equals 1,000 cm3, so 1 cm3 is the same as 1 mL.*

Table 2.1 Multiplicative Prefixes for SI Units

Prefix	Abbreviation	Multiplicative Amount
giga-	G	1,000,000,000 ×
mega-	M	1,000,000 ×
kilo-	k	1,000 ×
deci-	d	1/10 ×
centi-	c	1/100 ×
milli-	m	1/1,000 ×
micro-	μ*	1/1,000,000 ×
nano-	n	1/1,000,000,000 ×
pico-	p	1/1,000,000,000,000 ×
* The letter μ is the Greek letter lowercase equivalent to an m and is called "mu" (pronounced "myoo").		

To use the fractions to generate new units, simply combine the prefix with the unit itself; the abbreviation for the new unit is the combination of the abbreviation for the prefix and the abbreviation of the unit. For example, the kilometer (km) is 1,000 × meter, or 1,000 m. Thus, 5 kilometers (5 km) is equal to 5,000 m. Similarly, a millisecond (ms) is 1/1,000 × second, or one- thousandth of a second. Thus, 25 ms is 25 thousandths of a second. You will need to become proficient in combining prefixes and units. (You may recognize that one of our fundamental units, the kilogram, automatically has a prefix-unit combination, the kilogram. The word *kilogram* means 1,000 g.)

In addition to the fundamental units, SI also allows for **derived units** based on a fundamental unit or units. There are many derived units used in science. For example, the derived unit for area comes from the idea that area is defined as width times height. Because both width and height are lengths, they both have the fundamental unit of meter, so the unit of area is meter × meter, or meter^2 (m^2). This is sometimes spoken as "square meters." A unit with a prefix can also be used to derive a unit for area, so we can also have cm^2, mm^2, or km^2 as acceptable units for area.

Volume is defined as length times width times height, so it has units of meter × meter × meter or meter^3 (m^3), sometimes spoken as "cubic meters." The cubic meter is a rather large unit, however, so another unit is defined that is somewhat more manageable: the liter (L). A liter is 1/1,000th of a cubic meter and is a little more than 1 quart in volume. Prefixes can also be used with the liter unit, so we can speak of milliliters (1/1,000th of a liter; mL) and kiloliters (1,000 L; kL).

Another definition of a liter is one-tenth of a meter cubed. Because one-tenth of a meter is 10 cm, then a liter is equal to 1,000 cm^3 . Because 1 L equals 1,000 mL, we conclude that 1 mL equals 1 cm^3; thus, these units are interchangeable.

Units not only are multiplied together but also can be divided. For example, if you are traveling at one meter for every second of time elapsed, your velocity is 1 meter per second, or 1 m/s. The word *per* implies division, so velocity is determined by dividing a distance quantity by a time quantity. Other units for velocity include kilometers per hour (km/h) or even micrometers per nanosecond (μm/ns). Later, we will see other derived units that can be expressed as fractions.

EXAMPLE 2

a.   A human hair has a diameter of about 6.0×10^{-5} m. Suggest an appropriate unit for this measurement and write the diameter of a human hair in terms of that unit.

b.   What is the velocity of a car if it goes 25 m in 5.0 s?

Solution

a.   The scientific notation 10^{-5} is close to 10^{-6}, which defines the micro- prefix. Let us use micrometers as the unit for hair diameter. The number 6.0×10^{-5} can be written as 60×10^{-6}, and a micrometer is 10^{-6} m, so the diameter of a human hair is about 60 μm.

b.   If velocity is defined as a distance quantity divided by a time quantity, then velocity is 25 meters/5.0 seconds. Dividing the numbers gives us 25/5.0 = 5.0, and dividing the units gives us meters/second, or m/s. The velocity is 5.0 m/s.

Test Yourself

a.   Express the volume of an Olympic-sized swimming pool, 2,500,000 L, in more appropriate units.

b.   A common garden snail moves about 6.1 m in 30 min. What is its velocity in meters per minute (m/min)?

Answers

a.   2.5 ML

b.   0.203 m/min

KEY TAKEAWAYS

❖ Numbers tell "how much," and units tell "of what."

❖ Chemistry uses a set of fundamental units and derived units from SI units.

❖ Chemistry uses a set of prefixes that represent multiples or fractions of units.

❖ Units can be multiplied and divided to generate new units for quantities.

1. Identify the unit in each quantity.
   A. 2 boxes of crayons

   B. 3.5 grams of gold

2. Identify the unit in each quantity.
   A. 32 oz of cheddar cheese

   B. 0.045 cm^3 of water

3. Identify the unit in each quantity.
   A. 9.58 s (the current world record in the 100 m dash)

   B. 6.14 m (the current world record in the pole vault)

4. Identify the unit in each quantity.
   A. 2 dozen eggs

   B. 2.4 km/s (the escape velocity of the moon, which is the velocity you need at the surface to escape the moon's

   gravity)

5. Indicate what multiplier each prefix represents.
   A. k

   B. m

   C. M

6. Indicate what multiplier each prefix represents.
   A. c

   B. G

   C. μ

7. Give the prefix that represents each multiplier.
   A. 1/1,000th ×

   B. 1,000 ×

   C. 1,000,000,000 ×

8. Give the prefix that represents each multiplier.
   D. 1/1,000,000,000th ×

   E. 1/100th ×

   F. 1,000,000 ×

9. Complete the following table with the missing information.

Unit	Abbreviation
kilosecond	
	mL
	Mg
centimeter	

10.

Unit	Abbreviation
kilometer per second	
second	
	cm^3
	μL
nanosecond	

11. Express each quantity in a more appropriate unit. There may be more than one acceptable answer.

A. 3.44×10^{-6} s

B. 3,500 L

C. 0.045 m

12. Express each quantity in a more appropriate unit. There may be more than one acceptable answer.

A. 0.000066 m/s (Hint: you need consider only the unit in the numerator.)

B. b. 4.66×10^6 s

C. c. 7,654 L

13. Express each quantity in a more appropriate unit. There may be more than one acceptable answer.

   A. 43,600 mL

   B. 0.0000044 m

   C. 1,438 ms

14. Express each quantity in a more appropriate unit. There may be more than one acceptable answer.

   A. 0.000000345 m³

   B. 47,000,000 mm³

   C. 0.00665 L

15. Multiplicative prefixes are used for other units as well, such as computer memory. The basic unit of computer memory is the byte (b). What is the unit for one million bytes?

16. You may have heard the terms *microscale* or *nanoscale* to represent the sizes of small objects. What units of length do you think are useful at these scales? What fractions of the fundamental units of length are these units?

17. Acceleration is defined as a change in velocity per time. Propose a unit for acceleration in terms of the fundamental SI units.

18. Density is defined as the mass of an object divided by its volume. Propose a unit for density in terms of the fundamental SI units.

1.
    A. boxes of crayons
    B. grams

3.
    A. seconds
    B. meters

5.
    A. 1000
    B. 1/1000
    C. 1,000,000

7.
    A. 1/1,000th ×
    B. 1,000 ×
    C. 1,000,000,000 ×

9.

Unit	Abbreviation
kilosecond	ks
milliliter	mL
megagram	Mg
centimeter	cm

11.
    A. 3.44 μs
    B. 3.5 kL
    C. 4.5 cm

13.
    A. 43.6 L
    B. 4.4 μm
    C. 1.438 s

15. megabytes (Mb)

17. meters/second^2

3. SIGNIFICANT FIGURES

LEARNING OBJECTIVES

1. Apply the concept of significant figures to limit a measurement to the proper number of digits.

2. Recognize the number of significant figures in a given quantity.

3. Limit mathematical results to the proper number of significant figures.

If you use a calculator to evaluate the expression 337/217, you will get the following:

$$337 \div 217 = 1.5529953917$$

and so on for many more digits. Although this answer is correct, it is somewhat presumptuous. You start with two values that each have three digits, and the answer has *twelve* digits? That does not make much sense from a strict numerical point of view.

Consider using a ruler to measure the width of an object, as shown in Figure 2.6. The object is definitely more than 1 cm long, so we know that the first digit in our measurement is 1. We see by counting the tick marks on the ruler that the object is at least three ticks after the 1. If each tick represents 0.1 cm, then we know the object is at least 1.3 cm wide. But our ruler does not have any more ticks between the 0.3 and the 0.4 marks, so we can't know exactly how much the next decimal place is. But with a practiced eye we can estimate it. Let us estimate it as about six-tenths of the way between the third and fourth tick marks, which estimates our hundredths place as 6, so we identify a measurement of 1.36 cm for the width of the object.

Does it make any sense to try to report a thousandths place for the measurement? No, it doesn't; we are not exactly sure of the hundredths place (after all, it was an estimate only), so it would be fruitless to estimate a thousandths place. Our best measurement, then, stops at the hundredths place, and we report 1.36 cm as proper measurement.

This concept of reporting the proper number of digits in a measurement or a calculation is called **significant figures**. Significant figures (sometimes called significant digits) represent the limits of what values of a measurement or a calculation we are sure of. The convention for a measurement is that the quantity reported should be all known values and the first estimated value. The conventions for calculations are discussed as follows.

Figure 2.6: *Expressing Width - What is the proper way to express the width of this object?*

In many cases, you will be given a measurement. How can you tell by looking what digits are significant?

For example, the reported population of the United States is 306,000,000. Does that mean that it is *exactly* three hundred six million or is some estimation occurring?

The following conventions dictate which numbers in a reported measurement are significant and which are not significant:
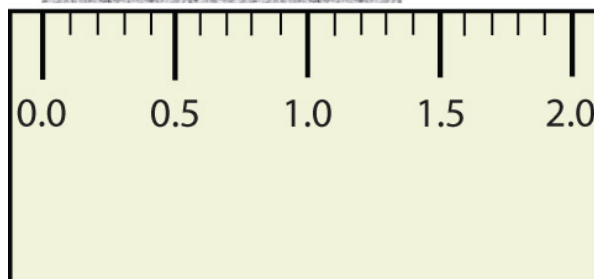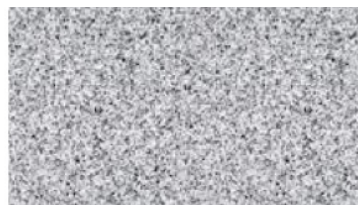
Significant Figures in Numbers	Examples (significant figures in bold)
Any nonzero digit is significant.	**13.4** (three significant figures)
Any zeros between nonzero digits (i.e., embedded zeros) are significant	**404.1** (four significant figures)
Leading zeros (zeros to the left of the first nonzero digit) are not significant.	0.0000**21** (two significant figures)
Trailing zeros (zeros at the end of a number) without a decimal point are not significant.	**4**000 (1 significant figure)
Trailing zeros with a decimal point are significant.	**4000.0** (5 significant figures)

So, by these rules, the population figure of the United States has only three significant figures: the 3, the 6, and the zero between them. The remaining six zeros simply put the 306 in the millions position. (See Figure 2.4 for another example.

Figure 2.4: *Significant Figures. How many of the numbers in this display are actually significant? Image used with permission (Public Domain).*

How are significant figures handled in calculations? It depends on what type of calculation is being performed. If the calculation is an addition or a subtraction, the rule is as follows: limit the reported answer to the rightmost column that all numbers have significant figures in common. For example, if you were to add 1.2 and 4.71, we note that the first number stops its significant figures in the tenths column, while the second number stops its significant figures in the hundredths column. We therefore limit our answer to the tenths column.

$$1.2$$
$$\underline{4.41}$$
$$5.61$$

↑ limit final answer to the tenths column: 5.6

We drop the last digit—the 1—because it is not significant to the final answer.

The dropping of positions in sums and differences brings up the topic of rounding. Although there are several conventions, in this text we will adopt the following rule: the final answer should be rounded up if the first dropped digit is 5 or greater and rounded down if the first dropped digit is less than 5.
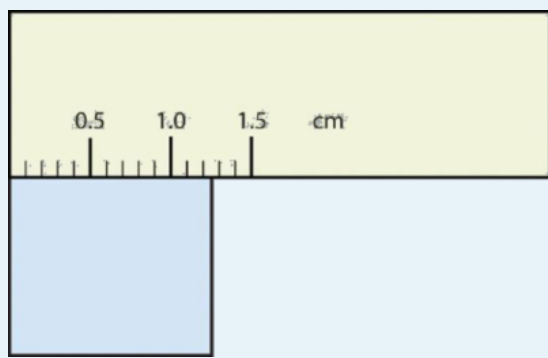
$$77.2$$
$$\underline{10.46}$$
$$87.66$$

↑ limit final answer to the tenths column and round up: 87.7

EXAMPLE 3

Use each diagram to report a measurement to the proper number of significant figures.

Solution

a. The arrow is between 4.0 and 5.0, so the measurement is at least 4.0. The arrow is between the third and fourth small tick marks, so it's at least 0.3. We will have to estimate the last place. It looks like about one-third of the way across the space, so let us estimate the hundredths place as 3. Combining the digits, we have a measurement of 4.33 psi (psi stands for "pounds per square inch" and is a unit of pressure, like air in a tire). We say that the measurement is reported to three significant figures.

b. The rectangle is at least 1.0 cm wide but certainly not 2.0 cm wide, so the first significant digit is 1. The rectangle's width is past the second tick mark but not the third; if each tick mark represents 0.1, then the rectangle is at least 0.2 in the next significant digit. We have to estimate the next place because there are no markings to guide us. It appears to be about halfway between 0.2 and 0.3, so we will estimate the next place to be a 5. Thus, the measured width of the rectangle is 1.25 cm. Again, the measurement is reported to three significant figures.

EXAMPLE 4

Express the final answer to the proper number of significant figures.

a. 101.2 + 18.702 = ?

b. 202.88 – 1.013 = ?

Solution

a. If we use a calculator to add these two numbers, we would get 119.902. However, most calculators do not understand significant figures, and we need to limit the final answer to the tenths place. Thus, we drop the 02 and report a final answer of 119.9 (rounding down).

b. A calculator would answer 201.867. However, we have to limit our final answer to the hundredths place. Because the first number being dropped is 7, which is greater than 7, we round up and report a final answer of 201.87.

Test Yourself

Express the answer for 3.445 + 90.83 – 72.4 to the proper number of significant figures.

Answer

21.9

If the operations being performed are multiplication or division, the rule is as follows: limit the answer to the number of significant figures that the data value with the least number of significant figures has. So if we are dividing 23 by 448, which have two and three significant figures each, we should limit the final reported answer to two significant figures (the lesser of two and three significant figures):

$$23 \div 448 = 0.051339286 \approx 0.051$$

The same rounding rules apply in multiplication and division as they do in addition and subtraction.

Express the final answer to the proper number of significant figures.

a. $76.4 \times 180.4 = ?$

b. $934.9 \div 0.00455 = ?$

Solution

a. The first number has three significant figures, while the second number has four significant figures. Therefore, we limit our final answer to three significant figures: $76.4 \times 180.4 = 13{,}782.56 = 13{,}800$.

b. The first number has four significant figures, while the second number has three significant figures. Therefore we limit our final answer to three significant figures: $934.9 \div 0.00455 = 205{,}472.5275\ldots = 205{,}000$.

Test Yourself

Express the final answer to the proper number of significant figures.

a. $22.4 \times 8.314 = ?$

b. $1.381 \div 6.02 = ?$

Answers

a. 186

b. 0.229

As you have probably realized by now, the biggest issue in determining the number of significant figures in a value is the zero. Is the zero significant or not? One way to unambiguously determine whether a zero is significant or not is to write a number in scientific notation. Scientific notation will include zeros in the coefficient of the number *only if they are significant*. Thus, the number 8.666×10^6 has four significant figures. However, the number 8.6660×10^6 has five significant figures. That last zero is significant; if it were not, it would not be written in the coefficient. So when in doubt about expressing the number of significant figures in a quantity, use scientific notation and include the number of zeros that are truly significant.

KEY TAKEAWAYS

❖ Significant figures in a quantity indicate the number of known values plus one place that is estimated.

❖ There are rules for which numbers in a quantity are significant and which are not significant.

❖ In calculations involving addition and subtraction, limit significant figures based on the rightmost place that all values have in common.

❖ In calculations involving multiplication and division, limit significant figures to the least number of significant figures in all the data values.
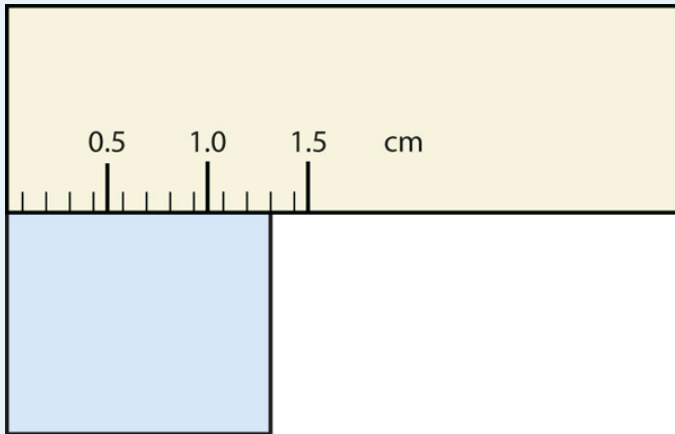
EXERCISES

1. Express each measurement to the correct number of significant figures.

A.
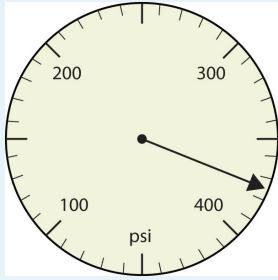
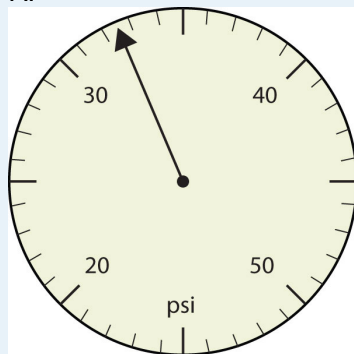B.
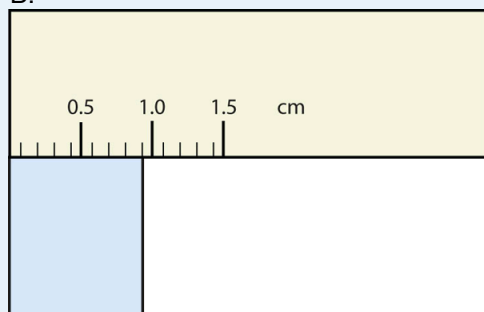
2. Express each measurement to the correct number of significant figures.

A.

B.

3. How many significant figures do these numbers have?
A. 23
B. 23.0
C. 0.00023
D. 0.0002302

4. How many significant figures do these numbers have?
A. 5.44×10^{8}
B. 1.008×10^{-5}
C. 43.09
D. 0.0000001381

5. How many significant figures do these numbers have?
A. 765,890
B. 765,890.0
C. 1.2000×10^{5}
D. 0.0005060

6. How many significant figures do these numbers have?
A. 0.009
B. 0.0000009
C. 65,444
D. 65,040

7. Compute and express each answer with the proper number of significant figures, rounding as necessary.
A. 56.0 + 3.44 = ?
B. 0.00665 + 1.004 = ?
C. 45.99 – 32.8 = ?
D. 45.99 – 32.8 + 75.02 = ?

8. Compute and express each answer with the proper number of significant figures, rounding as necessary.
A. $1.005 + 17.88 = ?$
B. $56{,}700 - 324 = ?$
C. $405{,}007 - 123.3 = ?$
D. $55.5 + 66.66 - 77.777 = ?$

9. Compute and express each answer with the proper number of significant figures, rounding as necessary.
A. $56.7 \times 66.99 = ?$
B. $1.000 \div 77 = ?$
C. $1.000 \div 77.0 = ?$
D. $6.022 \times 1.89 = ?$

10. Compute and express each answer with the proper number of significant figures, rounding as necessary.
A. $0.000440 \times 17.22 = ?$
B. $203{,}000 \div 0.044 = ?$
C. $67 \times 85.0 \times 0.0028 = ?$
D. $999{,}999 \div 3{,}310 = ?$

11. Write the number 87,449 in scientific notation with four significant figures.

12. Write the number 0.000066600 in scientific notation with five significant figures.

13. Write the number 306,000,000 in scientific notation to the proper number of significant figures.

14. Write the number 0.0000558 in scientific notation with two significant figures.

15. Perform each calculation and limit each answer to three significant figures.
A. $67{,}883 \times 0.004321 = ?$
B. $(9.67 \times 10^3) \times 0.0055087 = ?$

16. Perform each calculation and limit each answer to four significant figures.
A. $18{,}900 \times 76.33 \div 0.00336 = ?$
B. $0.77604 \div 76{,}003 \times 8.888 = ?$

ANSWERS

1.
A. 375 psi
B. 1.30 cm

3.
A. two
B. two
C. five
D. seven

5.
A. two
B. three
C. two
D. four

7.
E. five
F. seven
G. five
H. four

9.
A. 59.4
B. 1.011
C. 13.2
D. 88.2

11.
A. 3.80×10^3
B. 0.013
C. 0.0130
D. 11.4

13.
A. 8.745×10^4
B. b. 6.6600×10^{-5}

15
A. 293
B. 53.3

4. CONVERTING UNITS

In Section 2.2 "Expressing Units", we showed some examples of how to replace initial units with other units of the same type to get a numerical value that is easier to comprehend. In this section, we will formalize the process.

Consider a simple example: how many feet are there in 4 yards? Most people will almost automatically answer that there are 12 feet in 4 yards. How did you make this determination? Well, if there are 3 feet in 1 yard and there are 4 yards, then there are 4 × 3 = 12 feet in 4 yards.

This is correct, of course, but it is informal. Let us formalize it in a way that can be applied more generally. We know that 1 yard (yd) equals 3 feet (ft):

$$1 \text{ yd} = 3 \text{ ft}$$

In math, this expression is called an *equality*. The rules of algebra say that you can change (i.e., multiply or divide or add or subtract) the equality (as long as you don't divide by zero) and the new expression will still be an equality. For example, if we divide both sides by 2, we get

$$1/2 \text{ yd} = 3/2 \text{ ft}$$

We see that one-half of a yard equals 3/2, or one and a half, feet—something we also know to be true, so the above equation is still an equality. Going back to the original equality, suppose we divide both sides of the equation by 1 yard (number *and* unit):

$$1 \text{ yd} / 1 \text{ yd} = 3 \text{ ft} / 1 \text{ yd}$$

The expression is still an equality, by the rules of algebra. The left fraction equals 1. It has the same quantity in the numerator and the denominator, so it must equal 1. The quantities in the numerator and denominator cancel, both the number *and* the unit:

$$1 = 3 \text{ ft} / 1 \text{ yd}$$

When everything cancels in a fraction, the fraction reduces to 1:

$$1 = 3 \text{ ft}$$

We have an expression, 3 ft, that equals 1. This is a strange way to write 1, but it makes sense: 3 ft equal 1 yd, so the quantities in the numerator and denominator are the same quantity, just expressed with different units. The expression 3 ft is called a conversion factor, and it is used to formally change the unit of a quantity into another unit. (The process of converting units in such a formal fashion is sometimes called *dimensional analysis* or the *factor label method*.)

To see how this happens, let us start with the original quantity:

$$4 \text{ yd}$$

Now let us multiply this quantity by 1. When you multiply anything by 1, you don't change the value of the quantity. Rather than multiplying by just 1, let us write 1 as 3 ft:

$$4 \text{ yd} \times 3 \text{ ft}$$

The 4 yd term can be thought of as 4 yd; that is, it can be thought of as a fraction with 1 in the denominator. We are essentially multiplying fractions. If the same thing appears in the numerator and denominator of a fraction, they cancel. In this case, what cancels is the unit *yard*:

$$4 \text{ yd}$$

That is all that we can cancel. Now, multiply and divide all the numbers to get the final answer:

$$4 \times 3 \text{ ft} = 12 \text{ ft}$$

Again, we get an answer of 12 ft, just as we did originally. But in this case, we used a more formal procedure that is applicable to a variety of problems.

How many millimeters are in 14.66 m? To answer this, we need to construct a conversion factor between millimeters and meters and apply it correctly to the original quantity. We start with the definition of a millimeter, which is

$$1 \text{ mm} = 1/1{,}000 \text{ m}$$

The 1/1,000 is what the prefix *milli-* means. Most people are more comfortable working without fractions, so we will rewrite this equation by bringing the 1,000 into the numerator of the other side of the equation:

$$1{,}000 \text{ mm} = 1 \text{ m}$$

Now we construct a conversion factor by dividing one quantity into both sides. But now a question arises: which quantity do we divide by? It turns out that we have two choices, and the two choices will give us different conversion factors, both of which equal 1:

$$\frac{1{,}000 \text{ mm}}{1} = 1 \text{ m}$$

Which conversion factor do we use? The answer is based on *what unit you want to get rid of in your initial quantity*. The original unit of our quantity is meters, which we want to convert to millimeters. Because the original unit is as-

sumed to be in the numerator, to get rid of it, we want the meter unit in the *denominator*; then they will cancel. Therefore, we will use the second conversion factor. Canceling units and performing the mathematics, we get

$$14.66 \text{ m} \times 1{,}000 \text{ mm}$$

Note how m cancels, leaving mm, which is the unit of interest.

The ability to construct and apply proper conversion factors is a very powerful mathematical technique in chemistry. You need to master this technique if you are going to be successful in this and future courses.

EXAMPLE 7

a. Convert 35.9 kL to liters.

b. Convert 555 nm to meters.

Solution

a. We will use the fact that 1 kL = 1,000 L. Of the two conversion factors that can be defined, the one that will work is

1,000 L. Applying this conversion factor, we get

$$35.9 \text{ kL}$$

b. We will use the fact that 1 nm = 1/1,000,000,000 m, which we will rewrite as 1,000,000,000 nm

= 1 m, or 10^9 nm = 1 m. Of the two possible conversion factors, the appropriate one has the nm unit in the denominator: 1 m. Applying this conversion factor, we get

$$555 \text{ nm}$$

In the final step, we expressed the answer in scientific notation.

Test Yourself

1. Convert 67.08 µL to liters.

2. Convert 56.8 m to kilometers.

Answers

1. 6.708×10^{-5} L

2. 5.68×10^{-2} km

What if we have a derived unit that is the product of more than one unit, such as m^2? Suppose we want to convert square meters to square centimeters? The key is to remember that m^2 means m × m, which means we have *two* meter units in our derived unit. That means we have to include *two* conversion factors, one for each unit. For example, to convert 17.6 m^2 to square centimeters, we perform the conversion as follows:

$$17.6 \text{ m}$$

EXAMPLE 8

How many cubic centimeters are in 0.883 m^3?

Solution

With an exponent of 3, we have three length units, so by extension we need to use three conversion factors between meters and centimeters. Thus, we have

$$0.883 \text{ m3}$$

You should demonstrate to yourself that the three meter units do indeed cancel.

Test Yourself

How many cubic millimeters are present in 0.0923 m^3?

Answer

9.23×10^7 mm^3

Suppose the unit you want to convert is in the denominator of a derived unit; what then? Then, in the conversion factor, the unit you want to remove must be in the *numerator*. This will cancel with the original unit in the denominator and introduce a new unit in the denominator. The following example illustrates this situation.

Sometimes there will be a need to convert from one unit with one numerical prefix to another unit with a different numerical prefix. How do we handle those conversions? Well, you could memorize the conversion factors that interrelate all numerical prefixes. Or you can go the easier route: first convert the quantity to the base unit, the unit with no numerical prefix, using the definition of the original prefix.

Then convert the quantity in the base unit to the desired unit using the definition of the second prefix. You can do the conversion in two separate steps or as one long algebraic step. For example, to convert 2.77 kg to milligrams:

$$2.77 \text{ kg} \times 1{,}000 \text{ g}$$

$$2{,}770 \text{ g} \times 1{,}000 \text{ mg1 g}$$

Alternatively, it can be done in a single multistep process:

$$2.77 \text{ kg}$$

You get the same answer either way.

When considering the significant figures of a final numerical answer in a conversion, there is one important case where a number does not impact the number of significant figures in a final answer—the so-called exact number. An exact number is a number from a defined relationship, not a measured one. For example, the prefix *kilo-* means 1,000—*exactly* 1,000, no more or no less. Thus, in constructing the conversion factor

$$1,000 \; g$$

neither the 1,000 nor the 1 enter into our consideration of significant figures. The numbers in the numerator and denominator are defined exactly by what the prefix *kilo-*means. Another way of thinking about it is that these numbers can be thought of as having an infinite number of significant figures, such as

$$1,000.0000000000\ldots g$$

The other numbers in the calculation will determine the number of significant figures in the final answer.

EXAMPLE 10

A rectangular plot in a garden has the dimensions 36.7 cm by 128.8 cm. What is the area of the garden plot in square meters? Express your answer in the proper number of significant figures.

Solution

Area is defined as the product of the two dimensions, which we then have to convert to square meters and express our final answer to the correct number of significant figures, which in this case will be three

$$36.7 \text{ cm}$$

The 1 and 100 in the conversion factors do not affect the determination of significant figures because they are exact numbers, defined by the centi- prefix.

Test Yourself

What is the volume of a block in cubic meters whose dimensions are 2.1 cm × 34.0 cm × 118 cm?

Answer

0.0084 m^3

Chemistry Is Everywhere: The Gimli Glider

On July 23, 1983, an Air Canada Boeing 767 jet had to glide to an emergency landing at Gimli Industrial Park Airport in Gimli, Manitoba, because it unexpectedly ran out of fuel during flight. There was no loss of life in the course of the emergency landing, only some minor injuries associated in part with the evacuation of the craft after landing. For the remainder of its operational life (the plane was retired in 2008), the aircraft was nicknamed "the Gimli Glider."

The Gimli Glider is the Boeing 767 that ran out of fuel and glided to safety at Gimli Airport. The aircraft ran out of fuel because of confusion over the units used to express the amount of fuel.

Source: Photo courtesy of Will F., http://commons.wikimedia.org/wiki/File:Gimli_Glider_today.jpg.

The 767 took off from Montreal on its way to Ottawa, ultimately heading for Edmonton, Canada. About halfway through the flight, all the engines on the plane began to shut down because of a lack of fuel. When the final engine cut off, all electricity (which was generated by the engines) was lost; the plane became, essentially, a powerless glider. Captain Robert Pearson was an experienced glider pilot, although he had never flown a glider the size of a 767. First Officer Maurice Quintal quickly determined that the aircraft would not be able make it to Winnipeg, the next large airport. He suggested his old Royal Air Force base at Gimli Station, one of whose runways was still being used as a community airport. Between the efforts of the pilots and the flight crew, they managed to get the airplane safely on the ground (although with buckled landing gear) and all passengers off safely.

EXERCISES

1. Write the two conversion factors that exist between the two given units.
   A. milliliters and liters
   B. microseconds and seconds
   C. kilometers and meters

2. Write the two conversion factors that exist between the two given units.
   A. kilograms and grams
   B. milliseconds and seconds
   C. centimeters and meters

3. Perform the following conversions.
   A. 5.4 km to meters
   B. 0.665 m to millimeters
   C. 0.665 m to kilometers

5. Perform the following conversions.
   A. 90.6 mL to liters
   B. 0.00066 ML to liters
   C. 750 L to kiloliters

6. Perform the following conversions.
   A. 17.8 µg to grams
   B. 7.22×10^2 kg to grams
   C. 0.00118 g to nanograms

7. Perform the following conversions.
   A. 833 ns to seconds
   B. 5.809 s to milliseconds
   C. 2.77×10^6 s to megaseconds

8. Perform the following conversions.
   A. 9.44 m^2 to square centimeters
   B. 3.44×10^8 mm^3 to cubic meters

9. Perform the following conversions.
   A. 0.00444 cm^3 to cubic meters
   B. 8.11×10^2 m^2 to square nanometers

10. Why would it be inappropriate to convert square centimeters to cubic meters?

11. Why would it be inappropriate to convert from cubic meters to cubic seconds?
    A. 45.0 m/min to meters/second
    B. 0.000444 m/s to micrometers/second
    C. 60.0 km/h to kilometers/second

12. Perform the following conversions.
    A. 3.4×10^2 cm/s to centimeters/minute

    B. 26.6 mm/s to millimeters/hour

    C. 13.7 kg/L to kilograms/milliliters

    D. 0.674 kL to milliliters

    E. 2.81×10^{12} mm to kilometers

    F. 94.5 kg to milligrams

    G. 6.79×10^{-6} kg to micrograms

    H. 1.22 mL to kiloliters

    I. 9.508×10^{-9} ks to milliseconds

13. Perform the following conversions.
    A. 6.77×10^{14} ms to kiloseconds
    B. 34,550,000 cm to kilometers

14. Perform the following conversions.
    A. 4.701×10^{15} mL to kiloliters
    B. 8.022×10^{-11} ks to microseconds

15. Perform the following conversions. Note that you will have to convert units in both the numerator and the denominator.
    A. 88 ft/s to miles/hour (Hint: use 5,280 ft = 1 mi.)
    B. 0.00667 km/h to meters/second

16. Perform the following conversions. Note that you will have to convert units in both the numerator and the denominator.
    A. 3.88×10^2 mm/s to kilometers/hour
    B. 1.004 kg/L to grams/milliliter

17. What is the area in square millimeters of a rectangle whose sides are 2.44 cm × 6.077 cm? Express the answer to the proper number of significant figures.

18. What is the volume in cubic centimeters of a cube with sides of 0.774 m? Express the answer to the proper number of significant figures.

19. The formula for the area of a triangle is 1/2 × base × height. What is the area of a triangle in square centimeters if its base is 1.007 m and its height is 0.665 m? Express the answer to the proper number of significant figures.

20. The formula for the area of a triangle is 1/2 × base × height. What is the area of a triangle in square meters if its base is 166 mm and its height is 930.0 mm? Express the answer to the proper number of significant figures.

57

1.
1. 1,000 mL and 1 L

   1,000,000 μs and 1 s

   1,000 m and 1 km

d. 5,400 m

e. 665 mm

f. 6.65×10^{-4} km

3. a. 1.78×10^{-5} g

b. 7.22×10^{5} g

c. 1.18×10^{6} ng

5. a. 94,400 cm²

b. 0.344 m³

7. One is a unit of area, and the other is a unit of volume.

9. a. 0.75 m/s

b. 444 μm/s

c. 1.666×10^{-2} km/s

11. a. 674,000 mL

b. 2.81×10^{6} km

c. 9.45×10^{7} mg

13. a. 6.77×10^{8} ks

b. 345.5 km
15. a. 6.0×10^{1} mi/h

b. 0.00185 m/s

17. a. 1.48×10^{3} mm²

b. 3.35×10^{3} cm²

5. OTHER UNITS: TEMPERATURE AND DENSITY

There are other units in chemistry that are important, and we will cover others in 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:

$$°C = (°F - 32) \times 5/9$$

$$°F = (°C \times 9/5) + 32$$

Using these formulas, we can convert from one temperature scale to another. The number 32 in the formulas is exact and does not count in significant figure determination.

EXAMPLE 12

a. What is 98.6°F in degrees Celsius?

b. What is 25.0°C in degrees Fahrenheit?

Solution

a. Using the first formula from above, we have

$$°C = (98.6–32)$$

b. Using the second formula from above, we have

$$°F = (25.0 \times 95)$$

Test Yourself
1. Convert 0°F to degrees Celsius.

2. Convert 212°C to degrees Fahrenheit.

Answers
1. –17.8°C

2. 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 lower-case) 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:

$$K = °C + 273.15°$$

$$C = K - 273.15$$

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. 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 13

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

Solution

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

$$°C=(72.0–32)$$

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

$$K = 22.2°C + 273.15 = 295.4 \text{ K}$$

So, room temperature is about 295 K.

Test Yourself

What is 98.6°F on the Kelvin scale?

Answer

310.2 K

Figure 2.9 "Fahrenheit, Celsius, and Kelvin Temperatures" 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 don't get confused by their weather reports.)

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

density = mass / volume => d = 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/cm3, g/L, kg/L, and even kg/m3. Densities for some common substances are listed in Table 2.2 "Densities of Some Common Substances".
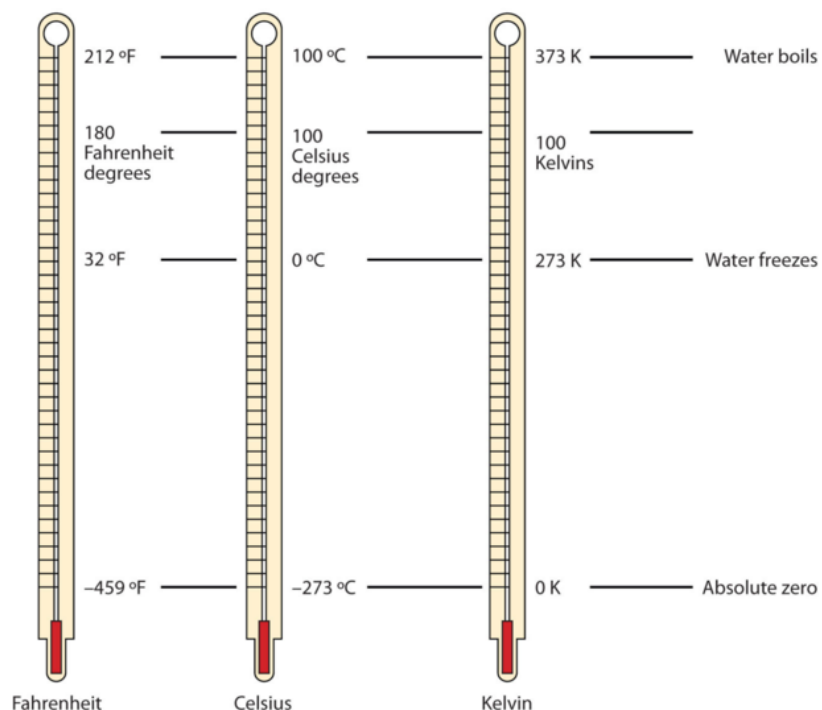
Figure 2.9: *Fahrenheit, Celsius, and Kelvin Temperatures - A comparison of the three temperature scales.*

Table 2.2 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 cm3. 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 2.2 "Densities of Some Common Substances"), 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.

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:

$$d=19.3 \text{ g/mL}=19.3 \text{ g}$$

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

$$d=19.3 \text{ g/mL}=19.3 \text{ g}$$

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:

$$1d=1 \text{ mL}$$

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:

$$45.9 \text{ g} \times 1 \text{ mL}$$

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

EXAMPLE 13

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

$$1 \, d = 1 \, cm3$$

We can use this expression as the conversion factor. So

Test Yourself

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.

EXAMPLE 14

What is the mass of 44.6 mL of mercury?

Solution

Use the density from Table 2.2 "Densities of Some Common Substances" as a conversion factor to go from volume to mass:

The mass of the mercury is 607 g.

Test Yourself

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

Answer

197 g

Food and Drink App: 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.

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.

<div style="background:green;color:white;text-align:center">KEY TAKEAWAYS</div>

❖ 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 a substance's mass and volume.

❖ Density can be used to calculate volume from a given mass or mass from a given volume.

EXERCISES

1. 37.0°C to kelvins

2. −37.0°C to kelvins

3. Convert 0 K to degrees Celsius. What is the significance of the temperature in degrees Celsius?

4. The hottest temperature ever recorded on the surface of the earth was 136°F in Libya in 1922. What is the temperature in degrees Celsius and in kelvins?

5. The coldest temperature ever recorded on the surface of the earth was −128.6°F in Vostok, Antarctica, in 1983. What is the temperature in degrees Celsius and in kelvins?

6. Give at least three possible units for density.

7. What are the units when density is inverted? Give three examples.

8. A sample of iron has a volume of 48.2 cm^3. What is its mass?

9. A sample of air has a volume of 1,015 mL. What is its mass?

10. The volume of hydrogen used by the *Hindenburg*, the German airship that exploded in New Jersey in 1937, was 2.000×10^8 L. If hydrogen gas has a density of 0.0899 g/L, what mass of hydrogen was used by the airship?

11. The volume of an Olympic-sized swimming pool is 2.50×10^9 cm^3. If the pool is filled with alcohol ($d = 0.789$ g/cm^3), what mass of alcohol is in the pool?

12. A typical engagement ring has 0.77 cm^3 of gold. What mass of gold is present?

13. What is the volume of 100.0 g of lead if lead has a density of 11.34 g/cm^3?

14. What is the volume of 255.0 g of uranium if uranium has a density of 19.05 g/cm^3?

15. What is the volume in liters of 222 g of neon if neon has a density of 0.900 g/L?

16. What is the volume in liters of 20.5 g of sulfur hexafluoride if sulfur hexafluoride has a density of 6.164 g/L?

17. Which has the greater volume, 100.0 g of iron ($d = 7.87$ g/cm^3) or 75.0 g of gold ($d = 19.3$ g/cm^3)?

18. Which has the greater volume, 100.0 g of hydrogen gas ($d = 0.0000899$ g/cm^3) or 25.0 g of argon gas ($d = 0.00178$ g/cm^3)?

ANSWERS

1.
    a. 124°C

    b. −159°C

    c. 122°F

    d. −58°F

3.
    a. 373 K

    b. 173 K

    c. −173°C

    d. 27°C

5. −273°C. This is the lowest possible temperature in degrees Celsius.

7. 57.8°C; 331 K

9. g/mL, g/L, and kg/L (answers will vary)

11. 379 g

13. 1.80×10^7 g

15. 15 g

17. 8.818 cm³

19. 247 L

21. The 100.0 g of iron has the greater volume.

6. END-OF-CHAPTER MATERIAL

1. Evaluate $0.00000000552 \times 0.0000000006188$ and express the answer in scientific notation. You may have to rewrite the original numbers in scientific notation first.

2. Evaluate $333,999,500,000 \div 0.00000000003396$ and express the answer in scientific notation. You may need to rewrite the original numbers in scientific notation first.

3. Express the number 6.022×10^{23} in standard notation.

4. Express the number 6.626×10^{-34} in standard notation.

5. When powers of 10 are multiplied together, the powers are added together. For example, $10^2 \times 10^3 = 10^{2+3} = 10^5$. With this in mind, can you evaluate $(4.506 \times 10^4) \times (1.003 \times 10^2)$ without entering scientific notation into your calculator?

6. When powers of 10 are divided into each other, the bottom exponent is subtracted from the top exponent. For example, $10^5/10^3 = 10^{5-3} = 10^2$. With this in mind, can you evaluate $(8.552 \times 10^6) \div (3.129 \times 10^3)$ without entering scientific notation into your calculator?

7. Consider the quantity two dozen eggs. Is the unit in this quantity "eggs" or "dozen eggs"? Justify your choice.

8. Fill in the blank: 1 km =_____μm.

9. Fill in the blank: 1 Ms =_____ns.

10. Fill in the blank: 1 cL =_____ML.

11. Fill in the blank: 1 mg =_____kg.

12. Express 67.3 km/h in meters/second.

13. Express 0.00444 m/s in kilometers/hour.

14. Using the idea that 1.602 km = 1.000 mi, convert a speed of 60.0 mi/h into kilometers/hour.

15. Using the idea that 1.602 km = 1.000 mi, convert a speed of 60.0 km/h into miles/hour.

16. Convert 52.09 km/h into meters/second.

17. Convert 2.155 m/s into kilometers/hour.

18. Use the formulas for converting degrees Fahrenheit into degrees Celsius to determine the relative size of the Fahrenheit degree over the Celsius degree.

19. Use the formulas for converting degrees Celsius into kelvins to determine the relative size of the Celsius degree over kelvins.

20. What is the mass of 12.67 L of mercury?

21. What is the mass of 0.663 m^3 of air?

22. What is the volume of 2.884 kg of gold?

23. What is the volume of 40.99 kg of cork? Assume a density of 0.22 g/cm^3.

ANSWERS

1. 3.42×10^{-18}

3. 602,200,000,000,000,000,000,000

5. 4.520×10^6

7. The quantity is two; dozen is the unit.

9. 1,000,000,000

11. 1/100,000,000

13. 18.7 m/s

15. 96.1 km/h

17. 14.47 m/s

19. One Fahrenheit degree is nine-fifths the size of a Celsius degree.

21. 1.72×10^5 g

23. 149 mL

CHAPTER 3:
ATOMS, MOLECULES, AND IONS

Opening Essay

Although not an SI unit, the angstrom (Å) is a useful unit of length. It is one ten-billionth of a meter, or 10^{-10} m. Why

is it a useful unit? The ultimate particles that compose all matter are about 10^{-10} m in size, or about 1 Å. This makes

the angstrom a natural—though not approved— unit for describing these particles.

The angstrom unit is named after Anders Jonas Ångström, a nineteenth-century Swedish physicist. Ångström's research dealt with light being emitted by glowing objects, including the sun. Ångström studied the brightness of the different colors of light that the sun emitted and was able to deduce that the sun is composed of the same kinds of matter that are present on the earth. By extension, we now know that all matter throughout the universe is similar to the matter that exists on our own planet.

Anders Jonas Ångstrom, a Swedish physicist, studied the light coming from the sun. His contributions to science were

sufficient to have a tiny unit of length named after him, the angstrom, which is one ten-billionth of a meter.
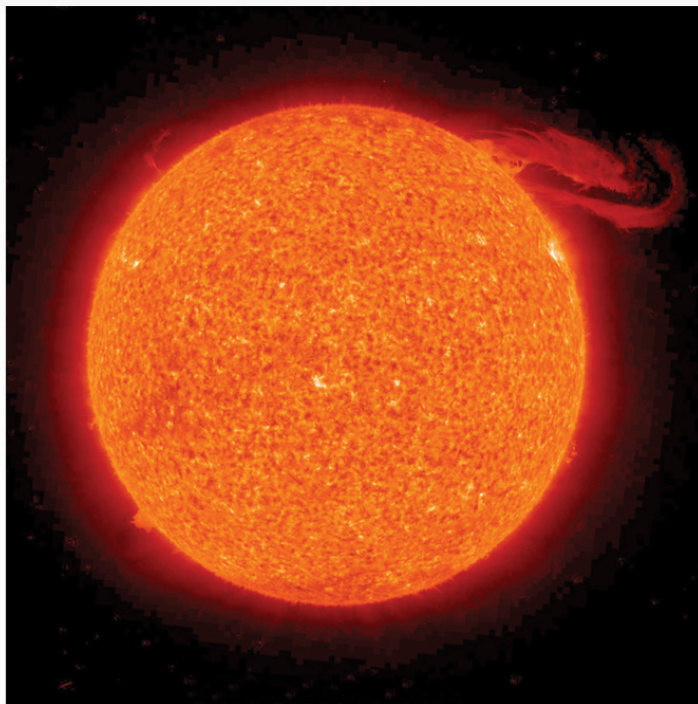
Source: Photo of the sun courtesy of NASA's Solar Dynamics Observatory

http://commons.wikimedia.org/wiki/File:The_Sun_by_the_Atmospheric_Imag[ing_Assembly_of_NASA%27s_So-](http://commons.wikimedia.org/wiki/File:The_Sun_by_the_Atmospheric_Imaging_Assembly_of_NASA%27s_Solar_Dynamics_Observatory_-_20100801.jpg)
[lar_Dynamics_Observatory_-_20100801.jpg](http://commons.wikimedia.org/wiki/File:The_Sun_by_the_Atmospheric_Imaging_Assembly_of_NASA%27s_Solar_Dynamics_Observatory_-_20100801.jpg).

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.

1. ATOMIC THEORY

LEARNING OBJECTIVES

1. State the modern atomic theory.

2. 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** 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 3.1 "Properties of the Three Subatomic Particles" summarizes the properties of these three subatomic particles.

Table 3.1 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** of the atom. 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. (See Figure 3.1 "The Structure of the Atom".)
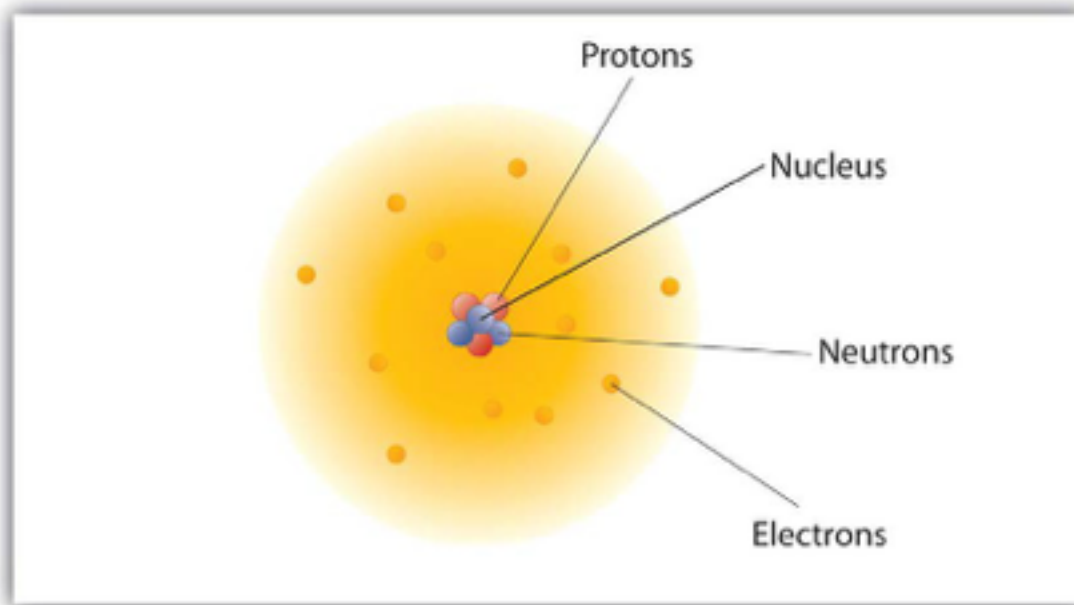
Figure 3.1 *The Structure of the Atom: Atoms have protons and neutrons in the center, making the nucleus, while the electrons orbit the nucleus.*

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** 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.

Test Yourself

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 3.2 "Names and Symbols of Common Elements" lists some common elements and their symbols. You should memorize the symbols in Table 3.2 "Names and Symbols of Common Elements", as this is how we will be representing elements throughout chemistry.

Table 3.2 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. A simple periodic table is shown in Figure 3.2 "A Simple Periodic Table", while a more extensive one is presented in Chapter 17 "Appendix: Periodic Table of the Elements". The elements on the periodic table are listed in order of ascending atomic number. The periodic table has a special shape that will become important to us when we consider the organization of electrons in atoms (see Chapter 8 "Electronic Structure"). 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 line splitting the right-hand part of the chart. All other elements are metals.

Figure 3.2 *A Simple Periodic Table*

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

$$^A_Z X$$

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

$$^{12}_6 C$$

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 26 F?

Solution

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

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

Test Yourself

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 an isotope of uranium that has 146 neutrons.

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.

EXERCISES

1. List the three statements that make up the modern atomic theory.

2. Explain how atoms are composed.

3. Which is larger, a proton or an electron?

4. Which is larger, a neutron or an electron?

5. What are the charges for each of the three subatomic particles?

6. Where is most of the mass of an atom located?

7. Sketch a diagram of a boron atom, which has five protons and six neutrons in its nucleus.

8. Sketch a diagram of a helium atom, which has two protons and two neutrons in its nucleus.

9. Define *atomic number*. What is the atomic number for a boron atom?

10. What is the atomic number of helium?

11. Define *isotope* and give an example.

12. What is the difference between deuterium and tritium?

13. Which pair represents isotopes?
    A. 26 F and 25 M

    B. 14 S and 15 P

14. Which pair represents isotopes?
    A. 20 C and 19 K

    B. 26 F and 26 F

    C. 92 U and 92 U

15. Give complete symbols of each atom, including the atomic number and the mass number.
    A. an oxygen atom with 8 protons and 8 neutrons

    B. a potassium atom with 19 protons and 20 neutrons

    C. a lithium atom with 3 protons and 4 neutrons

16. Give complete symbols of each atom, including the atomic number and the mass number.

    A. a magnesium atom with 12 protons and 12 neutrons

    B. a magnesium atom with 12 protons and 13 neutrons

    C. a xenon atom with 54 protons and 77 neutrons

17. Americium-241 is an isotope used in smoke detectors. What is the complete symbol for this isotope?

18. Carbon-14 is an isotope used to perform radioactive dating tests on previously living material. What is the complete symbol for this isotope?

19. Give atomic symbols for each element.
   A. sodium

   B. argon

   C. nitrogen

   D. radon

20. Give atomic symbols for each element.

   A.silver

   B.gold

   C.mercury

   D.iodine

21. Give the name of the element.

   A.Si

   B.Mn

   C.Fe

   D.Cr

22. Give the name of the element.

   A. F

   B. Cl

   C. Br

   D. I

ANSWERS

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

3. A proton is larger than an electron.

5. proton: 1+; electron: 1–; neutron: 0

7.

9. The atomic number is the number of protons in a nucleus. Boron has an atomic number of five.

11. Isotopes are atoms of the same element but with different numbers of neutrons.   and   are examples.

A.   isotopes

B.   not isotopes

C.   not isotopes

15.
A. a.

B. b. 19 K c.

17. . 95 A

19.
a.   Na
b.   Ar
c.   N
d.   Rn

21.
v.   silicon
w.   manganese
x.   iron
y.   chromium

2. MOLECULES AND NOMENCLATURE

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. Some elements exist naturally as molecules. For example, hydrogen and oxygen exist as two-atom molecules. Other elements also exist naturally as **diatomic molecules** (see Table 3.3 "Elements That Exist as Diatomic Molecules"). 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. 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 (see Figure 3.3 "Molecular Art of S"). 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.

Table 3.3 Elements That Exist as Diatomic Molecules

Hydrogen
Oxygen
Nitrogen
Fluorine
Chlorine
Bromine
Iodine
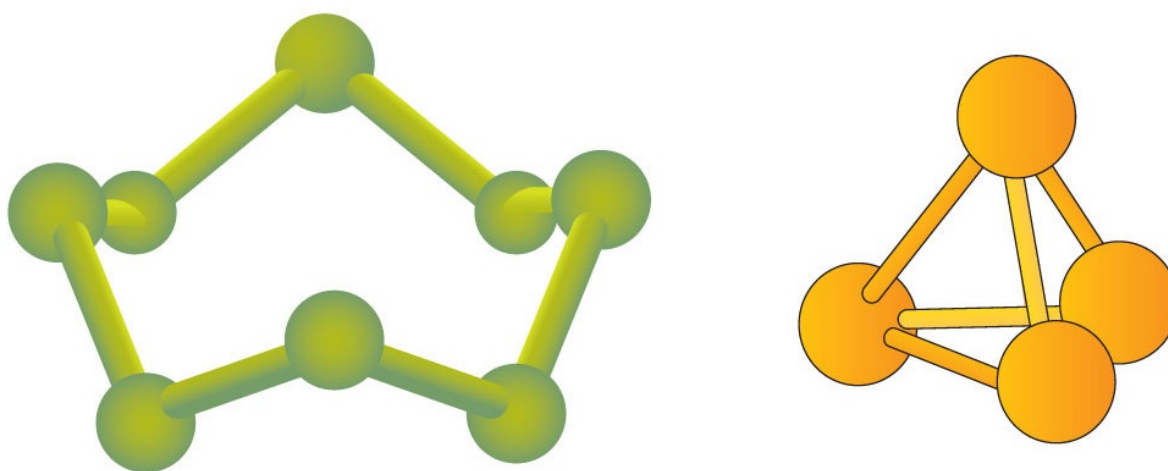
Figure 3.3: *Molecular Art of S8 and P4 Molecules - If each green ball represents a sulfur atom, then the diagram on the left represents an S8 molecule. The molecule on the right shows that one form of elemental phosphorus exists, as a four-atom molecule.*

Figure 3.3 "Molecular Art of S" 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**. In Chapter 9 "Chemical Bonds", 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 "Ions and Ionic Compounds".) 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. This is why you need to know the names and symbols of the elements in Table 3.2 "Names and Symbols of Common Elements".

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 3.4 "Numerical Prefixes Used in Naming Molecular Compounds". *Do not use the prefix* mono- *if there is only one atom of the first element.*

Table 3.4 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-

1. Name the second element by using three pieces:

   a. a numerical prefix indicating the number of atoms of the second element, plus

   b. the stem of the element name (e.g., *ox* for oxygen, *chlor* for chlorine, etc.), plus

   c. the suffix *-ide*.

2. Combine the two words, leaving a space between them.

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 3.4 "Numerical Prefixes Used in Naming Molecular Compounds") 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.

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 mol-

ecule. 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 3

a. A compound with one carbon atom and one oxygen atom is properly called carbon monoxide, not carbon monooxide.

b. There are two atoms of each element, selenium and bromine. According to the rules, the proper name here is *diselenium dibromide*.

Test Yourself

Name each molecule.

a. SF_4

b. P_2S_5

Answers

a. sulfur tetrafluoride

b. diphosphorus pentasulfide

EXAMPLE 4

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.

Test Yourself

Give the formula for each molecule.
a. disulfur difluoride

b. iodine pentabromide

Answers
a. S_2F_2

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.

EXERCISES

1. Which of these formulas represent molecules? State how many atoms are in each molecule.
   A. Fe

   B. PCl_3

   C. P_4

   D. Ar

2. Which of these formulas represent molecules? State how many atoms are in each molecule.
   A. I_2

   B. He

   C. H_2O

   D. Al

3. What is the difference between CO and Co?

4. What is the difference between H_2O and H_2O_2 (hydrogen peroxide)?

5. Give the proper formula for each diatomic element.

6. In 1986, when Halley's comet last passed the earth, astronomers detected the presence of S_2 in their telescopes. Why is sulfur not considered a diatomic element?

7. What is the stem of fluorine used in molecule names? CF_4 is one example.

8. What is the stem of selenium used in molecule names? $SiSe_2$ is an example.

9. Give the proper name for each molecule.
   A. PF_3

   B. $TeCl_2$

   C. N_2O_3

10. Give the proper name for each molecule.
    A. NO

    B. CS_2

    C. As_2O_3

11. Give the proper name for each molecule.
    A. XeF_2

    B. O_2F_2

    C. SF_6

12. Give the proper name for each molecule.
    A. P_4O_{10}

    B. B_2O_3

    C. P_2S_3

13. Give the proper name for each molecule.
    A. N_2O

    B. N_2O_4

    C. N_2O_5

ANSWERS

1.
A. not a molecule

B. a molecule; four atoms total

C. a molecule; four atoms total

D. not a molecule

3. CO is a compound of carbon and oxygen; Co is the element cobalt.

5. H_2, O_2, N_2, F_2, Cl_2, Br_2, I_2

7. *fluor-*

9.
A. phosphorus trifluoride

B. tellurium dichloride

C. dinitrogen trioxide

11.
A.   xenon difluoride

B.   dioxygen difluoride

C.   sulfur hexafluoride

13.
A. dinitrogen monoxide

B. dinitrogen tetroxide

C. dinitrogen pentoxide

15.
A.   a. N_2O_5

B. B_4C_3

C. PCl_5

17.
A.   a. O_2Cl_2

B. N_2S_3

C. XeF_4

19.
A.   a. IF_3

B. XeO_3

C. S_2F_{10}

3. MASSES OF ATOMS AND MOLECULES

LEARNING OBJECTIVE
1. 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.

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.

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) × 10 u	0.50 × 10 u	5.0 u
(50/100) × 11 u	0.50 × 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) × 10 u	0.20 × 10 u	2.0 u
(80/100) × 11 u	0.80 × 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 3.5 "Selected Atomic Masses of Some Elements" lists the atomic masses of some elements; a more expansive table is in Chapter 17 "Appendix: Periodic Table of the Elements". The atomic masses in Table 3.5 "Selected Atomic Masses of Some Elements" 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 3.5 Selected Atomic Masses of Some Elements

Element Name	Atomic Mass (u)		Element Name	Atomic Mass (u)
Aluminum	26.981		Molybdenum	95.94
Argon	39.948		Neon	20.180
Arsenic	74.922		Nickel	58.693
Barium	137.327		Nitrogen	14.007
Beryllium	9.012		Oxygen	15.999
Bismuth	208.980		Palladium	106.42
Boron	10.811		Phosphorus	30.974
Bromine	79.904		Platinum	195.084
Calcium	40.078		Potassium	39.098
Carbon	12.011		Radium	n/a
Chlorine	35.453		Radon	n/a
Cobalt	58.933		Rubidium	85.468
Copper	63.546		Scandium	44.956

Fluorine	18.998		Selenium	78.96
Gallium	69.723		Silicon	28.086
Germanium	72.64		Silver	107.868
Gold	196.967		Sodium	22.990
Helium	4.003		Strontium	87.62
Hydrogen	1.008		Sulfur	32.065
Iodine	126.904		Tantalum	180.948
Iridium	192.217		Tin	118.710
Iron	55.845		Titanium	47.867
Krypton	83.798		Tungsten	183.84
Lead	207.2		Uranium	238.029
Lithium	6.941		Xenon	131.293
Magnesium	24.305		Zinc	65.409
Manganese	54.938		Zirconium	91.224
Mercury	200.59		Molybdenum	95.94
Note: Atomic mass is given to three decimal places, if known.				

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:

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 N2O3

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

EXAMPLE 5

What is the molecular mass of each substance?

    a. NBr_3

    b. C_2H_6

Solution

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

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

The compound C_2H_6 also has a common name—ethane.

Test Yourself

What is the molecular mass of each substance?

    a. SO_2

    b. PF_3

Answers

    a. 64.063 u

    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.

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).
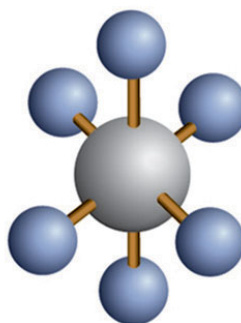
(a) (b) (c)

Figure 3.4: 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 SF6. (c) A high-voltage electrical switchgear assembly that would be filled with SF6 as a spark suppressant.

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.

EXERCISES

1. Define *atomic mass unit*. What is its abbreviation?

2. Define *atomic mass*. What is its unit?

3. Estimate the mass, in whole numbers, of each isotope.
   A. hydrogen-1

   B. hydrogen-3

   C. iron-56

4. Estimate the mass, in whole numbers, of each isotope.
   A. phosphorus-31

   B. carbon-14

   C. americium-241

5. Determine the atomic mass of each element, given the isotopic composition.
   a. lithium, which is 92.4% lithium-7 (mass 7.016 u) and 7.60% lithium-6 (mass 6.015 u)
   b. oxygen, which is 99.76% oxygen-16 (mass 15.995 u), 0.038% oxygen-17 (mass 16.999 u), and 0.205% oxygen-18 (mass 17.999 u)

6. Determine the atomic mass of each element, given the isotopic composition.

   A. neon, which is 90.48% neon-20 (mass 19.992 u), 0.27% neon-21 (mass 20.994 u), and 9.25% neon-22 (mass 21.991 u)

   B. uranium, which is 99.27% uranium-238 (mass 238.051 u) and 0.720% uranium-235 (mass 235.044 u)

7. How far off would your answer be from Exercise 5a if you used whole-number masses for individual isotopes of lithium?

8. How far off would your answer be from Exercise 6b if you used whole-number masses for individual isotopes of uranium?

9. What is the atomic mass of an oxygen atom?

10. What is the molecular mass of oxygen in its elemental form?

11. What is the atomic mass of bromine?

12. What is the molecular mass of bromine in its elemental form?

13. Determine the mass of each substance.
    A. F_2

    B. CO

    C. CO_2

16. Determine the mass of each substance.
   A.Kr

   B.KrF_4

   C.PF_5

17. Determine the mass of each substance.
   A. Na

   B. B_2O_3

   C. S_2Cl_2

18. Determine the mass of each substance.
   A. IBr_3

   B. N_2O_5

   C. CCl_4

19. Determine the mass of each substance.
   A. GeO_2

   B. IF_3

   C. XeF_6

20. Determine the mass of each substance.
   A. NO

   B. N_2O_4

   C. B_2O_3

   D. S_2Cl_2

21. Determine the mass of each substance.
   A. IBr_3

   B. N_2O_5

   C. CCl_4

22. Determine the mass of each substance.
   A. GeO_2

   B. IF_3

   C. XeF_6

23. Determine the mass of each substance.
   A. NO

   B. N_2O_4

   C. Ca

4. IONS AND IONIC COMPOUNDS

LEARNING OBJECTIVES

1. Know how ions form.

2. Learn the characteristic charges that ions have.

3. Construct a proper formula for an ionic compound.

4. 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 called 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. Table 3.6 "Monatomic Ions of Various Charges" lists some common ions in terms of how many electrons they lose (making cations) or gain (making anions). There are several things to notice about the ions in Table 3.6 "Monatomic Ions of Various Charges". 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, 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 Table 3.6 "Monatomic Ions of Various Charges"to memory, you will always know what charges most atoms form. (In Chapter 9 "Chemical Bonds", we will discuss *why* atoms form the charges they do.)

Table 3.6 Monatomic Ions of Various Charges

Ions formed by losing a single electron	
	H^+
	Na^+
	K^+
	Rb^+
	Ag^+
	Au^+

Ions formed by losing two electrons	
	Mg^{2+}
	Ca^{2+}
	Sr^{2+}
	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 a single electron	F^-
	Cl^-
	Br^-
	I^-
Ions formed by gaining two electrons	O^{2-}
	S^{2-}
	Se^{2-}
Ions formed by gaining three electrons	N^{3-}
	P^{3-}

Third, there are some exceptions to the previous point. A few elements, all metals, can form more than one possible charge. For example, iron atoms can form 2+ cations or 3+ cations. Cobalt is another element that can form more than one possible charged ion (2+ and 3+), while lead 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 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 paren-

theses 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 6

Test Yourself

a. P^{3-}

b. Sr^{2+}

Answers

a. the strontium cation
b. the phosphide anion

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. 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 3.5 "NaCl = Table Salt").

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. For the ionic compound between Mg^{2+} ions and Cl^- ions, we now consider the fact that the charges

Figure 3.5: *NaCl = Table Salt © Thinkstock The ionic compound NaCl is very common.*

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 7

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 .

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 8

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.

Test Yourself

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 (Figure 3.2 "A Simple 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 3.7 "Common Polyatomic Ions" 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 3.7 Common Polyatomic Ions

Name	Formula and Charge
ammonium	NH_4^+
acetate	$C_2H_3O_2^-$, or CH_3COO^-
bicarbonate (hydrogen carbonate)	HCO_3^-
bisulfate (hydrogen sulfate)	HSO_4^-

carbonate	CO_3^{2-}
chlorate	ClO_3^{-}
chromate	CrO_4^{2-}
cyanide	CN^{-}
dichromate	$Cr_2O_7^{2-}$
hydroxide	OH^{-}
nitrate	NO_3^{-}
nitrite	NO_2^{-}
peroxide	O_2^{2-}
perchlorate	ClO_4^{-}
phosphate	PO_4^{3-}
sulfate	SO_4^{2-}
sulfite	SO_3^{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 9

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 3.8 "Some Sodium Compounds Added to Food" 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.

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.

Table 3.8 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 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

Figure 3.6: *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.

EXERCISES

1. Explain how cations form.

1. Explain how anions form.

2. Give the charge each atom takes when it forms an ion

A. K

B. O

C. Co

1. Ca

2. I

3. Fe

a K^+ and S^{2-}

a Ag^+ and Br^-

a Sr^{2+} and N^{3-}

a. Give the formula and name for each ionic compound formed between the two listed ions.

a. Cu^{2+} and F^-

b. Ca^{2+} and O^{2-}

c. K^+ and P^{3-}

a. Give the formula and name for each ionic compound formed between the two listed ions.

a. Na^+ and N^{3-}

b. Co^{2+} and I^-

c. Au^{3+} and S^{2-}

a. Give the formula and name for each ionic compound formed between the two listed ions.
a. K^+ and SO_4

a. NH_4 and S

a. NH_4 and PO_4

a. Give the formula and name for each ionic compound formed between the two listed ions.
a. Ca^{2+} and NO_3

a. Ca^{2+} and NO_2

a. Sc^{3+} and $C_2H_3O_2$

a. Give the formula and name for each ionic compound formed between the two listed ions.

a. Pb^{4+} and $SO_4{}^{2-}$

a. Na^+ and I_3

a. Li^+ and Cr_2O_7

a. Give the formula and name for each ionic compound formed between the two listed ions.

a. $NH_4{}^+$ and N^{3-}

b. Mg^{2+} and $CO_3{}^{2-}$

a. Al^{3+} and OH^-

a. Give the formula and name for each ionic compound formed between the two listed ions.

a. Ag^+ and $SO_3{}^{2-}$

a. Na^+ and $HCO_3{}^-$

a. Fe^{3+} and $ClO_3{}^-$

a. Give the formula and name for each ionic compound formed between the two listed ions.

a. Rb^+ and O_2

a. Au^{3+} and $HSO_4{}^-$

a. Sr^{2+} and NO_2

a. What is the difference between SO_3 and $SO_3{}^{2-}$?

a. What is the difference between NO_2 and $NO_2{}^-$?

b. Cations form by losing electrons.

3. a. 1+

b. 2−

c. 2+, 3+

5. a. 1+

b. 1+, 3+

b. 1−

b. a. the potassium ion

c. the oxide ion

d. the cobalt(II) and cobalt(III) ions, respectively

b. a. the silver ion

c. the gold(I) and gold(III) ions, respectively

d. the bromide ion

b. a. magnesium chloride, $MgCl_2$

c. iron(II) oxide, FeO

d. iron(III) oxide, Fe_2O_3

b. a. copper(II) fluoride, CuF_2

c. calcium oxide, CaO

d. potassium phosphide, K_3P

15. a. potassium sulfate, K_2SO_4

b. ammonium sulfide, $(NH_4)_2S$

b. ammonium phosphate, $(NH_4)_3PO_4$

b. a. lead(IV) sulfate, $Pb(SO_4)_2$

c. sodium triiodide, NaI_3

d. lithium dichromate, $Li_2Cr_2O_7$

b. a. silver sulfite, Ag_2SO_3

c. sodium hydrogen carbonate, $NaHCO_3$

d. iron(III) chlorate, $Fe(ClO_3)_3$

21. SO_3 is sulfur trioxide, while SO_3^{2-} is the sulfite ion.

<table>
<tr><td colspan="2" align="center">LEARNING OBJECTIVES</td></tr>
<tr><td>1.</td><td>Define acid.</td></tr>
<tr><td>2.</td><td>Name a simple acid.</td></tr>
</table>

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. (We will expand on this definition in Chapter 12 "Acids and Bases".) 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 3.9 "Names and Formulas of Acids" 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 3.9 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 10

Name each acid without consulting Table 3.9 "Names and Formulas of Acids".

 a. HBr

 b. H_2SO_4

Solution

 a. 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.

 b. 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.

Test Yourself

Name each acid.

 a. HF

 b. HNO_2

Answers

 a. hydrofluoric acid

 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.

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.

1. Give the formula for each acid
    1. perchloric acid
    2. hydriodic acid
2. Give the formula for each acid

a. hydrosulfuric acid

b. phosphorous acid

a. Name each acid.

a. HF(aq)

b. HNO$_3$(aq)

c. H$_2$C$_2$O$_4$(aq)

a. Name each acid.

a. H$_2$SO$_4$(aq)

b. H$_3$PO$_4$(aq)

c. HCl(aq)

a. Name an acid found in food.

a. Name some properties that acids have in common.

ANSWERS

1. a. HClO$_4$(aq)

    b. HI(aq)

b. a. hydrofluoric acid

    c. nitric acid

    d. oxalic acid

5. oxalic acid (answers will vary)

5. END-OF-CHAPTER MATERIAL

ADDITIONAL EXERCISES

1. How many electrons does it take to make the mass of one proton?

2. How many protons does it take to make the mass of a neutron?

3. Dalton's initial version of the modern atomic theory says that all atoms of the same element are the same. Is this actually correct? Why or why not?

4. How are atoms of the same element the same? How are atoms of the same element different?

5. Give complete atomic symbols for the three known isotopes of hydrogen.

6. A rare isotope of helium has a single neutron in its nucleus. Write the complete atomic symbol of this isotope.

7. Use its place on the periodic table to determine if indium, In, atomic number 49, is a metal or a nonmetal.

8. Only a few atoms of astatine, At, atomic number 85, have been detected. On the basis of its position on the periodic table, would you expect it to be a metal or a nonmetal?

9. Americium-241 is a crucial part of many smoke detectors. How many neutrons are present in its nucleus.

10. Potassium-40 is a radioactive isotope of potassium that is present in the human body. How many neutrons are present in its nucleus?

11. Determine the atomic mass of ruthenium from the given abundance and mass data.

ANSWERS

1. about 1,800 electrons

3. It is not strictly correct because of the existence of isotopes.

5. H11, H12, and H13

7. It is a metal.

9. 146 neutrons

11. 101.065 u

13. 3.817×10^{-23} g

15. 2.991×10^{-23} g

17. ionic

19. a. Hg_2^{2+}

b. Hg_2Cl_2

21. uranyl fluoride, UO_2F_2; uranyl sulfate, UO_2SO_4; uranyl phosphate, $(UO_2)_3(PO_4)_2$

CHAPTER 4:

CHEMICAL REACTIONS AND EQUATIONS

Opening Essay

The space shuttle—and any other rocket-based system—uses chemical reactions to propel itself into space and maneuver itself when it gets into orbit. The rockets that lift the orbiter are of two different types. The three main engines are powered by reacting liquid hydrogen with liquid oxygen to generate water. Then there are the two solid rocket boosters, which use a solid fuel mixture that contains mainly ammonium perchlorate and powdered aluminum. The chemical reaction between these substances produces aluminum oxide, water, nitrogen gas, and hydrogen chloride. Although the solid rocket boosters each have a significantly lower mass than the liquid oxygen and liquid hydrogen tanks, they provide over 80% of the lift needed to put the shuttle into orbit—all because of chemical reactions.

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.

1. THE CHEMICAL EQUATION

LEARNING OBJECTIVES

1. Define chemical equation.
2. 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:

<div align="center">hydrogen reacts with oxygen to make water</div>

We can represent this chemical change more succinctly as

<div align="center">hydrogen + oxygen → water</div>

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

$$H_2 + O_2 \rightarrow H_2O$$

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:

$$H_2 + O_2 \rightarrow 2H_2O$$
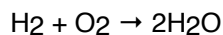
The 2 in front of the formula for water is called a **coefficient**. Now there is the same number of oxygen atoms in the reactants as there are in the product. But in satisfying the need for the same number of oxygen atoms on both sides of the reaction, we have also changed the number of hydrogen atoms 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:

$$2H_2 + O_2 \rightarrow 2H_2O$$
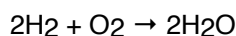
There are now four hydrogen atoms in the reactants and also four atoms of hydrogen in the product. There are two oxygen atoms in the reactants and two atoms of oxygen in the product. The law of conservation of matter has been satisfied. When the reactants and products of a chemical equation have the 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 1

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

a. Hydrogen and chlorine react to make HCl.
b. Ethane, C_2H_6, reacts with oxygen to make carbon dioxide and water.

Solution

a. 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: $H_2 + Cl_2 \rightarrow HCl$

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: $H_2 + Cl_2 \rightarrow 2HCl$

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

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

$$C_2H_6 + O_2 \rightarrow CO_2 + H_2O$$

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:

$$C_2H_6 + O_2 \rightarrow 2CO_2 + 3H_2O$$
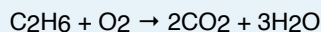
Now we have seven oxygen atoms in the products (four from the CO_2 and three from the H_2O). That means we need seven oxygen atoms in the reactants. However, because oxygen is a diatomic molecule, we can only get an even number of oxygen atoms at a time. We can achieve this by multiplying the other coefficients by 2:

$$2C_2H_6 + O_2 \rightarrow 4CO_2 + 6H_2O$$
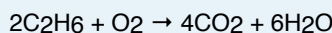
By multiplying everything else by 2, we don't unbalance the other elements, and we now get an even number of oxygen atoms in the product—14. We can get 14 oxygen atoms on the reactant side by having 7 oxygen molecules:

$$2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$$

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.

Test Yourself

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

Answer

$N_2 + 3H_2 \rightarrow 2NH_3$

113
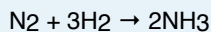
Many chemical equations also include phase labels for the substances: (s) for solid, (ℓ) for liquid, (g) for gas, and (aq) for aqueous (i.e., dissolved in water). Special conditions, such as temperature, may also be listed above the arrow. For example,

$$2NaHCO$$

KEY TAKEAWAYS

❖ A chemical equation is a concise description of a chemical reaction.

❖ Proper chemical equations are balanced.

EXERCISES

1. From the statement "nitrogen and hydrogen react to produce ammonia," identify the reactants and the products.

2. From the statement "sodium metal reacts with water to produce sodium hydroxide and hydrogen," identify the reactants and the products.

3. From the statement "magnesium hydroxide reacts with nitric acid to produce magnesium nitrate and water," identify the reactants and the products.

4. From the statement "propane reacts with oxygen to produce carbon dioxide and water," identify the reactants and the products.

5. Write and balance the chemical equation described by Exercise 1.

6. Write and balance the chemical equation described by Exercise 2.

7. Write and balance the chemical equation described by Exercise 3.

8. Write and balance the chemical equation described by Exercise 4. The formula for propane is C_3H_8.

9. Balance:_____$NaClO_3 \rightarrow$___$NaCl$ +_O_2

10. Balance:_____N_2 +_____$H_2 \rightarrow$____N_2H_4

11. Balance:_____Al +_____$O_2 \rightarrow$____Al_2O_3

12. Balance:_____C_2H_4 +__$O_2 \rightarrow$____CO_2 +_____H_2O

13. How would you write the balanced chemical equation in Exercise 12 if all the substances except water were gases and water itself were a liquid?

114

1. TYPES OF CHEMICAL REACTIONS:
SINGLE- AND DOUBLE-DISPLACEMENT REACTIONS

LEARNING OBJECTIVES

1. Recognize chemical reactions as single-replacement reactions and double-replacement reactions.

2. Use the periodic table, an activity series, or solubility rules to predict whether single- replacement reactions or double-replacement reactions will occur.

Up to 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. For example,

$$2HCl(aq) + Zn(s) \rightarrow ZnCl_2(aq) + H_2(g)$$
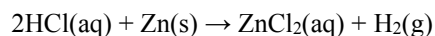
is an example of a single-replacement reaction. The hydrogen atoms in HCl are replaced by Zn atoms, and in the process a new element—hydrogen—is formed. Another example of a single-replacement reaction is

$$2NaCl(aq) + F_2(g) \rightarrow 2NaF(s) + Cl_2(g)$$
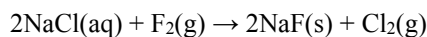
Here the negatively charged ion changes from chloride to fluoride. A typical characteristic of a single- replacement reaction is that there is one element as a reactant and another element as a product.

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 (see Figure 4.1 "Halogens on the Periodic Table"). 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

$$CaI_2(s) + Cl_2(g) \rightarrow CaCl_2(s) + I_2(s)$$
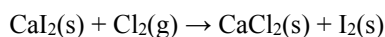
will occur, but the reaction

$$CaF_2(s) + Br_2(\ell) \rightarrow CaBr_2(s) + F_2(g)$$

115
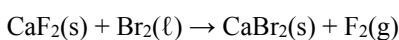
will not because bromine is below fluorine on the periodic table. This is just one of many ways the periodic table helps us understand chemistry.

Figure 4.1: *Halogens on the Periodic Table - The halogens are the elements in the next-to-last column on the periodic table.*

EXAMPLE 2

Will a single-replacement reaction occur? If so, identify the products.
1. $MgCl_2 + I_2 \rightarrow$?

2. $CaBr_2 + F_2 \rightarrow$?
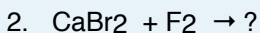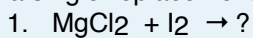
Solution
3. Because iodine is below chlorine on the periodic table, a single-replacement reaction will not occur.

4. 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.

Test Yourself

Will a single-replacement reaction occur? If so, identify the products.
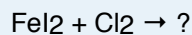
$FeI_2 + Cl_2 \rightarrow$?
Answer

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.

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 3

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.

Test Yourself

Use the activity series to predict the products, if any, of this equation.

$AlPO_4 + Mg \rightarrow$?

Answer

$Mg_3(PO_4)_2$ and Al
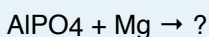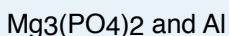
A double-replacement reaction occurs when parts of two ionic compounds are exchanged, making two new compounds. A characteristic of a double-replacement equation is that there are two compounds as reactants and two different compounds as products. An example is

$$CuCl_2(aq) + 2AgNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2AgCl(s)$$
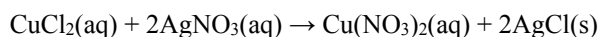
There are two equivalent ways of considering a double-replacement equation: either the cations are swapped, or the anions are swapped. (You cannot swap both; you would end up with the same substances you started with.) Either per-

spective 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 4

Predict the products of this double-replacement equation: $BaCl_2 + Na_2SO_4 \rightarrow$?

Solution

Thinking about the reaction as either switching the cations or switching the anions, we would expect the products to be $BaSO_4$ and $NaCl$.

Test Yourself

Predict the products of this double-replacement equation: $KBr + AgNO_3 \rightarrow$?

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 4.1 "Some Useful Solubility Rules"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 in Table 4.1 "Some Useful Solubility Rules". If a compound is soluble, we use the (aq) label with it, indicating 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 4.1 Some Useful Solubility Rules

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	Hg_2^{2+}, Pb^{2+}, Sr^{2+}, Ba^{2+}
These compounds generally do not dissolve in water (are insoluble):	**Exceptions:**
Compounds of CO_3 and PO_4	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

$$Na_2SO_4(aq) + SrCl_2(aq) \rightarrow 2NaCl(aq) + SrSO_4(s)$$
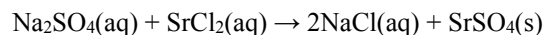
You would expect to see a visual change corresponding to $SrSO_4$ precipitating out of solution (Figure 4.2 "Double-Replacement Reactions").

Figure 4.2 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.

EXAMPLE 5

Will a double-replacement reaction occur? If so, identify the products.

1. $Ca(NO_3)_2 + KBr \rightarrow$?

2. $NaOH + FeCl_2 \rightarrow$?
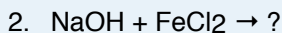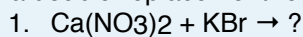
Solution

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

    $$2NaOH(aq) + FeCl_2(aq) \rightarrow 2NaCl(aq) + Fe(OH)_2(s)$$
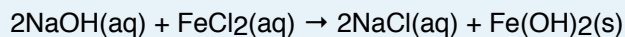
Test Yourself

Will a double-replacement equation occur? If so, identify the products.

$Sr(NO_3)_2 + KCl \rightarrow$?
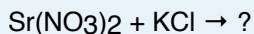
Answer

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.

EXERCISES

1. Assuming that each single-replacement reaction occurs, predict the products and write each balanced chemical equation.

   A. $Sn + H_2SO_4 \rightarrow$?

   B. $Al + NiBr_2 \rightarrow$?

2. Assuming that each single-replacement reaction occurs, predict the products and write each balanced chemical equation.

   A. $Mg + HCl \rightarrow$?

   B. $HI + Br_2 \rightarrow$?

3. Use the periodic table or the activity series to predict if each single-replacement reaction will occur and, if so, write a balanced chemical equation.

   A. $FeCl_2 + Br_2 \rightarrow$?

   B. $Fe(NO_3)_3 + Al \rightarrow$?

4. Use the periodic table or the activity series to predict if each single-replacement reaction will occur and, if so, write a balanced chemical equation.

   A. $Zn + Fe_3(PO_4)_2 \rightarrow$?

   B. $Ag + HNO_3 \rightarrow$?

5. Use the periodic table or the activity series to predict if each single-replacement reaction will occur and, if so, write a balanced chemical equation.

   A. $NaI + Cl_2 \rightarrow$?

   B. $AgCl + Au \rightarrow$?

6. Use the periodic table or the activity series to predict if each single-replacement reaction will occur and, if so, write a balanced chemical equation.

   A. $Pt + H_3PO_4 \rightarrow$?

   B. $Li + H_2O \rightarrow$? (Hint: treat H_2O as if it were composed of H^+ and OH^- ions.)

7. Assuming that each double-replacement reaction occurs, predict the products and write each balanced chemical equation.

   A. $Zn(NO_3)_2 + NaOH \rightarrow$?

   B. $HCl + Na_2S \rightarrow$?

8. Assuming that each double-replacement reaction occurs, predict the products and write each balanced chemical equation.

   A. $Ca(C_2H_3O_2)_2 + HNO_3 \rightarrow$?

   B. $Na_2CO_3 + Sr(NO_2)_2 \rightarrow$?

9. Assuming that each double-replacement reaction occurs, predict the products and write each balanced chemical equation.

   A. $Pb(NO_3)_2 + KBr \rightarrow$?

   B. $K_2O + MgCO_3 \rightarrow$?

10. Assuming that each double-replacement reaction occurs, predict the products and write each balanced chemical equation.

    A. $Sn(OH)_2 + FeBr_3 \rightarrow$?

    B. $CsNO_3 + KCl \rightarrow$?

11. Use the solubility rules to predict if each double-replacement reaction will occur and, if so, write a balanced chemical equation.

    A. $Pb(NO_3)_2 + KBr \rightarrow$?

    B. $K_2O + Na_2CO_3 \rightarrow$?

12. Use the solubility rules to predict if each double-replacement reaction will occur and, if so, write a balanced chemical equation.

  A. $Na_2CO_3 + Sr(NO_2)_2 \rightarrow$?

  B. $(NH_4)_2SO_4 + Ba(NO_3)_2 \rightarrow$?

13. Use the solubility rules to predict if each double-replacement reaction will occur and, if so, write a balanced chemical equation.

  A. $K_3PO_4 + SrCl_2 \rightarrow$?

  B. $NaOH + MgCl_2 \rightarrow$?

14. Use the solubility rules to predict if each double-replacement reaction will occur and, if so, write a balanced chemical equation.

  A. $KC_2H_3O_2 + Li_2CO_3 \rightarrow$?

  B. $KOH + AgNO_3 \rightarrow$?

ANSWERS

1. One element replaces another element in a compound.

3. a. $Zn + Fe(NO_3)_2 \rightarrow Zn(NO_3)_2 + Fe$

   b. $3F_2 + 2FeI_3 \rightarrow 3I_2 + 2FeF_3$

5. a. $Sn + H_2SO_4 \rightarrow SnSO_4 + H_2$

   b. $2Al + 3NiBr_2 \rightarrow 2AlBr_3 + 3Ni$

7. a. No reaction occurs.

   b. $Fe(NO_3)_3 + Al \rightarrow Al(NO_3)_3 + Fe$

9. a. $2NaI + Cl_2 \rightarrow 2NaCl + I_2$

   b. No reaction occurs.

11. a. $Zn(NO_3)_2 + 2NaOH \rightarrow Zn(OH)_2 + 2NaNO_3$

   b. $2HCl + Na_2S \rightarrow 2NaCl + H_2S$

13. a. $Pb(NO_3)_2 + 2KBr \rightarrow PbBr_2 + 2KNO_3$

   b. $K_2O + MgCO_3 \rightarrow K_2CO_3 + MgO$

15. a. $Pb(NO_3)_2 + 2KBr \rightarrow PbBr_2(s) + 2KNO_3$

   b. No reaction occurs.

17. a. $2K_3PO_4 + 3SrCl_2 \rightarrow Sr_3(PO_4)_2(s) + 6KCl$

   b. $2NaOH + MgCl_2 \rightarrow 2NaCl + Mg(OH)_2(s)$

2. IONIC EQUATIONS: A CLOSER LOOK

LEARNING OBJECTIVES

1. Write ionic equations for chemical reactions between ionic compounds.

2. 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 dissolving 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:

$$NaCl(s) \xrightarrow{H_2O} Na^+(aq) + Cl^-(aq)$$
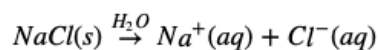
When NaCl dissolves in water, the ions separate and go their own way in solution; the ions are now written with their respective charges, and the (aq) phase label emphasizes that they are dissolved (Figure 3. "Ionic Solutions"). This process is called dissociation; we say that the ions *dissociate*.
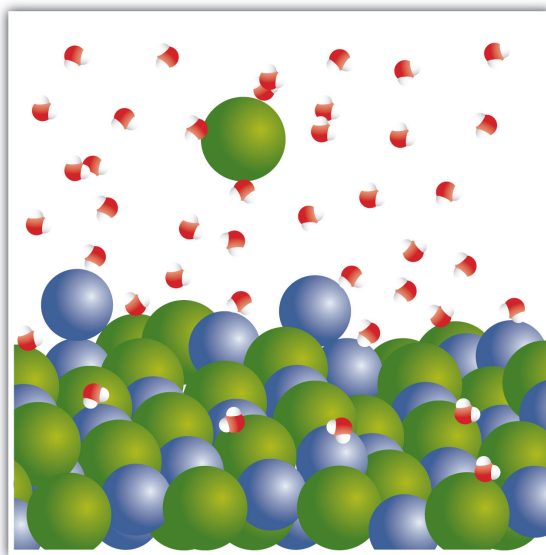
Figure 4.3: *Ionic Solutions - When an ionic compound dissociates in water, water molecules surround each ion and separate it from the rest of the solid. Each ion goes its own way in solution.*

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 CaCl2 dissolves, the one Ca^{2+} ion and the two Cl^- ions separate from each other:

$$CaCl_2(s) \xrightarrow{H_2O} Ca^{2+}(aq) + Cl^-(aq) + Cl^-(aq)$$

$$CaCl_2(s) \xrightarrow{H_2O} Ca^{2+}(aq) + 2Cl^-(aq)$$
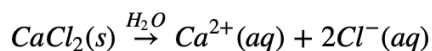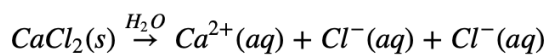
That is, the two chloride ions go off on their own. They do not remain as Cl_2 (that would be elemental chlorine; these are chloride ions); they do not stick together to make Cl_2^- or Cl_2^{2-}. They become dissociated ions in their own right. Polyatomic ions also retain their overall identity when they are dissolved.

EXAMPLE 6

Write the chemical equation that represents the dissociation of each ionic compound.

    a. KBr

    b. Na_2SO_4

Solution

    a. $KBr(s) \rightarrow K^+(aq) + Br^-(aq)$

    b. 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

$$Na_2SO_4(s) \rightarrow 2Na^+(aq) + SO_4^{2-}(aq)$$
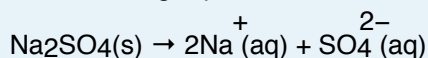
Test Yourself

Write the chemical equation that represents the dissociation of $(NH_4)_2S$.

Answer

$$(NH_4)_2S(s) \rightarrow 2NH_4^+(aq) + S^{2-}(aq)$$
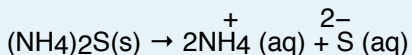
When chemicals in solution react, the proper way of writing the chemical formulas of the dissolved ionic compounds is in terms of the dissociated ions, not the complete ionic formula.

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 separated ions:

$$Na^+(aq) + Cl^-(aq) + Ag^+(aq) + NO_3^-(aq) \rightarrow AgCl(s) + Na^+(aq) + NO_3^-(aq)$$
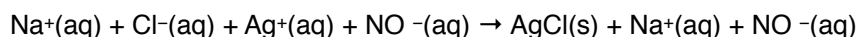
This is more representative of what is occurring in the solution.

EXAMPLE 7

Write the complete ionic equation for each chemical reaction.

    a. $KBr(aq) + AgC_2H_3O_2(aq) \rightarrow KC_2H_3O_2(aq) + AgBr(s)$

    b. $MgSO_4(aq) + Ba(NO_3)_2(aq) \rightarrow Mg(NO_3)_2(aq) + BaSO_4(s)$

Solution

For any ionic compound that is aqueous, we will write the compound as separated ions.

a. The complete ionic equation is

$$K^+(aq) + Br^-(aq) + Ag^+(aq) + C_2H_3O_2^-(aq) \rightarrow K^+(aq) + C_2H_3O_2^-(aq) + AgBr(s)$$

b. The complete ionic equation is

$$Mg^{2+}(aq) + SO_4^{2-}(aq) + Ba^{2+}(aq) + 2NO_3^-(aq) \rightarrow Mg^{2+}(aq) + 2NO_3^-(aq) + BaSO_4(s)$$
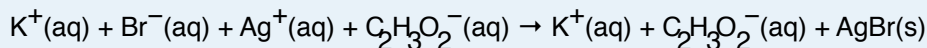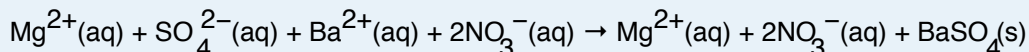
Test Yourself

Write the complete ionic equation for

$CaCl_2(aq) + Pb(NO_3)_2(aq) \rightarrow Ca(NO_3)_2(aq) + PbCl_2(s)$

Answer

$$Ca^{2+}(aq) + 2Cl^-(aq) + Pb^{2+}(aq) + 2NO_3^-(aq) \rightarrow Ca^{2+}(aq) + 2NO_3^-(aq) + PbCl_2(s)$$
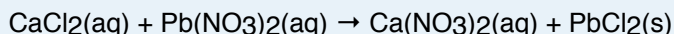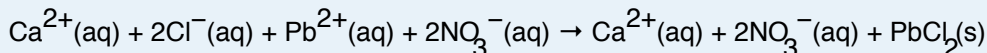
You may notice that in a complete ionic equation, some ions do not change their chemical form; they stay exactly the same on the reactant and product sides of the equation. For example, in

$$Na^+(aq) + Cl^-(aq) + Ag^+(aq) + NO^-(aq) \rightarrow AgCl(s) + Na^+(aq) + NO^-(aq)$$
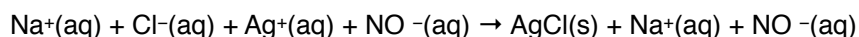
the $Ag^+(aq)$ and $Cl^-(aq)$ ions become $AgCl(s)$, but the $Na^+(aq)$ ions and the $NO_3^-(aq)$ ions stay as $Na^+(aq)$ ions and $NO_3^-(aq)$ ions. These two ions are examples of **spectator ions**, ions that do nothing in the overall course of a chemical reaction. They are present, but they do not 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:

$$\cancel{Na^+}(aq) + Cl^-(aq) + Ag^+(aq) + \cancel{NO_3^-}(aq) \rightarrow AgCl(s) + \cancel{Na^+}(aq) + \cancel{NO_3^-}(aq)$$
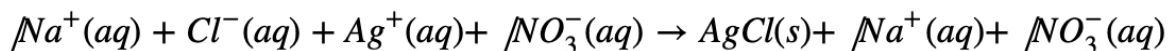
What remains when the spectator ions are removed is called the **net ionic equation**, which represents the actual chemical change occurring between the ionic compounds:

$$Cl^-(aq) + Ag^+(aq) \rightarrow AgCl(s)$$
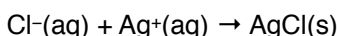
It is important to reiterate that the spectator ions are still present in solution, but they don't experience any net chemical change, so they are not written in a net ionic equation.

Write the net ionic equation for each chemical reaction:

a. $K^+(aq) + Br^-(aq) + Ag^+(aq) + C_2H_3O_2^-(aq) \rightarrow K^+(aq) + C_2H_3O_2^-(aq) + AgBr(s)$

b. $Mg^{2+}(aq) + SO_4^{2-}(aq) + Ba^{2+}(aq) + 2NO_3^-(aq) \rightarrow Mg^{2+}(aq) + 2NO_3^-(aq) + BaSO_4(s)$
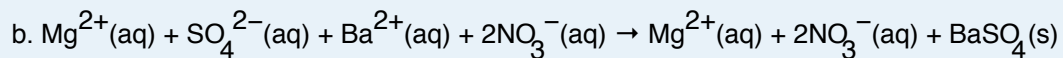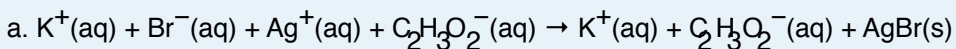
Solution

a. In the first equation, the $K^+(aq)$ and $C_2H_3O_2^-(aq)$ ions are spectator ions, so they are canceled:

$$\cancel{K^+(aq)} + Br^-(aq) + Ag^+(aq) + \cancel{C_2H_3O_2^-(aq)} \rightarrow K^+(aq) + \cancel{C_2H_3O_2^-(aq)} + AgBr(s)$$
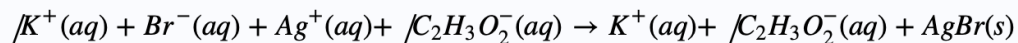
The net ionic equation is $Br^-(aq) + Ag^+(aq) \rightarrow AgBr(s)$

b. 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
$SO_4^{2-}(aq) + Ba^{2+}(aq) \rightarrow BaSO_4(s)$
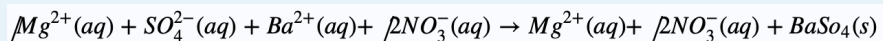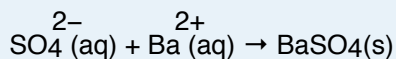
Test Yourself

Write the net ionic equation for
$CaCl_2(aq) + Pb(NO_3)_2(aq) \rightarrow Ca(NO_3)_2(aq) + PbCl_2(s)$

Answer

$Pb^{2+}(aq) + 2Cl^-(aq) \rightarrow PbCl_2(s)$
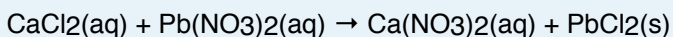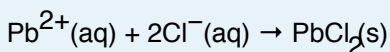
EXAMPLE 8

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 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. 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!

Fig. 4.4: The Grand Canyon © Thinkstock - *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.*

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.

EXERCISES

1. Write a chemical equation that represents $NaBr(s)$ dissociating in water.

2. Write a chemical equation that represents $SrCl_2(s)$ dissociating in water.

3. Write a chemical equation that represents $(NH_4)_3PO_4(s)$ dissociating in water.

4. Write a chemical equation that represents $Fe(C_2H_3O_2)_3(s)$ dissociating in water.

5. Write the complete ionic equation for the reaction of $FeCl_2(aq)$ and $AgNO_3(aq)$. You may have to consult the solubility rules.

6. Write the complete ionic equation for the reaction of $BaCl_2(aq)$ and $Na_2SO_4(aq)$. You may have to consult the solubility rules.

7. Write the complete ionic equation for the reaction of $KCl(aq)$ and $NaC_2H_3O_2(aq)$. You may have to consult the solubility rules.

8. Write the complete ionic equation for the reaction of $Fe_2(SO_4)_3(aq)$ and $Sr(NO_3)_2(aq)$. You may have to consult the solubility rules.

9. Write the net ionic equation for the reaction of $FeCl_2(aq)$ and $AgNO_3(aq)$. You may have to consult the solubility rules.

10. Write the net ionic equation for the reaction of $BaCl_2(aq)$ and $Na_2SO_4(aq)$. You may have to consult the solubility rules.

11. Write the net ionic equation for the reaction of $KCl(aq)$ and $NaC_2H_3O_2(aq)$. You may have to consult the solubility rules.

12. Write the net ionic equation for the reaction of $Fe_2(SO_4)_3(aq)$ and $Sr(NO_3)_2(aq)$. You may have to consult the solubility rules.

13. Identify the spectator ions in Exercises 9 and 10.

14. Identify the spectator ions in Exercises 11 and 12.
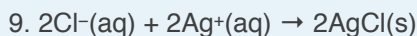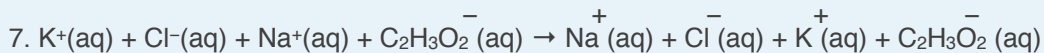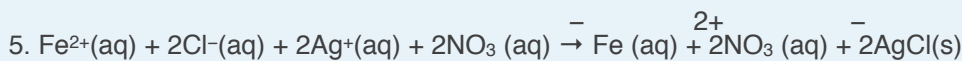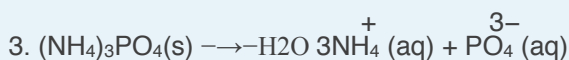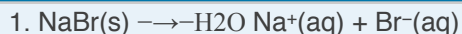
3. COMPOSITION, DECOMPOSITION, AND COMBUSTION REACTIONS

LEARNING OBJECTIVES

1. Recognize composition, decomposition, and combustion reactions.
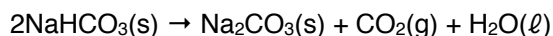
2. Predict the products of a combustion reaction.

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

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(\ell)$$
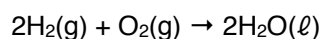
water is produced from hydrogen and oxygen. Although there are two molecules of water being produced, there is only one substance—water—as a product. So this is a composition reaction.

A **decomposition reaction** starts from a single substance and produces more than one substance; that is, it decomposes. One substance as a reactant and more than one substance as the products is the key characteristic of a decomposition reaction. For example, in the decomposition of sodium hydrogen carbonate (also known as sodium bicarbonate),

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(\ell)$$

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.

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:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$
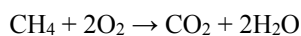
Kerosene can be approximated with the formula $C_{12}H_{26}$, and its combustion equation is

$$2C_{12}H_{26} + 37O_2 \rightarrow 24CO_2 + 26H_2O$$
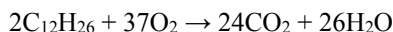
Sometimes fuels contain oxygen atoms, which must be counted when balancing the chemical equation. One common fuel is ethanol, C_2H_5OH, whose combustion equation is

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$$
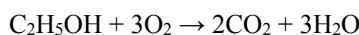
If nitrogen is present in the original fuel, it is converted to N_2, not to a nitrogen-oxygen compound. Thus, for the combustion of the fuel dinitroethylene, whose formula is $C_2H_2N_2O_4$, we have

$$2C_2H_2N_2O_4 + O_2 \rightarrow 4CO_2 + 2H_2O + 2N_2$$
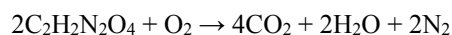
EXAMPLE 9

Complete and balance each combustion equation.

    a. the combustion of propane, C_3H_8

    b. the combustion of ammonia, NH_3

Solution

    c. The products of the reaction are CO_2 and H_2O, so our unbalanced equation is $C_3H_8 + O_2 \rightarrow CO_2 + H_2O$

        Balancing (and you may have to go back and forth a few times to balance this), we get

        $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$
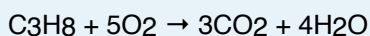
    d. The nitrogen atoms in ammonia will react to make N_2, while the hydrogen atoms will react with O_2 to make H_2O:
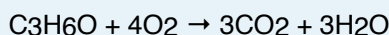
$$NH_3 + O_2 \rightarrow N_2 + H_2O$$
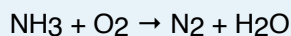
    To balance this equation without fractions (which is the convention), we get $4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$

Test Yourself

Complete and balance the combustion equation for cyclopropanol, C_3H_6O.

Answer

$C_3H_6O + 4O_2 \rightarrow 3CO_2 + 3H_2O$

EXERCISES

1.   Which is a composition reaction and which is not?
     A. $NaCl + AgNO_3 \rightarrow AgCl + NaNO_3$

     B. $CaO + CO_2 \rightarrow CaCO_3$

2.   Which is a composition reaction and which is not?
     A. $H_2 + Cl_2 \rightarrow 2HCl$

     B. $2HBr + Cl_2 \rightarrow 2HCl + Br_2$

3.   Which is a composition reaction and which is not?
     A. $2SO_2 + O_2 \rightarrow 2SO_3$

     B. $6C + 3H_2 \rightarrow C_6H_6$

4.   Which is a composition reaction and which is not?
     A. $4Na + 2C + 3O_2 \rightarrow 2Na_2CO_3$

     B. $Na_2CO_3 \rightarrow Na_2O + CO_2$

5.   Which is a decomposition reaction and which is not?

     A. $HCl + NaOH \rightarrow NaCl + H_2O$

     B. $CaCO_3 \rightarrow CaO + CO_2$

6.   Which is a decomposition reaction and which is not?

     A. $3O_2 \rightarrow 2O_3$

     B. $2KClO_3 \rightarrow 2KCl + 3O_2$

7.   Which is a decomposition reaction and which is not?

     A. $Na_2O + CO_2 \rightarrow Na_2CO_3$

     B. $H_2SO_3 \rightarrow H_2O + SO_2$

8.   Which is a decomposition reaction and which is not?

     A. $2C_7H_5N_3O_6 \rightarrow 3N_2 + 5H_2O + 7CO + 7C$

     B. $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$

9.   Which is a combustion reaction and which is not?

     A. $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$

     B. $2Fe_2S_3 + 9O_2 \rightarrow 2Fe_2O_3 + 6SO_2$

10. Which is a combustion reaction and which is not?

     A. $CH_4 + 2F_2 \rightarrow CF_4 + 2H_2$

     B. $2H_2 + O_2 \rightarrow 2H_2O$

11. Which is a combustion reaction and which is not?

    A. $P_4 + 5O_2 \rightarrow 2P_2O_5$

    B. $2Al_2S_3 + 9O_2 \rightarrow 2Al_2O_3 + 6SO_2$

12. Which is a combustion reaction and which is not?

    A. $C_2H_4 + O_2 \rightarrow C_2H_4O_2$

    B. $C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$

13. Is it possible for a composition reaction to also be a combustion reaction? Give an example to support your case.

14. Is it possible for a decomposition reaction to also be a combustion reaction? Give an example to support your case.

15. Complete and balance each combustion equation.

    a. $C_4H_9OH + O_2 \rightarrow$?

    b. $CH_3NO_2 + O_2 \rightarrow$?

16. Complete and balance each combustion equation.

    a. $B_2H_6 + O_2 \rightarrow$? (The oxide of boron formed is B_2O_3.)

    b. $Al_2S_3 + O_2 \rightarrow$? (The oxide of sulfur formed is SO_2.)

    c. $Al_2S_3 + O_2 \rightarrow$? (The oxide of sulfur formed is SO_3.)

ANSWERS

1. A. not composition

    B. composition

3. A. composition

    B. composition

5. A. not decomposition

    B. decomposition

7. A. not decomposition

    B. decomposition

9. A. combustion

    B. combustion

11. A. combustion

    B. combustion

13. Yes; $2H_2 + O_2 \rightarrow 2H_2O$ (answers will vary)

15. A. $C_4H_9OH + 6O_2 \rightarrow 4CO_2 + 5H_2O$

    B. $4CH_3NO_2 + 3O_2 \rightarrow 4CO_2 + 6H_2O + 2N_2$

4. NEUTRALIZATION REACTIONS

LEARNING OBJECTIVES

1. Identify an acid and a base.
2. Identify a neutralization reaction and predict its products.

In Chapter 3 "Atoms, Molecules, and Ions", Section 3.5 "Acids", 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 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

$$\text{acid} + \text{base} \rightarrow \text{water} + \text{salt}$$
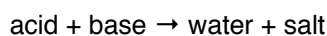
where the term salt is generally used to define any ionic compound (soluble or insoluble) that is formed from a reaction between an acid and a base. (In chemistry, the word *salt* refers to more than just table salt.) For example, the balanced chemical equation for the reaction between HCl(aq) and KOH(aq) is

$$HCl(aq) + KOH(aq) \rightarrow H_2O(\ell) + KCl(aq)$$
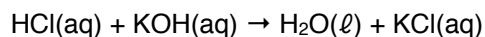
where the salt is KCl. By counting the number of atoms of each element, we find that only one water molecule is formed as a product. However, in the reaction between HCl(aq) and Mg(OH)2(aq), additional molecules of HCl and H2O are required to balance the chemical equation:

$$2HCl(aq) + Mg(OH)_2(aq) \rightarrow 2H_2O(\ell) + MgCl_2(aq)$$
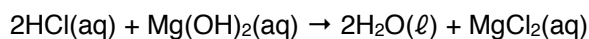
Here, the salt is MgCl2. (This is one of several reactions that take place when a type of antacid—a base—is used to treat stomach acid.)
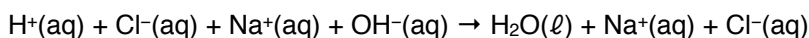
Neutralization reactions are one type of chemical reaction that proceeds even if one reactant is not in the aqueous phase. For example, the chemical reaction between HCl(aq) and Fe(OH)3(s) still proceeds according to the equation

$$3HCl(aq) + Fe(OH)_3(s) \rightarrow 3H_2O(\ell) + FeCl_3(aq)$$
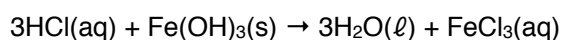
even though $Fe(OH)_3$ is not soluble. When one realizes that $Fe(OH)_3(s)$ is a component of rust, this explains why some cleaning solutions for rust stains contain acids—the neutralization reaction produces products that are soluble and wash away. (Washing with acids like HCl is one way to remove rust 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),

$$HCl(aq) + NaOH(aq) \rightarrow H_2O(\ell) + NaCl(aq)$$
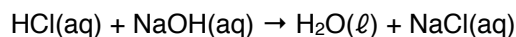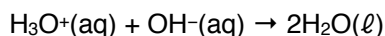
the complete ionic reaction is

$$H^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \rightarrow H_2O(\ell) + Na^+(aq) + Cl^-(aq)$$

The $Na^+(aq)$ and $Cl^-(aq)$ ions are spectator ions, so we can remove them to have

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(\ell)$$
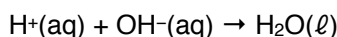
as the net ionic equation. If we wanted to write this in terms of the hydronium ion, $H_3O^+(aq)$, we would write it as

$$H_3O^+(aq) + OH^-(aq) \rightarrow 2H_2O(\ell)$$

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:

$$2H^+(aq) + 2Cl^-(aq) + Cr(OH)_2(s) \rightarrow 2H_2O(\ell) + Cr^{2+}(aq) + 2Cl^-(aq)$$
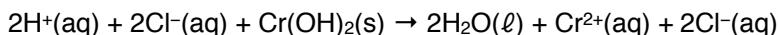
The chloride ions are the only spectator ions here, so the net ionic equation is

$$2H^+(aq) + Cr(OH)_2(s) \rightarrow 2H_2O(\ell) + Cr^{2+}(aq)$$
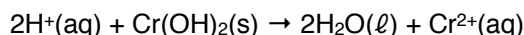
EXAMPLE 12

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 $2-C_2O_4$.)

Solution

The products of the neutralization reaction will be water and calcium oxalate:

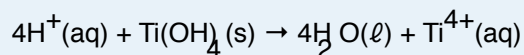$$H_2C_2O_4(s) + Ca(OH)_2(s) \rightarrow 2H_2O(\ell) + CaC_2O_4(s)$$
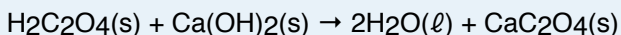
Because nothing is dissolved, there are no substances to separate into ions, so the net ionic equation is the equation of the three solids and one liquid.

Test Yourself

What is the net ionic equation between $HNO_3(aq)$ and $Ti(OH)_4(s)$?

Answer

$$4H^+(aq) + Ti(OH)_4(s) \rightarrow 4H_2O(\ell) + Ti^{4+}(aq)$$

Acid Name	Acid Formula	Use and Appearance
acetic acid	$HC_2H_3O_2$	flavoring; found in vinegar
adipic acid	$H_2C_6H_8O_4$	flavoring; found in processed foods and some antacids
alginic acid	various	thickener; found in drinks, ice cream, and weight loss products
ascorbic acid	$HC_6H_7O_6$	antioxidant, also known as vitamin C; found in fruits and vegetables
benzoic acid	$HC_6H_5CO_2$	preservative; found in processed foods
citric acid	$H_3C_6H_5O_7$	flavoring; found in citrus fruits
dehydroacetic acid	$HC_8H_7O_4$	preservative, especially for strawberries and squash
erythrobic acid	$HC_6H_7O_6$	antioxidant; found in processed foods
fatty acids	various	thickener and emulsifier; found in processed foods
fumaric acid	$H_2C_4H_2O_4$	flavoring; acid reactant in some baking powders
glutamic acid	$H_2C_5H_7NO_4$	flavoring; found in processed foods and in tomatoes, some cheeses, and
lactic acid	$HC_3H_5O_3$	flavoring; found in wine, yogurt, cottage cheese, and other sour milk pro
malic acid	$H_2C_4H_4O_5$	flavoring; found in apples and unripe fruit
phosphoric acid	H_3PO_4	flavoring; found in some colas
propionic acid	$HC_3H_5O_2$	preservative; found in baked goods
sorbic acid	$HC_6H_7O_2$	preservative; found in processed foods
stearic acid	$HC_{18}H_{35}O_2$	anticaking agent; found in hard candies
succinic acid	$H_2C_4H_4O_4$	flavoring; found in wine and beer
tartaric acid	$H_2C_4H_4O_6$	flavoring; found in grapes, bananas, and tamarinds

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.
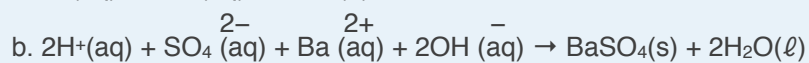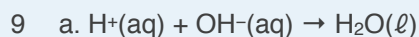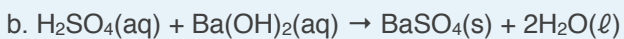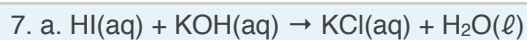
EXERCISES

1. What is the Arrhenius definition of an acid?

2. What is the Arrhenius definition of a base?

3. Predict the products of each acid-base combination listed. Assume that a neutralization reaction occurs.

   1. HCl and KOH

   2. H_2SO_4 and KOH

   3. H_3PO_4 and $Ni(OH)_2$

4. Predict the products of each acid-base combination listed. Assume that a neutralization reaction occurs.

   1. HBr and $Fe(OH)_3$

   2. HNO_2 and $Al(OH)_3$

   3. $HClO_3$ and $Mg(OH)_2$

5. Write a balanced chemical equation for each neutralization reaction in Exercise 3.

6. Write a balanced chemical equation for each neutralization reaction in Exercise 4.

7. Write a balanced chemical equation for the neutralization reaction between each given acid and base. Include the proper phase labels.

   1. $HI(aq) + KOH(aq) \rightarrow$?

   2. $H_2SO_4(aq) + Ba(OH)_2(aq) \rightarrow$?

8. Write a balanced chemical equation for the neutralization reaction between each given acid and base. Include the proper phase labels.

   1. $HNO_3(aq) + Fe(OH)_3(s) \rightarrow$?

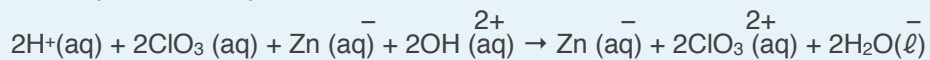   2. $H_3PO_4(aq) + CsOH(aq) \rightarrow$?

9. Write the net ionic equation for each neutralization reaction in Exercise 7.

10. Write the net ionic equation for each neutralization reaction in Exercise 8.

11. Write the complete and net ionic equations for the neutralization reaction between $HClO_3(aq)$ and $Zn(OH)_2(s)$. Assume the salt is soluble.

12. Write the complete and net ionic equations for the neutralization reaction between $H2C2O4(s)$ and $Sr(OH)2(aq)$. Assume the salt is insoluble.

13. Explain why the net ionic equation for the neutralization reaction between $HCl(aq)$ and $KOH(aq)$ is the same as the net ionic equation for the neutralization reaction between $HNO3(aq)$ and RbOH.

14. Write the complete and net ionic equations for the neutralization reaction between $HCl(aq)$ and $KOH(aq)$ using the hydronium ion in place of $H+$. What difference does it make when using the hydronium ion?

15. Write the complete and net ionic equations for the neutralization reaction between $HClO3(aq)$ and $Zn(OH)2(s)$ using the hydronium ion in place of $H+$. Assume the salt is soluble. What difference does it make when using the hydronium ion?

ANSWERS

1. An Arrhenius acid increases the amount of H^+ ions in an aqueous solution.

3.
  a. KCl and H_2O

  d. K_2SO_4 and H_2O

  e. $Ni_3(PO_4)_2$ and H_2O

5. a. HCl + KOH → KCl + H_2O

  b. H_2SO_4 + 2KOH → K_2SO_4 + $2H_2O$

  c. $2H_3PO_4$ + $3Ni(OH)_2$ → $Ni_3(PO_4)_2$ + $6H_2O$

7. a. $HI(aq) + KOH(aq) \rightarrow KCl(aq) + H_2O(\ell)$

   b. $H_2SO_4(aq) + Ba(OH)_2(aq) \rightarrow BaSO_4(s) + 2H_2O(\ell)$

9 a. $H^+(aq) + OH^-(aq) \rightarrow H_2O(\ell)$

   b. $2H^+(aq) + SO_4^{2-}(aq) + Ba^{2+}(aq) + 2OH^-(aq) \rightarrow BaSO_4(s) + 2H_2O(\ell)$

11. Complete ionic equation:

   $2H^+(aq) + 2ClO_3^-(aq) + Zn^{2+}(aq) + 2OH^-(aq) \rightarrow Zn^{2+}(aq) + 2ClO_3^-(aq) + 2H_2O(\ell)$

   Net ionic equation:

   $2H^+(aq) + 2OH^-(aq) \rightarrow 2H_2O(\ell)$
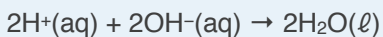
13. Because the salts are soluble in both cases, the net ionic reaction is just $H^+(aq) + OH^-(aq)$

   $\rightarrow H_2O(\ell)$.

15. Complete ionic equation:

   $H_3O^+(aq) + Cl^-(aq) + K^+(aq) + OH^-(aq) \rightarrow 2H_2O(\ell) + K^+(aq) + Cl^-(aq)$

   Net ionic equation: $H_3O^+(aq) + OH^-(aq) \rightarrow 2H_2O(\ell)$
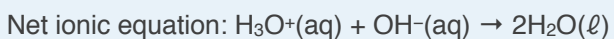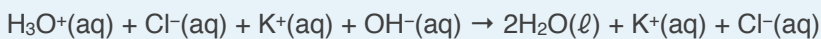
   The difference is simply the presence of an extra water molecule as a product.

5. OXIDATION-REDUCTION REACTIONS
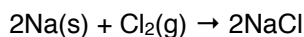
Consider this chemical reaction:

$$2Na(s) + Cl_2(g) \rightarrow 2NaCl$$

The reactants are elements, and it is assumed that they are electrically neutral; they have the same number of electrons as protons. The product, however, is ionic; it is composed of Na^+ and Cl^- ions. Somehow, the individual sodium atoms as reactants had to lose an electron to make the Na^+ ion, while the chlorine atoms as reactants had to each gain an electron to become the Cl^- ion. This reaction involves the transfer of electrons between atoms.

In reality, electrons are lost by some atoms and gained by other atoms 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. In reality, 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 an artificial count called the **oxidation number** to keep track of electrons in atoms. Oxidation numbers are assigned to atoms based on a series of rules. Oxidation numbers are not necessarily equal to the charge on the atom; we must keep the concepts of charge and oxidation numbers separate.

The rules for assigning oxidation numbers to atoms are as follows:

1. Atoms in their elemental state are assigned an oxidation number of 0.

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, which differentiates them from charges.

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).

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).

Let us work through a few examples for practice. In H_2, both hydrogen atoms have an oxidation number of 0, by rule 1. In NaCl, sodium has an oxidation number of +1, while chlorine has an oxidation number of −1, by rule 2. In H_2O, the hydrogen atoms each have an oxidation number of +1, while the oxygen has an oxidation number of −2, even though hydrogen and oxygen do not exist as ions in this compound as per rule 3. By contrast, by rule 3 in hydrogen peroxide (H_2O_2), each hydrogen atom has an oxidation number of +1, while each oxygen atom has an oxidation number of −1.

We can use rule 4 to determine oxidation numbers for the atoms in SO_2. Each oxygen 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 sulfur atom is assigned an oxidation number of +4. Does this mean that the sulfur atom has a 4+ charge on it? No, it only means that the sulfur atom is assigned a +4 oxidation number by our rules of apportioning electrons among the atoms in a compound.

EXAMPLE 13

The compound barium nitrate can be separated into two parts: the Ba^{2+} ion and the nitrate ion. Considering these separately, the Ba^{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 oxygens. According to rule 4, the sum of the oxidation number 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 nitrogen atom and −1 represents the charge on the species. Evaluating,

$$x + (-6) = -1 \quad x = +5$$

Thus, the oxidation number on the N atom in the nitrate ion is +5.

Test Yourself

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*. Oxidation and reduction are thus also defined in terms of increasing or decreasing oxidation numbers, respectively.

In this introduction to oxidation-reduction reactions, we are using straightforward examples. However, oxidation reactions can become quite complex; the following equation represents a redox reaction:

$$6H^+(aq) + 2MnO_4^-(aq) + 5H_2O_2(\ell) \longrightarrow 2Mn^{2+}(aq) + 5O_2(g) + 8H_2O(\ell)$$

ox #   +7   −1   +2   0
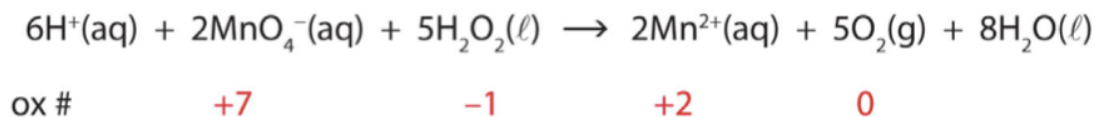
To demonstrate that this is a redox reaction, the oxidation numbers of the species being oxidized and reduced are listed; can you determine what is being oxidized and what is being reduced? This is also an example of a net ionic reaction; spectator ions that do not change oxidation numbers are not displayed in the equation.

- ❖ 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 of oxidation number (a loss of electrons); reduction is a decrease in oxidation number (a gain of electrons).

EXERCISES

1 Is

$$2K(s) + Br_2(\ell) \rightarrow 2KBr(s)$$
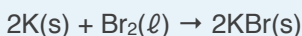
an oxidation-reduction reaction? Explain your answer.

2 Is the reaction

$$NaCl(aq) + AgNO_3(aq) \rightarrow NaNO_3(aq) + AgCl(s)$$
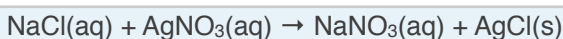
an oxidation-reduction reaction? Explain your answer.

3 In the reaction

$$2Ca(s) + O_2(g) \rightarrow 2CaO$$
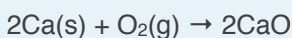
indicate what has lost electrons and what has gained electrons.

4 In the reaction

$$16Fe(s) + 3S_8(s) \rightarrow 8Fe_2S_3(s)$$
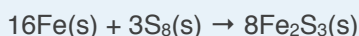
indicate what has lost electrons and what has gained electrons.

5 In the reaction

$$2Li(s) + O_2(g) \rightarrow Li_2O_2(s)$$
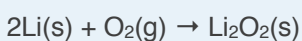
indicate what has been oxidized and what has been reduced.

6 In the reaction

$$2Ni(s) + 3I_2(s) \rightarrow 2NiI_3(s)$$
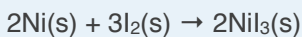
indicate what has been oxidized and what has been reduced.

7 What are two different definitions of oxidation?

8 What are two different definitions of reduction?

9 Assign oxidation numbers to each atom in each substance.

   a. P_4

   b. SO_2

   a. SO_2^{2-}

   b. $Ca(NO_3)_2$

142

10. Assign oxidation numbers to each atom in each substance.
    1. PF_5
    2. $(NH_4)_2S$
    3. Hg
    4. Li_2O_2 (lithium peroxide)

11. Assign oxidation numbers to each atom in each substance.
    1. CO
    2. CO_2
    3. $NiCl_2$
    4. $NiCl_3$

12. Assign oxidation numbers to each atom in each substance.
    1. NaH (sodium hydride)
    2. NO_2
    3.
    1. NO_2^-
    2. $AgNO_3$

13. Assign oxidation numbers to each atom in each substance.
    1. CH_2O
    2. NH_3
    3. Rb_2SO_4
    4. $Zn(C_2H_3O_2)_2$

14. Assign oxidation numbers to each atom in each substance.
    1. C_6H_6
    2. $B(OH)_3$
    3. Li_2S
    4. Au

15. Identify what is being oxidized and reduced in this redox equation by assigning oxidation numbers to the atoms.

$$2NO + Cl_2 \rightarrow 2NOCl$$

16. Identify what is being oxidized and reduced in this redox equation by assigning oxidation numbers to the atoms

$$Fe + SO_3 \rightarrow FeSO_3$$

17. Identify what is being oxidized and reduced in this redox equation by assigning oxidation numbers to the atoms.

$$2KrF_2 + 2H_2O \rightarrow 2Kr + 4HF + O_2$$
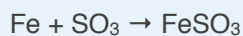
18. Identify what is being oxidized and reduced in this redox equation by assigning oxidation numbers to the atoms.

$$SO_3 + SCl_2 \rightarrow SOCl_2 + SO_2$$
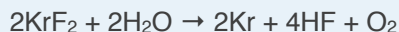
19. Identify what is being oxidized and reduced in this redox equation by assigning oxidation numbers to the atoms.

$$2K + MgCl_2 \rightarrow 2KCl + Mg$$
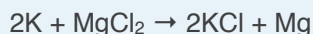
20. Identify what is being oxidized and reduced in this redox equation by assigning oxidation numbers to the atoms.

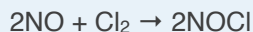$$C_7H_{16} + 11O_2 \rightarrow 7CO_2 + 8H_2O$$

ANSWERS

1. Yes; both K and Br are changing oxidation numbers.

3. Ca has lost electrons, and O has gained electrons.

5. Li has been oxidized, and O has been reduced.

7. loss of electrons; increase in oxidation number

9. a. P: 0

    b.   S: +4; O: –2

    c.   S: +2; O: –2

    d. Ca: 2+; N: +5; O: –2

11. a.   C: +2; O: –2

    b.   C: +4; O: –2

    c.   Ni: +2; Cl: –1

    d.   Ni: +3; Cl: –1

13. a. C: 0; H: +1; O: –2

    b. N: –3; H: +1

    c.   Rb: +1; S: +6; O: –2

    d. Zn: +2; C: 0; H: +1; O: –2

15. N is being oxidized, and Cl is being reduced.

17. O is being oxidized, and Kr is being reduced.

19. K is being oxidized, and Mg is being reduced.

6. END-OF-CHAPTER MATERIAL

1. Chemical equations can also be used to represent physical processes. Write a chemical reaction for the boiling of water, including the proper phase labels.

2. Chemical equations can also be used to represent physical processes. Write a chemical reaction for the freezing of water, including the proper phase labels.

3. Explain why $4Na(s) + 2Cl_2(g) \rightarrow 4NaCl(s)$ should not be considered a proper chemical equation.

4. Explain why $H_2(g) + 1/2O_2(g) \rightarrow H_2O(\ell)$ should not be considered a proper chemical equation.

5. Does the chemical reaction represented by $3Zn(s) + 2Al(NO_3)_3(aq) \rightarrow 3Zn(NO_3)_2(aq) + 2Al(s)$ proceed as written? Why or why not?

6. Does the chemical reaction represented by $2Au(s) + 2HNO_3(aq) \rightarrow 2AuNO_3(aq) + H_2(g)$ proceed as written? Gold is a relatively useful metal for certain applications, such as jewelry and electronics. Does your answer suggest why this is so?

7. Explain what is wrong with this double-replacement reaction. $NaCl(aq) + KBr(aq) \rightarrow NaK(aq) + ClBr(aq)$

8. Predict the products of and balance this double-replacement reaction. $Ag_2SO_4(aq) + SrCl_2(aq) \rightarrow$?

9. Write the complete and net ionic equations for this double-replacement reaction. $BaCl_2(aq) + Ag_2SO_4(aq) \rightarrow$?

10. Write the complete and net ionic equations for this double-replacement reaction. $Ag_2SO_4(aq) + SrCl_2(aq) \rightarrow$?

11. Identify the spectator ions in this reaction. What is the net ionic equation? $NaCl(aq) + KBr(aq) \rightarrow NaBr(aq) + KCl(aq)$

12. Complete this reaction and identify the spectator ions. What is the net ionic equation? $3H_2SO_4(aq) + 2Al(OH)_3(s) \rightarrow$?

13. Can a reaction be a composition reaction and a redox reaction at the same time? Give an example to support your answer.

14. Can a reaction be a combustion reaction and a redox reaction at the same time? Give an example to support your answer.

15. Can a reaction be a decomposition reaction and a redox reaction at the same time? Give an example to support your answer.

16. Can a reaction be a combustion reaction and a double-replacement reaction at the same time? Give an example to support your answer.

17. Why is CH_4 not normally considered an acid?

18. Methyl alcohol has the formula CH_3OH. Why would methyl alcohol not normally be considered a base?

19. What are the oxidation numbers of the nitrogen atoms in these substances?

   1. N_2

   2. NH_3

   3. NO

   4. N_2O

   5. NO_2

   6. N_2O_4

   7. N_2O_5

   8. $NaNO_3$

20. What are the oxidation numbers of the sulfur atoms in these substances?

   1. SF_6

   2. Na_2SO_4

   3. K_2SO_3

   4. SO_3

   5. SO_2

   6. S_8

   7. e. Na_2S

21. Disproportion is a type of redox reaction in which the same substance is both oxidized and reduced. Identify the element that is disproportionating and indicate the initial and final oxidation numbers of that element.
   $2CuCl(aq) \rightarrow CuCl_2(aq) + Cu(s)$

22. Disproportion is a type of redox reaction in which the same substance is both oxidized and reduced. Identify the element that is disproportionating and indicate the initial and final oxidation numbers of that element.
   $3Cl_2(g) + 6OH^-(aq) \rightarrow 5Cl^-(aq) + ClO_3 (aq) + 3H_2O(\ell)$
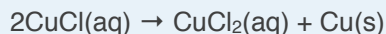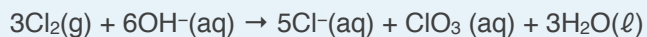
ANSWERS

1. $H_2O(\ell) \rightarrow H_2O(g)$

3. The coefficients are not in their lowest whole-number ratio.

5. No; zinc is lower in the activity series than aluminum.

7. In the products, the cation is pairing with the cation, and the anion is pairing with the anion.

9. Complete ionic equation: $Ba^{2+}(aq) + 2Cl^-(aq) + 2Ag^+(aq) + SO_4(aq) \rightarrow BaSO_4(s) + 2AgCl(s)$
   2–Net ionic equation: The net ionic equation is the same as the complete ionic equation.

11. Each ion is a spectator ion; there is no overall net ionic equation.

13. Yes; $H_2 + Cl_2 \rightarrow 2HCl$ (answers will vary)

15. Yes; $2HCl \rightarrow H_2 + Cl_2$ (answers will vary)

17. It does not increase the H^+ ion concentration; it is not a compound of H^+.

19. a. 0

    b. –3

    c. +2

    d. +1

    e. +4

    f. +4

    g. +5

    h. +5

21. Copper is disproportionating. Initially, its oxidation number is +1; in the products, its oxidation numbers are +2

    and 0, respectively.

CHAPTER 5:

STOICHIOMETRY AND THE MOLE

Opening Essay

At Contrived State University in Anytown, Ohio, a new building was dedicated in March 2010 to house the College of Education. The 100,000-square-foot building has enough office space to accommodate 86 full-time faculty members and 167 full-time staff.

In a fit of monetary excess, the university administration offered to buy new furniture (desks and chairs) and computer workstations for all faculty and staff members moving into the new building. However, to save on long-term energy and materials costs, the university offered to buy only 1 laser printer per 10 employees, with the plan to network the printers together.

How many laser printers did the administration have to buy? It is rather simple to show that 26 laser printers are needed for all the employees. However, what if a chemist was calculating quantities for a chemical reaction? Interestingly enough, similar calculations can be performed for chemicals as well as laser printers.

Figure 5.1 Outfitting a New Building

In filling a new office building with furniture and equipment, managers do calculations similar to those performed by scientists doing chemical reactions.

Source: Photo courtesy of Benjamin Benschneider, Cleveland State University.

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.

1. STOICHIOMETRY

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 H2. If the chemical reaction follows the balanced chemical equation

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(\ell)$$
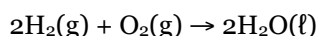
then what mass of oxygen do you need to make water?

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:

$$2 \text{ c mix} + 1 \text{ egg} + 1/2 \text{ c milk} \rightarrow 1 \text{ batch of pancakes}$$
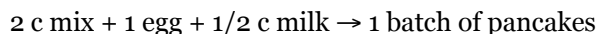
If you have 9 c of pancake mix, how many eggs and how much milk do you need? It might take a little bit of work, but eventually you will find you need 4½ eggs and 2¼ c milk.

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, similar to the way we constructed a conversion factor between feet and yards in - ball-ch02. 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:

$$2 \text{ c pancake mix} \Leftrightarrow 1 \text{ egg} \Leftrightarrow 1/2 \text{ c milk}$$
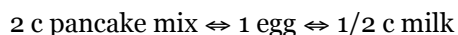
where ™ is the mathematical symbol for "is equivalent to." This does not mean that 2 c of pancake mix equal 1 egg.

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,

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

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:

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

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:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(\ell)$$
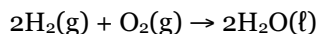
We can interpret this as, literally, "two hydrogen molecules react with one oxygen molecule to make two water molecules." That interpretation leads us directly to some equivalences, just as our pancake recipe did:

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

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:

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

Note how the unit *molecules H_2* 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.

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

$$Fe_2O_3(s) + 3SO_3(g) \rightarrow Fe_2(SO_4)_3$$
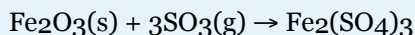
Solution

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

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

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

Test Yourself

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 $N_2 + 3H_2 \rightarrow 2NH_3$?

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:

$$\frac{2 \; atoms \; H}{1 \; molecule \; H_2O} \qquad \frac{1 \; molecule \; H_2O}{1 \; atom \; O}$$

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

EXAMPLE 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:

Test Yourself

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

Answer

259 molecules

KEY TAKEAWAY

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

EXERCISES

1. Think back to the pound cake recipe. What possible conversion factors can you construct relating the compo- nents of the recipe?

2. Think back to the pancake recipe. What possible conversion factors can you construct relating the components of the recipe?

3. What are all the conversion factors that can be constructed from the balanced chemical reaction $2H_2(g) + O_2(g) \rightarrow 2H_2O(\ell)$?

4. What are all the conversion factors that can be constructed from the balanced chemical reaction $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$?

5. Given the chemical equation $Na(s) + H_2O(\ell) \rightarrow NaOH(aq) + H_2(g)$
   1. Balance the equation.
   2. How many molecules of H_2 are produced when 332 atoms of Na react?

6. Given the chemical equation $S(s) + O_2(g) \rightarrow SO_3(g)$
   1. Balance the equation.
   2. How many molecules of O_2 are needed when 38 atoms of S react?

7. For the balanced chemical equation
   1. $6H^+(aq) + 2MnO_4^-(aq) + 5H_2O_2(\ell) \rightarrow 2Mn^{2+}(aq) + 5O_2(g) + 8H_2O(\ell)$
   2. how many molecules of H_2O are produced when 75 molecules of H_2O_2 react?

8. For the balanced chemical reaction $2C_6H_6(\ell) + 15O_2(g) \rightarrow 12CO_2(g) + 6H_2O(\ell)$ how many molecules of CO_2 are produced when 56 molecules of C_6H_6 react?

9. Given the balanced chemical equation $Fe_2O_3(s) + 3SO_3(g) \rightarrow Fe_2(SO_4)_3$ how many molecules of $Fe_2(SO_4)_3$ are produced if 321 atoms of S are reacted?

10. For the balanced chemical equation $CuO(s) + H_2S(g) \rightarrow CuS + H_2O(\ell)$, how many molecules of CuS are formed if 9,044 atoms of H react?

11. For the balanced chemical equation $Fe_2O_3(s) + 3SO_3(g) \rightarrow Fe_2(SO_4)_3$ suppose we need to make 145,000 molecules of $Fe_2(SO_4)_3$. How many molecules of SO_3 do we need?

12. One way to make sulfur hexafluoride is to react thioformaldehyde, CH_2S, with elemental fluorine: $CH_2S + 6F_2 \rightarrow CF_4 + 2HF + SF_6$. If 45,750 molecules of SF_6 are needed, how many molecules of F_2 are required?

13. Construct the three independent conversion factors possible for these two reactions
    1. $2H_2 + O_2 \rightarrow 2H_2O$
    2. $H_2 + O_2 \rightarrow H_2O_2$

14. Why are the ratios between H_2 and O_2 different?

15. The conversion factors are different because the stoichiometries of the balanced chemical reactions are different.

16. Construct the three independent conversion factors possible for these two reactions:
    1. $2Na + Cl_2 \rightarrow 2NaCl$
    2. $4Na + 2Cl_2 \rightarrow 4NaCl$

17. What similarities, if any, exist in the conversion factors from these two reactions?

ANSWERS

5. a. $2Na(s) + 2H_2O(\ell) \rightarrow 2NaOH(aq) + H_2(g)$

   b. 166 molecules

7. 120 molecules

9. 107 molecules

11. 435,000 molecules

2. THE MOLE

LEARNING OBJECTIVES

1. Describe the unit *mole*.

2. 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 don't 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. What we need is 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 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), which is also known as the *Avogadro constant*, after Amadeo Avogadro, an Italian chemist who first proposed its importance.

> *Test Yourself*
>
> 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:

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

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.

Test Yourself

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.

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:

Test Yourself

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 7

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

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

Test Yourself

If the density of benzene, C6H6, is 0.879 g/mL, how many moles are present in 17.9 mL of benzene?

Answer

0.201 mol

KEY TAKEAWAYS

❖   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.

EXERCISES

1. How many atoms are present in 4.55 mol of Fe?

2. How many atoms are present in 0.0665 mol of K?

3. How many molecules are present in 2.509 mol of H_2S?

4. How many molecules are present in 0.336 mol of acetylene (C_2H_2)?

5. How many moles are present in 3.55×10^{24} Pb atoms?

6. How many moles are present in 2.09×10^{22} Ti atoms?

7. How many moles are present in 1.00×10^{23} PF_3 molecules?

8. How many moles are present in 5.52×10^{25} penicillin molecules?

9. Determine the molar mass of each substance.

    1. Si

    2. SiH_4

    3. K_2O

10. Determine the molar mass of each substance.

    1. Cl_2

    2. $SeCl_2$

    3. $Ca(C_2H_3O_2)_2$

11. Determine the molar mass of each substance.

    1. Al

    2. Al_2O_3

    3. $CoCl_3$

12. Determine the molar mass of each substance.

    1. O_3

    2. NaI

    3. C12H22O11

13. What is the mass of 4.44 mol of Rb?

14. What is the mass of 0.311 mol of Xe?

15. What is the mass of 12.34 mol of $Al_2(SO_4)_3$?

16. What is the mass of 0.0656 mol of $PbCl_2$?

17. How many moles are present in 45.6 g of CO?

18. How many moles are present in 0.00339 g of LiF?

19. How many moles are present in 1.223 g of SF_6?

20. How many moles are present in 48.8 g of $BaCO_3$?

21. How many moles are present in 54.8 mL of mercury if the density of mercury is 13.6 g/mL?

22. How many moles are present in 56.83 mL of O_2 if the density of O_2 is 0.00133 g/mL?

ANSWERS

1. 2.74×10^{24} atoms

3. 1.511×10^{24} molecules

5. 5.90 mol

7. 0.166 mol

9. a.   28.086 g

    b.   32.118 g

    c.   94.195 g

11. a.   26.981 g

    b.   101.959 g

    c.   165.292 g

13. 379 g

15. 4,222 g

17. 1.63 mol

19. 0.008374 mol

21. 3.72 mol

3. THE MOLE IN CHEMICAL REACTIONS

LEARNING OBJECTIVES

1. Balance a chemical equation in terms of moles.

2. Use the balanced equation to construct conversion factors in terms of moles.

3. Calculate moles of one substance from moles of another substance using a balanced chemical equation.

Consider this balanced chemical equation:

$$2H_2 + O_2 \rightarrow 2H_2O$$
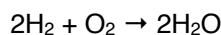
We interpret this as "two molecules of hydrogen react with one molecule of oxygen to make two molecules of water." The chemical equation is balanced as long as the coefficients are in the ratio 2:1:2. For instance, this chemical equation is also balanced:

$$100H_2 + 50O_2 \rightarrow 100H_2O$$
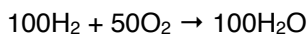
This equation is not conventional—because convention says that we use the lowest ratio of coefficients— but it is balanced. So is this chemical equation:

$$5,000H_2 + 2,500O_2 \rightarrow 5,000H_2O$$

Again, this is not conventional, but it is still balanced. Suppose we use a much larger number:

$$12.044 \times 10^{23}\ H_2 + 6.022 \times 10^{23}\ O_2 \rightarrow 12.044 \times 10^{23}\ H_2O$$
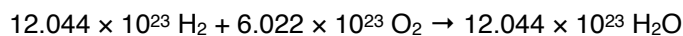
These coefficients are also in the ratio of 2:1:2. But these numbers are related to the number of things in a mole: the first and last numbers are two times Avogadro's number, while the second number is Avogadro's number. That means that the first and last numbers represent 2 mol, while the middle number is just 1 mol. Well, why not just use the number of moles in balancing the chemical equation?

$$2H_2 + O_2 \rightarrow 2H_2O$$
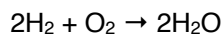
is the same balanced chemical equation we started with! What this means is that chemical equations are not just balanced in terms of molecules; *they are also balanced in terms of moles*. We can just as easily read this chemical equation as "two moles of hydrogen react with one mole of oxygen to make two moles of water." All balanced chemical reactions are balanced in terms of moles.

Test Yourself

Interpret this balanced chemical equation in terms of moles.
$$N_2 + 3H_2 \rightarrow 2NH_3$$
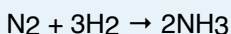
Answer

One mole of elemental nitrogen reacts with three moles of elemental hydrogen to produce two moles of ammonia.

In Chapter 4 "Chemical Reactions and Equations", Section 4.1 "The Chemical Equation", we stated that a chemical equation is simply a recipe for a chemical reaction. As such, chemical equations also give us equivalences—equivalences

between the reactants and the products. However, now we understand that these equivalences are expressed in terms of moles. Consider the chemical equation

$$2H_2 + O_2 \rightarrow 2H_2O$$
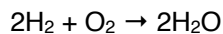
This chemical reaction gives us the following equivalences:

$$2 \text{ mol } H_2 \text{ ™ } 1 \text{ mol } O_2 \text{ ™ } 2 \text{ mol } H_2O$$
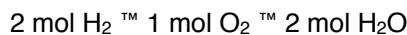
Any two of these quantities can be used to construct a conversion factor that lets us relate the number of moles of one substance to an equivalent number of moles of another substance. If, for example, we want to know how many moles of oxygen will react with 17.6 mol of hydrogen, we construct a conversion 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:

$$17.6 \text{ } \cancel{mol \, H_2} \times \frac{1 \text{ } mol \, O_2}{2 \text{ } \cancel{mol \, H_2}} = 8.80 \text{ } mol \, O_2$$

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 8

For the balanced chemical equation

$2C_4H_{10}(g) + 13O_2 \rightarrow 8CO_2(g) + 10H_2O(\ell)$
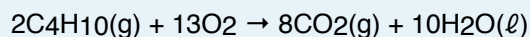
if 154 mol of O_2 are reacted, how many moles of CO_2 are produced?

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 mol O_2 ⇔ 8 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 don't contribute to the number of significant figures in the final answer.

Test Yourself
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.

EXERCISES

1. Express in mole terms what this chemical equation means. $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

2. Express in mole terms what this chemical equation means. $Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$

3. How many molecules of each substance are involved in the equation in Exercise 1 if it is interpreted in terms of moles?

4. How many molecules of each substance are involved in the equation in Exercise 2 if it is interpreted in terms of moles?

5. For the chemical equation $2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$ what equivalences can you write in terms of moles? Use the $\Leftrightarrow$ sign.

6. For the chemical equation $2Al + 3Cl_2 \rightarrow 2AlCl_3$ what equivalences can you write in terms of moles? Use the $\Leftrightarrow$ sign.

7. Write the balanced chemical reaction for the combustion of C_5H_{12} (the products are CO_2 and H_2O) and determine how many moles of H_2O are formed when 5.8 mol of O_2 are reacted.

8. Write the balanced chemical reaction for the formation of $Fe_2(SO_4)_3$ from Fe_2O_3 and SO_3 and determine how many moles of $Fe_2(SO_4)_3$ are formed when 12.7 mol of SO_3 are reacted.

9. For the balanced chemical equation $3Cu(s) + 2NO_3 (aq) + 8H (aq) \rightarrow 3Cu (aq) + 4H_2O(\ell) + 2NO(g)$ how many moles of Cu^{2+} are formed when 55.7 mol of H^+ are reacted?

10. For the balanced chemical equation $Al(s) + 3Ag^+(aq) \rightarrow Al^{3+}(aq) + 3Ag(s)$ how many moles of Ag are produced when 0.661 mol of Al are reacted?

11. For the balanced chemical reaction $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(\ell)$ how many moles of H_2O are produced when 0.669 mol of NH_3 react?

12. For the balanced chemical reaction $4NaOH(aq) + 2S(s) + 3O_2(g) \rightarrow 2Na_2SO_4(aq) + 2H_2O(\ell)$ how many moles of Na_2SO_4 are formed when 1.22 mol of O_2 react?

13. For the balanced chemical reaction $4KO_2(s) + 2CO_2(g) \rightarrow 2K_2CO_3(s) + 3O_2(g)$ determine the number of moles of both products formed when 6.88 mol of KO_2 react.

14. For the balanced chemical reaction $2AlCl_3 + 3H_2O(\ell) \rightarrow Al_2O_3 + 6HCl(g)$ determine the number of moles of both products formed when 0.0552 mol of $AlCl_3$ react.

4. MOLE-MASS AND MASS-MASS CALCULATIONS

LEARNING OBJECTIVES

1. From a given number of moles of a substance, calculate the mass of another substance involved using the balanced chemical equation.

2. From a given mass of a substance, calculate the moles of another substance involved using the balanced chemical equation.

3. 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

$$2Al + 3Cl_2 \rightarrow 2AlCl_3$$
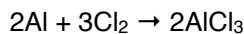
Suppose we know we have 123.2 g of Cl_2. How can we determine how many moles of $AlCl_3$ we will get when the reaction is complete? First and foremost, *chemical equations are not balanced in terms of grams; they are balanced in terms of moles*. So to use the balanced chemical equation to relate an amount 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:

$$123.2 \ g\ Cl_2 \times \frac{1 \ mol \ Cl_2}{70.90 \ g\ Cl_2} = 1.738 \ mol \ Cl_2$$

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 AlCl3 if we react 123.2 g of Cl2.

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 10

How many moles of HCl will be produced when 249 g of $AlCl_3$ are reacted according to this chemical equation?

$$2AlCl_3 + 3H_2O(\ell) \rightarrow Al_2O_3 + 6HCl(g)$$
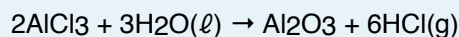
Solution

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:

$$249 \; g \, AlCl_3 \times \frac{1 \, mol \, AlCl_3}{133.33 \; g \, AlCl_3} = 1.87 \, mol \, AlCl_3$$

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:

Applying this conversion factor to the quantity of $AlCl_3$, we get

$$1.87 \; mol \, AlCl_3 \times \frac{6 \, mol \, HCl}{2 \; mol \, AlCl_3} = 5.61 \, mol \, HCl$$

Alternatively, we could have done this in one line:

$$249 \; g \, AlCl_3 \times \frac{1 \; mol \, AlCl_3}{133.33 \; g \, AlCl_3} \times \frac{6 \, mol \, HCl}{2 \; mol \, AlCl_3} = 5.60 \, mol \, HCl$$

The last digit in our final answer is slightly different because of rounding differences, but the answer is essentially the same.

Test Yourself

How many moles of Al_2O_3 will be produced when 23.9 g of H_2O are reacted according to this chemical equation?

$$2AlCl_3 + 3H_2O(\ell) \rightarrow Al_2O_3 + 6HCl(g)$$
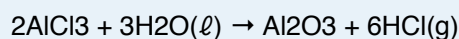
Answer

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 11

How many grams of NH3 will be produced when 33.9 mol of H2 are reacted according to this chemical equation?

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
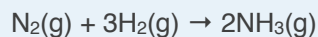
The conversions are the same, but they are applied in a different order. Start by using the balanced chemical equation to convert to moles of another substance and then use its molar mass to determine the mass of the final substance. In two steps, we have:

$$33.9 \; \cancel{mol \, H_2} \times \frac{2 \, mol \, NH_3}{3 \; \cancel{mol \, H_2}} = 22.6 \, mol \, NH_3$$

Now, using the molar mass of NH3, which is 17.03 g/mol, we get

$$22.6 \; \cancel{mol \, NH_3} \times \frac{17.03 \, g \, NH_3}{1 \; \cancel{mol \, NH_3}} = 385 \, g \, NH_3$$

Test Yourself

How many grams of N2 are needed to produce 2.17 mol of NH3 when reacted according to this chemical equation?

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$
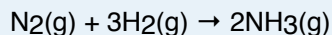
Answer

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 SO3 that can be produced by the reaction of 45.3 g of SO2 and O2:

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$$
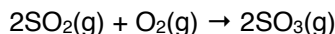
First, we convert the given amount, 45.3 g of SO2, to moles of SO2 using its molar mass (64.06 g/mol):

$$45.3 \; \cancel{g \, SO_2} \times \frac{1 \, mol \, SO_2}{64.06 \; \cancel{g \, SO_2}} = 0.707 \, mol \, SO_2$$

Second, we use the balanced chemical reaction to convert from moles of SO2 to moles of SO3:

$$0.707 \; \cancel{mol \, SO_2} \times \frac{2 \; mol \, SO_3}{2 \; \cancel{mol \, SO_2}} = 0.707 \; mol \, SO_3$$

Finally, we use the molar mass of SO3 (80.06 g/mol) to convert to the mass of SO3:

$$0.707 \; \cancel{mol \, SO_3} \times \frac{80.06 \; g \, SO_3}{1 \; \cancel{mol \, SO_3}} = 56.6 \; g \, SO_3$$

We can also perform all three steps sequentially, writing them on one line as

$$45.3 \; \cancel{g \, SO_2} \times \frac{1 \; mol \, SO_2}{64.06 \; \cancel{g \, SO_2}} \times \frac{2 \; mol \, SO_3}{2 \; \cancel{mol \, SO_2}} \times \frac{80.06 \; g \, SO_3}{1 \; \cancel{mol \, SO_3}} = 56.6 \; g \, SO_3$$

We get the same answer. Note how the initial and all the intermediate units cancel, leaving 56.6 grams of SO3, which is what we are looking for, as our final answer.

EXAMPLE 12

What mass of Mg will be produced when 86.4 g of K are reacted?

$$MgCl2(s) + 2K(s) \rightarrow Mg(s) + 2KCl(s)$$
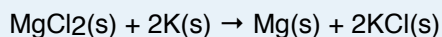
Solution

We will simply follow the steps

$$mass \; K \rightarrow mol \; K \rightarrow mol \; Mg \rightarrow mass \; Mg$$
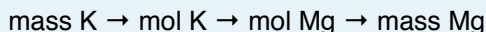
In addition to the balanced chemical equation, we need the molar masses of K (39.09 g/mol) and Mg (24.31 g/mol). In one line,

$$86.4 \; \cancel{g \, K} \times \frac{1 \; mol \, K}{39.09 \; \cancel{g \, K}} \times \frac{1 \; \cancel{mol \, Mg}}{2 \; \cancel{mol \, K}} \times \frac{24.31 \; g \, Mg}{1 \; \cancel{mol \, Mg}} = 26.87 \; g \, Mg$$

Test Yourself

What mass of H2 will be produced when 122 g of Zn are reacted?

$$Zn(s) + 2HCl(aq) \rightarrow ZnCl2(aq) + H2(g)$$

Answer

3.77 g

EXERCISES

1. What mass of CO_2 is produced by the combustion of 1.00 mol of CH_4?

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell)$$
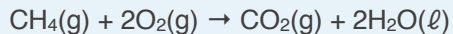
2. What mass of H_2O is produced by the combustion of 1.00 mol of CH_4?

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell)$$
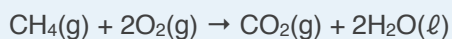
3. What mass of HgO is required to produce 0.692 mol of O_2?

4. What mass of MnO_2 is produced when 445 g of H_2O are reacted?

$$H_2O(\ell) + 2MnO_4\ (aq) + Br\ (aq) \rightarrow BrO_3\ (aq) + 2MnO_2(s) + 2OH\ (aq)$$
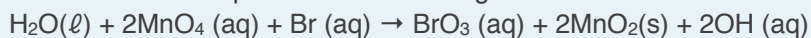
5. What mass of $PbSO_4$ is produced when 29.6 g of H_2SO_4 are reacted?

$$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(\ell)$$
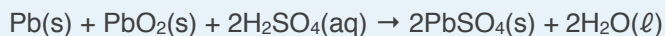
6. If 83.9 g of ZnO are formed, what mass of Mn_2O_3 is formed with it?

$$Zn(s) + 2MnO_2(s) \rightarrow ZnO(s) + Mn_2O_3(s)$$
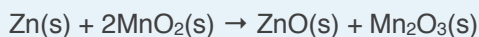
7. If 14.7 g of NO_2 are reacted, what mass of H_2O is reacted with it?

$$3NO_2(g) + H_2O(\ell) \rightarrow 2HNO_3(aq) + NO(g)$$
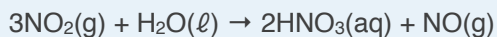
8. If 88.4 g of CH_2S are reacted, what mass of HF is produced?

$$CH_2S + 6F_2 \rightarrow CF_4 + 2HF + SF_6$$
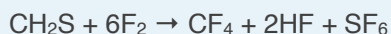
9. If 100.0 g of Cl_2 are needed, what mass of NaOCl must be reacted?
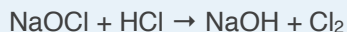
$$NaOCl + HCl \rightarrow NaOH + Cl_2$$

5. YIELDS

LEARNING OBJECTIVE

1. 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 "Chemical Equilibrium"). 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:

$$\text{percent yield} = \text{actual yield/theoretical yield} \times 100\%$$

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.

171

EXAMPLE 13

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?

$Zn(s) + 2HNO_3(aq) \rightarrow Zn(NO_3)_2(aq) + H_2(g)$
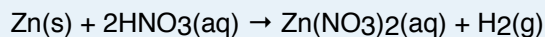
Solution

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

$$30.5 \text{ g Zn} \times \frac{1 \text{ mol Zn}}{65.39 \text{ g Zn}} \times \frac{1 \text{ mol Zn(NO}_3)_2}{1 \text{ mol Zn}} \times \frac{189.41 \text{ g Zn(NO}_3)_2}{1 \text{ mol Zn(NO}_3)_2} = 88.3 \text{ g Zn(NO}_3)_2$$

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:

$$\frac{65.2 \text{ g Zn(NO}_3)_2}{88.3 \text{ g Zn(NO}_3)_2} \times 100\% = 73.8\%$$

The worker achieved almost three-fourths of the possible yield.

Test Yourself
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?

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$
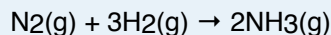
Answer

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
intermediate A → intermediate B
intermediate B → intermediate C
intermediate C → intermediate D
intermediate D → purified albuterol
overall percent yield = 70% × 100% × 40% × 72% × 35% = 7.5%   percent yield = 35%
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.

EXERCISES

1. What is the difference between the theoretical yield and the actual yield?

2. What is the difference between the actual yield and the percent yield?

3. A worker isolates 2.675 g of SiF_4 after reacting 2.339 g of SiO_2 with HF. What are the theoretical yield and the actual yield? $SiO_2(s) + 4HF(g) \rightarrow SiF_4(g) + 2H_2O(\ell)$

4. A worker synthesizes aspirin, $C_9H_8O_4$, according to this chemical equation. If 12.66 g of $C_7H_6O_3$ are reacted and 12.03 g of aspirin are isolated, what are the theoretical yield and the actual yield? $C_7H_6O_3 + C_4H_6O_3 \rightarrow C_9H_8O_4 + HC_2H_3O_2$

5. A chemist decomposes 1.006 g of $NaHCO_3$ and obtains 0.0334 g of Na_2CO_3. What are the theoretical yield and the actual yield?

$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(\ell) + CO_2(g)$
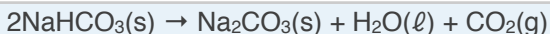
6. A chemist combusts a 3.009 g sample of C_5H_{12} and obtains 3.774 g of H_2O. What are the theoretical yield and the actual yield? $C_5H_{12}(\ell) + 8O_2(g) \rightarrow 5CO_2 + 6H_2O(\ell)$

7. What is the percent yield in Exercise 3?

8. What is the percent yield in Exercise 4?

9. What is the percent yield in Exercise 5?

10. What is the percent yield in Exercise 6?

ANSWERS

1. Theoretical yield is what you expect stoichiometrically from a chemical reaction; actual yield is what you actually get from a chemical reaction.

3. theoretical yield = 4.052 g; actual yield = 2.675 g

5. theoretical yield = 0.635 g; actual yield = 0.0334 g

7. 66.02%

9. 5.26%

6. LIMITING REAGENTS

One additional assumption we have made about chemical reactions—in addition to the assumption that reactions proceed all the way to completion—is that all the reactants are present in the proper quantities to react to products. This is not always the case.

Consider Figure 5.2 "Making Water". Here 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.
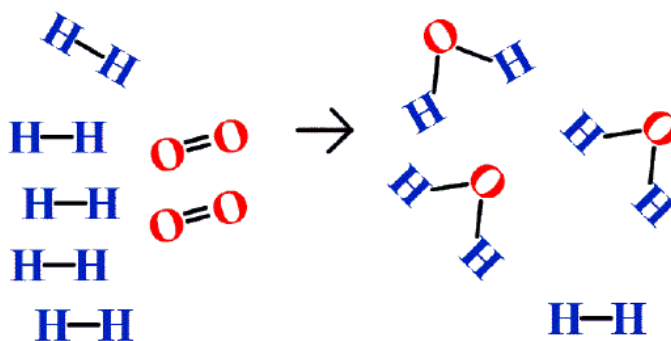
Figure 5.2: *Making Water - In this scenario for making water molecules, we run out of O atoms before we use up all the H atoms. Similar situations exist for many chemical reactions when one reactant runs out before the other.*

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:

$$4As(s) + 3O_2(g) \rightarrow 2As_2O_3(s)$$
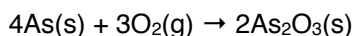
Suppose we start a reaction with 50.0 g of As and 50.0 g of O_2. Which one is the limiting reagent? We need to perform two mole-mass calculations, each assuming that each reactant reacts completely. Then we compare the amount of the product produced by each and determine which is less.

The calculations are as follows:

$$50.0 \ g\cancel{As} \times \frac{1 \ \cancel{mol \ As}}{74.92 \ g\cancel{As}} \times \frac{2 \ mol \ As_2O_3}{4 \ \cancel{mol \ As}} = 0.334 \ mol \ As_2O_3$$

$$50.0 \ g\cancel{O_2} \times \frac{1 \ \cancel{mol \ O_2}}{32.00 \ g\cancel{O_2}} \times \frac{2 \ mol \ As_2O_3}{3 \ \cancel{mol \ O_2}} = 1.04 \ mol \ As_2O_3$$

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,

$$50.0 \ g\cancel{As} \times \frac{1 \ \cancel{mol \ As}}{74.92 \ g\cancel{As}} \times \frac{3 \ \cancel{mol \ O_2}}{4 \ \cancel{mol \ As}} \times \frac{32.00 \ g \ O_2}{1 \ \cancel{mol \ O_2}} = 16.0 \ g \ O_2 \ reacted$$

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.

KEY TAKEAWAYS
❖ The limiting reagent is that 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.

7. END-OF-CHAPTER MATERIAL

ADDITIONAL EXERCISES

1. How many molecules of O_2 will react with 6.022×10^{23} molecules of H_2 to make water? The reaction is $2H_2(g) + O_2(g) \rightarrow 2H_2O(\ell)$.

2. How many molecules of H_2 will react with 6.022×10^{23} molecules of N_2 to make ammonia? The reaction is $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$.

3. How many moles are present in 6.411 kg of CO_2? How many molecules is this?

4. How many moles are present in 2.998 mg of SCl_4? How many molecules is this?

5. What is the mass in milligrams of 7.22×10^{20} molecules of CO_2?

6. What is the mass in kilograms of 3.408×10^{25} molecules of SiS_2?

7. What is the mass in grams of 1 molecule of H_2O?

8. What is the mass in grams of 1 atom of Al?

9. What is the volume of 3.44 mol of Ga if the density of Ga is 6.08 g/mL?

10. What is the volume of 0.662 mol of He if the density of He is 0.1785 g/L?

11. For the chemical reaction $2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(\ell)$ assume that 13.4 g of C_4H_{10} reacts completely to products. The density of CO_2 is 1.96 g/L. What volume in liters of CO_2 is produced?

12. For the chemical reaction $2GaCl_3(s) + 3H_2(g) \rightarrow 2Ga(\ell) + 6HCl(g)$ if 223 g of $GaCl_3$ reacts completely to products and the density of Ga is 6.08 g/mL, what volume in milliliters of Ga is produced?

13. Calculate the mass of each product when 100.0 g of CuCl react according to the reaction $2CuCl(aq) \rightarrow CuCl_2(aq) + Cu(s)$
What do you notice about the sum of the masses of the products? What concept is being illustrated here?

14. Calculate the mass of each product when 500.0 g of $SnCl_2$ react according to the reaction

$2SnCl_2(aq) \rightarrow SnCl_4(aq) + Sn(s)$

What do you notice about the sum of the masses of the products? What concept is being illustrated here?

15. What mass of CO_2 is produced from the combustion of 1 gal of gasoline? The chemical formula of gasoline can be approximated as C_8H_{18}. Assume that there are 2,801 g of gasoline per gallon.

16. What mass of H_2O is produced from the combustion of 1 gal of gasoline? The chemical formula of gasoline can be approximated as C_8H_{18}. Assume that there are 2,801 g of gasoline per gallon.

17. A chemical reaction has a theoretical yield of 19.98 g and a percent yield of 88.40%. What is the actual yield?

18. A chemical reaction has an actual yield of 19.98 g and a percent yield of 88.40%. What is the theoretical yield?

19. Given the initial amounts listed, what is the limiting reagent, and how much of the other reactants are in excess?

$$\underset{35.0\,g}{P_4} + \underset{12.7\,g}{3NaOH} + \underset{9.33\,g}{3H_2O} \rightarrow 2Na_2HPO_4 + PH_3$$

20. Given the initial amounts listed, what is the limiting reagent, and how much of the other reactants are in excess?

$$\underset{46.3\,g}{2NaCrO_2} + \underset{88.2\,g}{3NaBrO_4} + \underset{32.5\,g}{2NaOH} \rightarrow 3NaBrO_3 + 2Na_2CrO_4 + H_2O$$

21. Verify that it does not matter which product you use to predict the limiting reagent by using both products in this combustion reaction to determine the limiting reagent and the amount of the reactant in excess. Initial amounts of each reactant are given.

$$\underset{26.3\,g}{C_3H_8} + \underset{21.8\,g}{5O_2} \rightarrow 3CO_2(g) + 4H_2O(l)$$
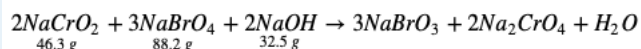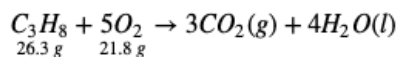
22. Just in case you suspect Exercise 21 is rigged, do it for another chemical reaction and verify that it does not matter which product you use to predict the limiting reagent by using both products in this combustion reaction to determine the limiting reagent and the amount of the reactant in excess. Initial amounts of each reactant are given.

$$\underset{35.0\,g}{2P_4} + \underset{12.7\,g}{6NaOH} + \underset{9.33\,g}{6H_2O} \rightarrow 3Na_2HPO_4 + 5PH_3$$
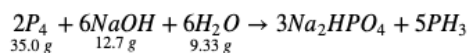
ANSWERS

1. 1.2044×10^{24} molecules

3. 145.7 mol; 8.77×10^{25} molecules

5. 52.8 mg

7. 2.99×10^{-23} g

9. 39.4 mL

11. 20.7 L

13. 67.91 g of $CuCl_2$; 32.09 g of Cu. The two masses add to 100.0 g, the initial amount of starting material, demonstrating the law of conservation of matter.

15. 8,632 g

17. 17.66 g

19. The limiting reagent is NaOH; 21.9 g of P_4 and 3.61 g of H_2O are left over.

21. Both products predict that O_2 is the limiting reagent; 20.3 g of C_3H_8 are left over.

CHAPTER 6: GASES

Opening Essay

Perhaps one of the most spectacular chemical reactions involving a gas occurred on May 6, 1937, when the German airship *Hindenburg* exploded on approach to the Naval Air Station in Lakehurst, New Jersey. The actual cause of the explosion is still unknown, but the entire volume of hydrogen gas used to float the airship, about 200,000 m3, burned in less than a minute.

Thirty-six people, including one on the ground, were killed.

Hydrogen is the lightest known gas. Any balloon filled with hydrogen gas will float in air if its mass is not too great. This makes hydrogen an obvious choice for flying machines based on balloons—airships, dirigibles, and blimps. However, hydrogen also has one obvious drawback: it burns in air according to the well-known chemical equation

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(\ell)$$
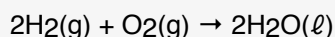
So although hydrogen is an obvious choice, it is also a dangerous choice.

Helium gas is also lighter than air and has 92% of the lifting power of hydrogen. Why, then, was helium not used in the *Hindenburg*? In the 1930s, helium was much more expensive. In addition, the best source of helium at the time was the United States, which banned helium exports to pre–World War II Germany. Today all airships use helium, a legacy of the Hindenburg disaster.

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.

1. KINETIC THEORY OF GASES

LEARNING OBJECTIVES

1. State the major concepts behind the kinetic theory of gases.

2. 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**. It 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 6.1 "The Kinetic Theory of Gases" shows a representation of how we mentally picture the gas phase.
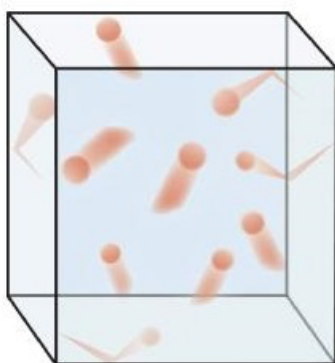
Figure 6.1 *The Kinetic Theory of Gases The kinetic theory of gases describes this state of matter as composed of tiny particles in constant motion with a lot of distance between the particles.*

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 so well that the kinetic theory of gases is well accepted by the scientific community.

2. PRESSURE

LEARNING OBJECTIVES

1. Define *pressure*.

2. Learn the units of pressure and how to convert between them.

The kinetic theory of gases indicates that gas particles are always in motion and are colliding with other particles and the walls of the container holding them. Although collisions with container walls are elastic (i.e., there is no net energy gain or loss because of the collision), a gas particle does exert a force on the wall during the collision. The accumulation of all these forces distributed over the area of the walls of the container causes something we call pressure. **Pressure** (P) is defined as the force of all the gas particle/wall collisions divided by the area of the wall:

All gases exert pressure; it is one of the fundamental measurable quantities of this phase of matter. Even our atmosphere exerts pressure—in this case, the gas is being "held in" by the earth's gravity, rather than the gas being in a container. The pressure of the atmosphere is about 14.7 pounds of force for every square inch of surface area: 14.7 lb/in^2.

Pressure has a variety of units. The formal, SI-approved unit of pressure is the *pascal* (Pa), which is defined as 1 N/m^2 (one newton of force over an area of one square meter). However, this is usually too small in magnitude to be useful. A common unit of pressure is the atmosphere (atm), which was originally defined as the average atmospheric pressure at sea level.

However, "average atmospheric pressure at sea level" is difficult to pinpoint because of atmospheric pressure variations. A more reliable and common unit is **millimeters of mercury** (mmHg), which is the amount of pressure exerted by a column of mercury exactly 1 mm high. An equivalent unit is the **torr**, which equals 1 mmHg. (The torr is named after Evangelista Torricelli, a seventeenth-century Italian scientist who invented the mercury barometer.) With these definitions of pressure, the atmosphere unit is redefined: 1 atm is defined as exactly 760 mmHg, or 760 torr. We thus have the following equivalences:

$$1 \text{ atm} = 760 \text{ mmHg} = 760 \text{ torr}$$

We can use these equivalences as with any equivalences—to perform conversions from one unit to another. Relating these to the formal SI unit of pressure, 1 atm = 101,325 Pa.

EXAMPLE 1

How many atmospheres are there in 595 torr?

Solution

Using the pressure equivalences, we construct a conversion factor between torr and atmospheres:

Thus, because the numbers in the conversion factor are exact, the number of significant figures in the final answer is determined by the initial value of pressure.

Test Yourself

How many atmospheres are there in 1,022 torr?

Answer

1.345 atm

KEY TAKEAWAYS

1. Pressure is a force exerted over an area.
2. Pressure has several common units that can be converted.

3. GAS LAWS

1. Learn what is meant by the term *gas laws*.

2. Learn and apply Boyle's law.

3. Learn and apply Charles's law.

When seventeenth-century scientists began studying the physical properties of gases, they noticed some simple relationships between some of the measurable properties of the gas. Take pressure (P) and volume (V), for example. Scientists noted that for a given amount of a gas (usually expressed in units of moles [n]), if the temperature (T) of the gas was kept constant, pressure and volume were related: As one increases, the other decreases. As one decreases, the other increases. We say that pressure and volume are *inversely related*. There is more to it, however: pressure and volume of a given amount of gas at constant temperature are *numerically* related. If you take the pressure value and multiply it by the volume value, the product is a constant for a given amount of gas at a constant temperature:

$$P \times V = \text{constant at constant } n \text{ and } T$$

If either volume or pressure changes while amount and temperature stay the same, then the other property must change so that the product of the two properties still equals that same constant. That is, if the original conditions are labeled $P1$ and $V1$ and the new conditions are labeled $P2$ and $V2$, we have

$$P_1 V_1 = \text{constant} = P_2 V_2$$

where the properties are assumed to be multiplied together. Leaving out the middle part, we have simply

$$P_1 V_1 = P_2 V_2 \text{ at constant } n \text{ and } T$$

This equation is an example of a gas law. A **gas law** is a simple mathematical formula that allows you to model, or predict, the behavior of a gas. This particular gas law is called **Boyle's law**, after the English scientist Robert Boyle, who first announced it in 1662. Figure 6.2 "Boyle's Law" shows two representations of how Boyle's law works.

V= large
P= small

V= small
P= large

V

P
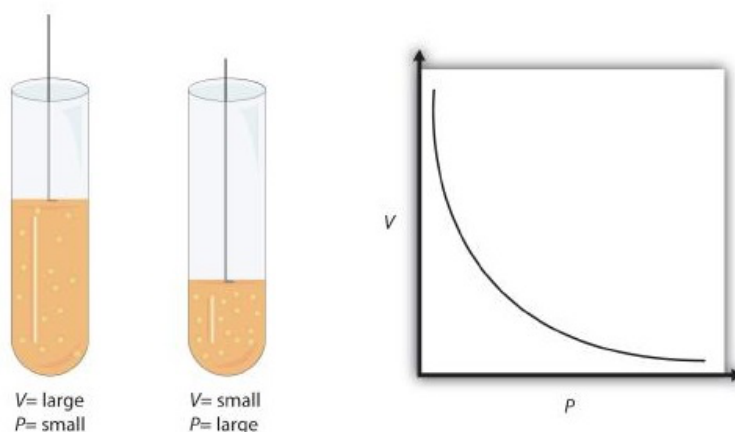
Figure 6.2: *Boyle's Law A piston having a certain pressure and volume (left piston) will have half the volume when its pressure is twice as much (right piston). One can also plot P versus V for a given amount of gas at a certain temperature; such a plot will look like the graph on the right.*

Boyle's law is an example of a second type of mathematical problem we see in chemistry—one based on a mathematical formula. Tactics for working with mathematical formulas are different from tactics for working with conversion factors. First, most of the questions you will have to answer using formulas are word-type questions, so the first step is to identify what quantities are known and assign them to variables. Second, in most formulas, some mathematical rearrangements (i.e., algebra) must be performed to solve for an unknown variable. The rule is that to find the value of the unknown variable, you must mathematically isolate the unknown variable *by itself and in the numerator* of one side of the equation. Finally, units must be consistent. For example, in Boyle's law there are two pressure variables; they must have the same unit. There are also two volume variables; they also must have the same unit. In most cases, it won't matter *what* the unit is, but the unit must be the *same* on both sides of the equation.

As mentioned, you can use any units for pressure or volume, but both pressures must be expressed in the same units, and both volumes must be expressed in the same units.

There are other measurable characteristics of a gas. One of them is temperature (T). Perhaps one can vary the temperature of a gas sample and note what effect it has on the other properties of the gas. Early scientists did just this, discovering that if the amount of a gas and its pressure are kept constant, then changing the temperature changes the volume (V). As temperature increases, volume increases; as temperature decreases, volume decreases. We say that these two characteristics are *directly related*.

A mathematical relationship between V and T should be possible except for one thought: what temperature scale should we use? We know from Chapter 2 "Measurements" that science uses several possible temperature scales. Experiments show that the volume of a gas is related to its *absolute temperature in Kelvin, not its temperature in degrees Celsius*. If the temperature of a gas is expressed in kelvins, then experiments show that the *ratio* of volume to temperature is a constant:

$$V/T = \text{constant}$$

We can modify this equation as we modified Boyle's law: the initial conditions V_1 and T_1 have a certain value, and the value must be the same when the conditions of the gas are changed to some new conditions V_2 and T_2, as long as pressure and the amount of the gas remain constant. Thus, we have another gas law:

$$V_1/T_1 = V_2/T_2 \text{ at constant P and n}$$

This gas law is commonly referred to as **Charles's law**, after the French scientist Jacques Charles, who performed experiments on gases in the 1780s. The tactics for using this mathematical formula are similar to those for Boyle's law. To determine an unknown quantity, use algebra to isolate the unknown variable by itself and in the numerator; the units of similar variables must be the same. But we add one more tactic: all temperatures must be expressed in the absolute temperature scale (Kelvin). As a reminder, we review the conversion between the absolute temperature scale and the Celsius temperature scale:

$$K = °C + 273$$

where K represents the temperature in kelvins, and °C represents the temperature in degrees Celsius. Figure 6.3 "Charles's Law" shows two representations of how Charles's law works.
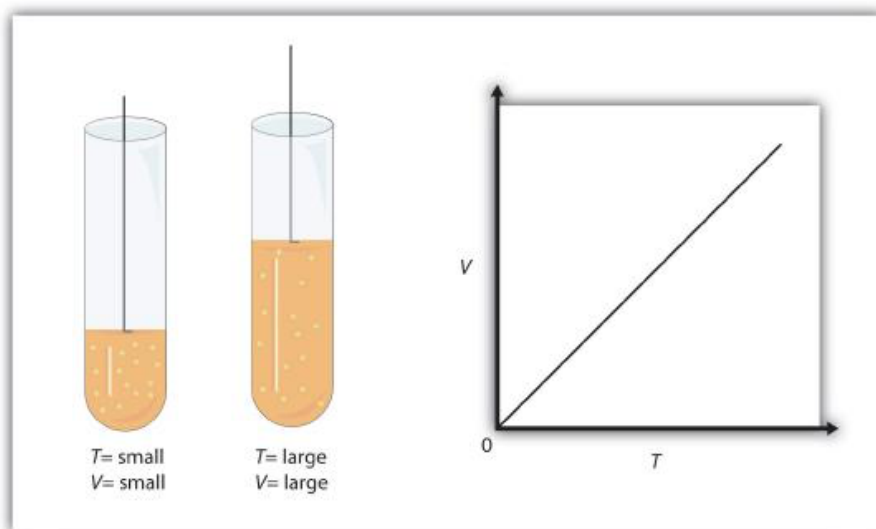
Figure 6.3: *Charles's Law A piston having a certain volume and temperature (left piston) will have twice the volume when its temperature is twice as much (right piston). One can also plot V versus T for a given amount of gas at a certain pressure; such a plot will look like the graph on the right.*

It is more mathematically complicated if a final temperature must be calculated because the T variable is in the denominator of Charles's law. There are several mathematical ways to work this, but perhaps the simplest way is to take the reciprocal of Charles's law. That is, rather than write it as

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

write the equation as

$$\frac{T_1}{V_1} = \frac{T_2}{V_2}$$

It is still an equality and a correct form of Charles's law, but now the temperature variable is in the numerator, and the algebra required to predict a final temperature is simpler.

4. OTHER GAS LAWS

1. Review other simple gas laws.

2. Learn and apply the combined gas law.

You may notice in Boyle's law and Charles's law that we actually refer to four physical properties of a gas: pressure (P), volume (V), temperature (T), and amount (in moles; n). We do this because these are the only four independent physical properties of a gas. There are other physical properties, but they are all related to one (or more) of these four properties.

Boyle's law is written in terms of two of these properties, with the other two being held constant. Charles's law is written in terms of two different properties, with the other two being held constant. It may not be surprising to learn that there are other gas laws that relate other pairs of properties—as long as the other two are held constant. Here we will mention a few.

Gay-Lussac's law relates pressure with absolute temperature. In terms of two sets of data, Gay-Lussac's law is

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \quad \text{at constant } V \text{ and } n$$

Note that it has a structure very similar to that of Charles's law, only with different variables—pressure instead of volume. *Avogadro's law* introduces the last variable for amount. The original statement of Avogadro's law states that equal volumes of different gases at the same temperature and pressure contain the same number of particles of gas. Because the number of particles is related to the number of moles (1 mol = 6.022×10^{23} particles), Avogadro's law essentially states that equal volumes of different gases at the same temperature and pressure contain the same *amount* (moles, particles) of gas. Put mathematically into a gas law, Avogadro's law is

$$\frac{V_1}{n_1} = \frac{V_2}{n_2} \quad \text{at constant } P \text{ and } T$$

(First announced in 1811, it was Avogadro's proposal that volume is related to the number of particles that eventually led to naming the number of things in a mole as Avogadro's number.) Avogadro's law is useful because for the first time we are seeing amount, in terms of the number of moles, as a variable in a gas law.

The variable n in Avogadro's law can also stand for the number of moles of gas in addition to number of particles.

One thing we notice about all the gas laws is that, collectively, volume and pressure are always in the numerator, and temperature is always in the denominator. This suggests that we can propose a gas law that combines pressure, volume, and temperature. This gas law is known as the combined gas law, and its mathematical form is

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad \text{at constant } n$$

This allows us to follow changes in all three major properties of a gas. Again, the usual warnings apply about how to solve for an unknown algebraically (isolate it on one side of the equation in the numerator), units (they must be the same for the two similar variables of each type), and units of temperature must be in kelvins.

As with other gas laws, if you need to determine the value of a variable in the denominator of the combined gas law, you can either cross-multiply all the terms or just take the reciprocal of the combined gas law. Remember, the variable you are solving for must be in the numerator and all by itself on one side of the equation.

KEY TAKEAWAYS

1. There are other gas laws that relate any two physical properties of a gas.

2. The combined gas law relates pressure, volume, and temperature of a gas.

5. THE IDEAL GAS LAW AND SOME APPLICATIONS

LEARNING OBJECTIVES

1. Learn the ideal gas law.

2. Apply the ideal gas law to any set of conditions of a gas.

3. 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

$$PV/nT = constant$$

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

$$PV/nT = R$$

which is usually rearranged as

$$PV = nRT$$

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 6.1 "Values of the Ideal Gas Law Constant " lists the numerical values of R.

Table 6.1 Values of the Ideal Gas Law Constant R

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

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.

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

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:

$$(1\,atm)V = (1\,mol)(0.08205)(L.atm/mol.K)(273K)$$

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 (Figure 6.4 "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.

Figure 6.4: *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*

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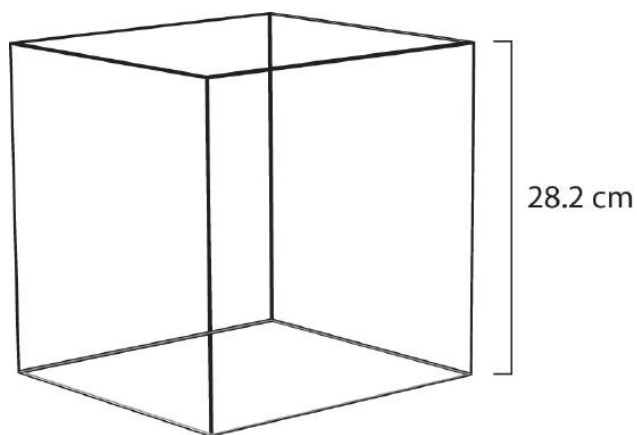
The ideal gas law can also be used to determine the densities of gases. Density, recall, is defined as the mass of a substance divided by its volume:

$$d = m/V$$

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

$$density = molar\ mass/molar\ volume$$

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.
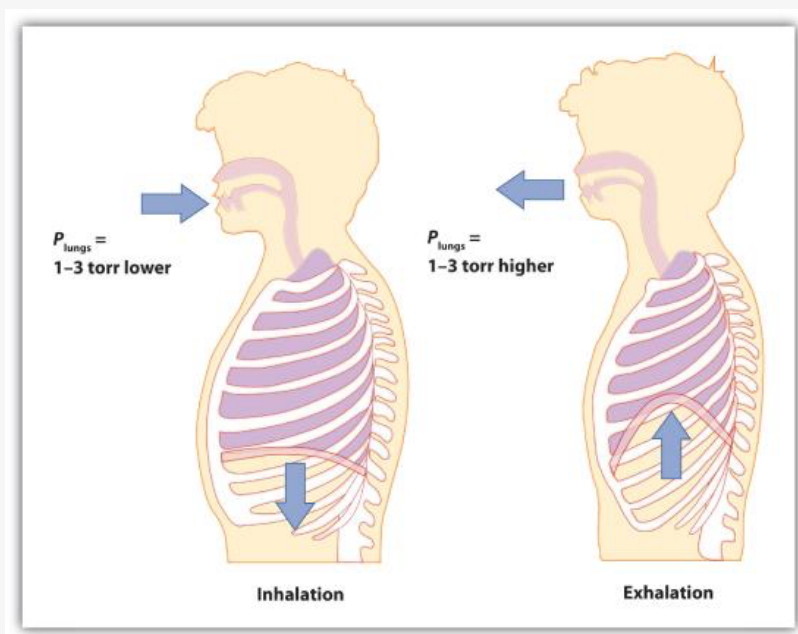
Figure 6.5: *Breathing Mechanics Breathing involves pressure differences between the inside of the lungs and the air outside. The pressure differences are only a few torr.*

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:

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

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.

6. GAS MIXTURES

LEARNING OBJECTIVE

1. Learn Dalton's law of partial pressures.

One of the properties of gases is that they mix with each other. When they do so, they become a solution— a homogeneous mixture. Some of the properties of gas mixtures are easy to determine if we know the composition of the gases in the mix.

In gas mixtures, each component in the gas phase can be treated separately. Each component of the mixture shares the same temperature and volume. (Remember that gases expand to fill the volume of their container; gases in a mixture continue to do that as well.) However, each gas has its own pressure. The **partial pressure** of a gas, P_i, is the pressure that an individual gas in a mixture has. Partial pressures are expressed in torr, millimeters of mercury, or atmospheres like any other gas pressure; however, we use the term *pressure* when talking about pure gases and the term *partial pressure* when we are talking about the individual gas components in a mixture.

Dalton's law of partial pressures states that the total pressure of a gas mixture, P_{tot}, is equal to the sum of the partial pressures of the components, P_i:

$$P_{tot} = P_1 + P_2 + P_3 + \ldots = \sum_{\#of\ gases} P_i$$

Although this may seem to be a trivial law, it reinforces the idea that gases behave independently of each other.

One of the reasons we have to deal with Dalton's law of partial pressures is because gases are frequently collected by bubbling through water. As we will see in Chapter 10 "Solids and Liquids", liquids are constantly evaporating into a vapor until the vapor achieves a partial pressure characteristic of the substance and the temperature. This partial pressure is called a **vapor pressure**. Table 6.2 "Vapor Pressure of Water versus Temperature" lists the vapor pressures of H_2O versus temperature. Note that if a substance is normally a gas under a given set of conditions, the term *partial pressure* is used; the term *vapor pressure* is reserved for the partial pressure of a vapor when the liquid is the normal phase under a given set of conditions.

Table 6.2 Vapor Pressure of Water versus Temperature

Temperature (°C)	Vapor Pressure (torr)
5	6.54
10	9.21
15	12.79
20	17.54
21	18.66
22	19.84
23	21.08
24	22.39
25	23.77
30	31.84
35	42.20
40	55.36
50	92.59
60	149.5
70	233.8
80	355.3
90	525.9
100	760.0

Any time a gas is collected over water, the total pressure is equal to the partial pressure of the gas *plus* the vapor pressure of water. This means that the amount of gas collected will be less than the total pressure suggests.

Finally, we introduce a new unit that can be useful, especially for gases. The mole fraction, χ_i, is the ratio of the number of moles of component *i* in a mixture divided by the total number of moles in the sample:

(χ is the lowercase Greek letter *chi*.) Note that mole fraction is *not* a percentage; its values range from 0 to 1. For example, consider the combination of 4.00 g of He and 5.0 g of Ne. Converting both to moles, we get

$$4.00 \; \cancel{g \, He} \times \frac{1 \, mol \, He}{4.00 \; \cancel{g \, He}} = 1.00 \, mol \, He \; and \; 5.0 \; \cancel{g \, Ne} \times \frac{1 \, mol \, Ne}{20.0 \; \cancel{g \, Ne}} = 0.25 \, mol \, Ne$$

The total number of moles is the sum of the two mole amounts:

$$total \; moles = 1.00 \; mol + 0.025 \; mol = 1.25 \; mol$$

The mole fractions are simply the ratio of each mole amount and the total number of moles, 1.25 mol:

$$\chi_{He} = \frac{1.00 \; \cancel{mol}}{1.25 \; \cancel{mol}} = 0.800$$

$$\chi_{Ne} = \frac{0.25 \; \cancel{mol}}{1.25 \; \cancel{mol}} = 0.200$$

The sum of the mole fractions equals exactly 1.

For gases, there is another way to determine the mole fraction. When gases have the same volume and temperature (as they would in a mixture of gases), the number of moles is proportional to partial pressure, so the mole fractions for a gas mixture can be determined by taking the ratio of partial pressure to total pressure:

$$\chi_i = \frac{P_i}{P_{tot}}$$

This expression allows us to determine mole fractions without calculating the moles of each component directly.

KEY TAKEAWAYS
❖ The pressure of a gas in a gas mixture is termed the *partial pressure*.
❖ Dalton's law of partial pressure says that the total pressure in a gas mixture is the sum of the individual partial pressures.
❖ Collecting gases over water requires that we take the vapor pressure of water into account.
❖ Mole fraction is another way to express the amounts of components in a mixture.

CHAPTER 7: ENERGY AND CHEMISTRY

Opening Essay

It takes energy to launch a spaceship into space. If it takes 1 energy unit to warm 0.25 g of water by 1°C, then it takes over 15,100 energy units to put that 0.25 g of water into earth orbit. The most powerful engines designed to lift rockets into space were part of the Saturn V rocket, that was built by the National Aeronautics and Space Administration (NASA). The rocket had three stages, with the first stage having the capability of launching about 3.5 million kg of mass. About 2.3 million kg was the actual fuel for the first stage; rockets in space have the unpleasant task of having to take their own chemicals with them to provide thrust.

Having to carry its own fuel puts a lot of mass burden on an engine in space. This is why NASA is developing other types of engines to minimize fuel mass. An ion thruster uses xenon atoms that have had at least one electron removed from their atoms. The resulting ions can be accelerated by electric fields, causing a thrust. Because xenon atoms are very large for atoms, the thrusting efficiency is high even though the actual thrust is low. Because of this, ion engines are useful only in space.
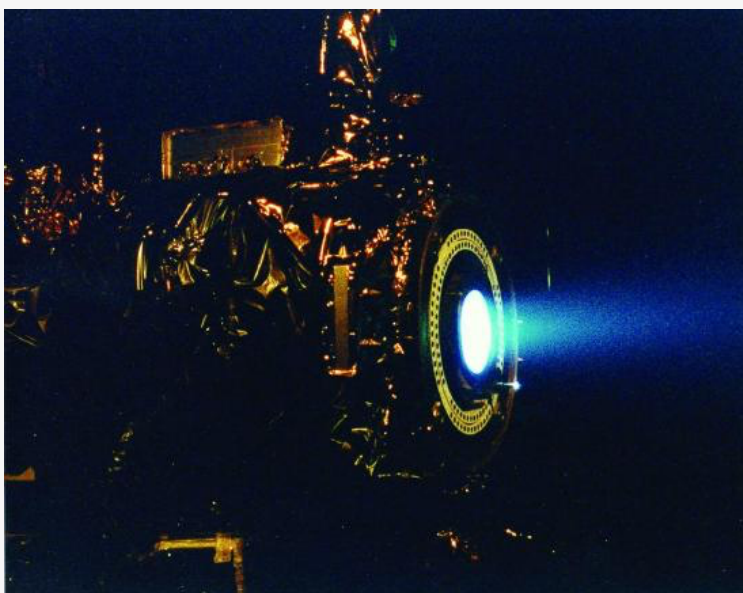
Ion drives have low thrust but high efficiency. They have already been used on several space missions, including NASA's Deep Space 1spacecraft and Japan's Hayabusa asteroid sampling probe.
Source: Photo courtesy of NASA,http://commons.wikimedia.org/wiki/File:Ion_Engine_Test_Firing_-_GPN-2000-000482.jpg.

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). As such, it is only natural that the study of chemistry involves energy.

1. ENERGY

LEARNING OBJECTIVES

1. Define *energy*.

2. Know the units of energy.

3. Understand the law of conservation of energy.

Energy is the ability to do work. Think about it: when you have a lot of energy, you can do a lot of work; but if you're low on energy, you don't want to do much work. Work (w) itself is defined as a force (F) operating over a distance (Δx):

$$w = F \times \Delta x$$

In SI, force has units of newtons (N), while distance has units of meters. Therefore, work has units of N·m. This compound unit is redefined as a **joule** (J):

$$1 \text{ joule} = 1 \text{ newton·meter} 1 \text{ J} = 1 \text{ N·m}$$

Because energy is the ability to do work, energy is also measured in joules. This is the primary unit of energy we will use here.

How much is 1 J? It is enough to warm up about one-fourth of a gram of water by 1°C. It takes about 12,000 J to warm a cup of coffee from room temperature to 50°C. So a joule is not a lot of energy. It will not be uncommon to measure energies in thousands of joules, so the kilojoule (kJ) is a common unit of energy, with 1 kJ equal to 1,000 J.

An older—but still common—unit of energy is the *calorie*. The calorie (cal) was originally defined in terms of warming up a given quantity of water. The modern definition of calorie equates it to joules:

$$1 \text{ cal} = 4.184 \text{ J}$$

One area where the calorie is used is in nutrition. Energy contents of foods are often expressed in calories. However, the calorie unit used for foods is actually the kilocalorie (kcal). Most foods indicate this by spelling the word with a capital C—Calorie. Figure 7.1 "Calories on Food Labels" shows one example. So be careful counting calories when you eat!

Figure 7.1: This label expresses the energy content of the food, but in Calories (which are actually kilocalories).

EXAMPLE 1

The label in Figure 7.1 "Calories on Food Labels" states that the serving has 38 Cal. How many joules is this?

Solution

We recognize that with a capital C, the Calories unit is actually kilocalories. To determine the number of joules, we convert first from kilocalories to calories (using the definition of the *kilo-* prefix) and then from calories to joules (using the relationship between calories and joules). So

Test Yourself

A serving of breakfast cereal usually has 110 Cal. How many joules of energy is this?

Answer

460,000 J

In the study of energy, we use the term system to describe the part of the universe under study: a beaker, a flask, or a container whose contents are being observed and measured. An isolated system is a system that does not allow a transfer of energy or matter into or out of the system. A good approximation of an isolated system is a closed, insulated thermos-type bottle. The fact that the thermos-type bottle is closed keeps matter from moving in or out, and the fact that it is insulated keeps energy from moving in or out. One of the fundamental ideas about the total energy of an isolated system is that is does not increase or decrease. When this happens to a quantity, we say that the quantity is *conserved*. The statement that the total energy of an isolated system does not change is called the **law of conservation of energy**. As a scientific law, this concept occupies the highest level of understanding we have about the natural universe.

2. WORK AND HEAT

LEARNING OBJECTIVES

1. Define a type of work in terms of pressure and volume.

2. Define *heat*.

3. Relate the amount of heat to a temperature change.

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 (Figure 7.2 "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.

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.
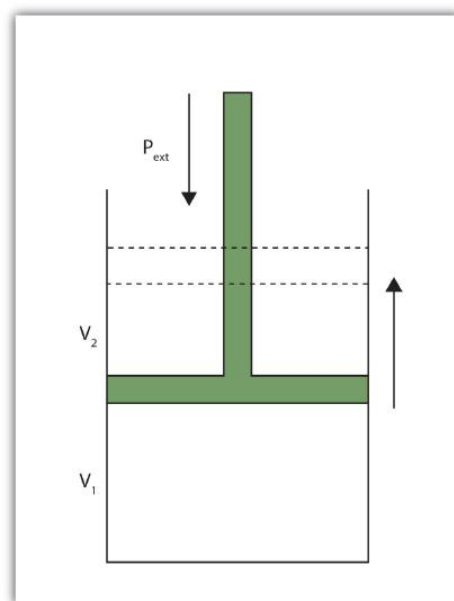
Figure 7.2: Volume versus Pressure - When a gas expands against an external pressure, the gas does work.

EXAMPLE 2

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:

$\Delta V = V_{final} - V_{initial} = 6.19\ L - 3.44\ L = 2.75\ L$

Now we can use the definition of work to determine the work done:

$w = -P_{ext} \cdot \Delta V = -(1.26\ atm)(2.75\ L) = -3.47\ L \cdot atm$

Now we construct a conversion factor from the relationship between liter·atmospheres and joules:

$$-3.47\ \cancel{L.\,atm} \times \times \frac{101.32\ J}{1\ \cancel{L.\,atm}} = -351\ J$$

We limit the final answer to three significant figures, as appropriate.

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 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

$$q \propto m \times \Delta T$$

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**:

$$q = mc\Delta T$$

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 depending on what the unit of ΔT is. You may note a depar-

ture 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 3

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:

$$\Delta T = 76°C - 22°C = 54°C$$

Now we can use the expression for q, substitute for all variables, and solve for heat:

$$q = (25.0\,g)(0.449\frac{J}{g \cdot °C})(54°C) = 610\,J$$

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.

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 4

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,

$$5{,}408 \text{ J} = (373 \text{ g})c(104°C)$$

We divide both sides of the equation by 373 g and 104°C:

Combining the numbers and bringing together all the units, we get

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 7.1 "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.

Table 7.1 Specific Heats of Various Substances

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

EXERCISES

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 7.1 "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 7.1 "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 7.1 "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 7.1 "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 7.1 "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 7.1 "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?

18. A sample of He goes from 19.4°C to 55.9°C when 448 J of energy are added. What is the mass of the helium? How many moles of helium is this?

3. ENTHALPY AND CHEMICAL REACTIONS

LEARNING OBJECTIVES

1. Define *enthalpy*.

2. Properly express the enthalpy change of chemical reactions.

3. 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 "Gases" and our definition of work in Section 7.2 "Work and Heat" 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:

$$\Delta H \equiv q \text{ at constant pressure}$$

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

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(\ell) \quad \Delta H = -570 \text{ kJ}$$

205
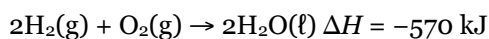
A chemical equation that includes an enthalpy change is called a **thermochemical equation**. A thermochemical equation is assumed to refer to the equation in molar quantities, which means it must be interpreted in terms of moles, not individual molecules.

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**.

What does it mean if the ΔH 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) in Figure 7.3 "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) in Figure 7.3 "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.
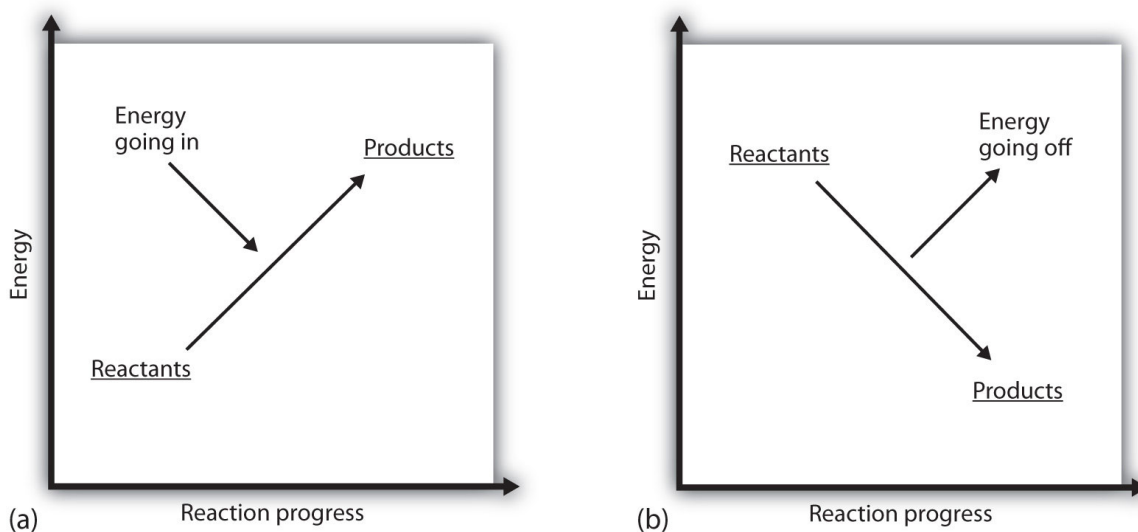
Figure 7.3: *Reaction Energy (a) In an endothermic reaction, the energy of the system increases (i.e., moves higher on the vertical scale of energy). (b) In an exothermic reaction, the energy of the system decreases (i.e., moves lower on the vertical scale of energy).*
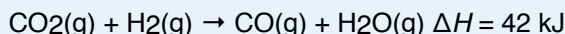
How are ΔH values measured experimentally? Actually, ΔH is not measured; q is measured. But the measurements are performed under conditions of constant pressure, so ΔH is equal to the q measured. Experimentally, q is measured by taking advantage of the equation

$$q = mc\Delta T$$

We pre-measure 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**.

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 Figure 7.4 "Calorimeters" for an example setup). The thermometer measures the temperature change as the following chemical reaction occurs:

$$NaOH (aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(\ell)$$
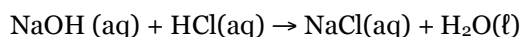
An observer notes that the temperature increases from 22.4°C to 29.1°C. Assuming that the heat capacities and densities of the solutions are the same as those of pure water, we now have the information we need to determine the enthalpy change of the chemical reaction. The total amount of solution is 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 (Table 7.1 "Specific Heats of Various Substances"):

Solving for q, we get

$$q = 5,600 \text{ J} \equiv \Delta H$$

for the reaction. 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:

$$\Delta H = -5,600 \text{ J for the reaction}$$

Thus, we have the following thermochemical equation for the chemical reaction that occurred in the calorimeter:

$$\frac{1}{10}NaOH(aq) + \frac{1}{10}HCl(aq) \rightarrow \frac{1}{10}NaCl(aq) + \frac{1}{10}H_2O(l) \ \Delta H = -5600 \ J$$
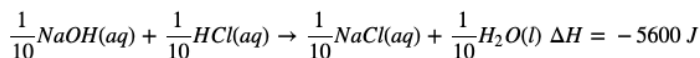
The 1/10 coefficients are present to remind us that we started with one-tenth of a mole of each reactant, so we make one-tenth of a mole of each product. Typically, however, we report thermochemical equations in terms of moles, not one-tenth of a mole. To scale up to molar quantities, we must multiply the coefficients by 10. However, when we do this, we get 10 times as much energy. Thus, we have

$$NaOH \ (aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(\ell) \ \Delta H = -56{,}000 \ J$$
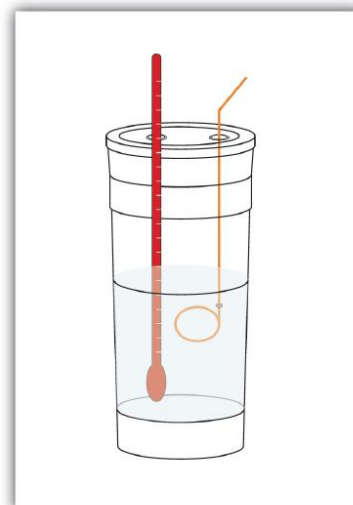
Figure 7.4: *Calorimeters - A simple calorimeter can be constructed from some nested foam coffee cups, a cover, a thermometer, and a stirrer.*

The ΔH can be converted into kJ units, so our final thermochemical equation is

$$NaOH \ (aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(\ell) \ \Delta H = -56 \ kJ$$

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 4

Test Yourself

In a calorimeter at constant pressure, 0.10 mol of $CH_4(g)$ and 0.20 mol of $O_2(g)$ are reacted.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell)$$
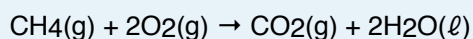
The reaction warms 750.0 g of H_2O by 28.4°C. What is ΔH for the reaction on a molar scale?

Answer

–891 kJ

208

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.

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 Figure 7.3 "Reaction Energy" for an example.)

12. Draw an energy level diagram for the chemical reaction in Exercise 9. (See Figure 7.3 "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?
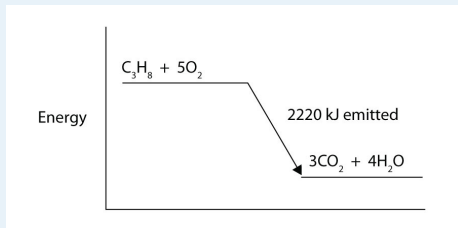
4. STOICHIOMETRY CALCULATIONS USING ENTHALPY

LEARNING OBJECTIVE

1. Perform stoichiometry calculations using energy changes from thermochemical equations.

In Chapter 5 "Stoichiometry and the Mole", we related quantities of one substance to another in a chemical equation by performing calculations that used the balanced chemical equation; the balanced chemical equation provided equivalences that we used to construct conversion factors. For example, in the balanced chemical equation

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(\ell)$$
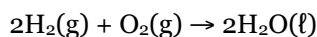
we recognized the equivalences

$$2 \text{ mol } H_2 \Leftrightarrow 1 \text{ mol } O_2 \Leftrightarrow 2 \text{ mol } H_2O$$

where $\Leftrightarrow$ is the mathematical symbol for "is equivalent to." In our thermochemical equation, however, we have another quantity—energy change:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(\ell) \ \Delta H = -570 \text{ kJ}$$
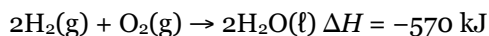
This new quantity allows us to add another equivalence to our list:

$$2 \text{ mol } H_2 \Leftrightarrow 1 \text{ mol } O_2 \Leftrightarrow 2 \text{ mol } H_2O \Leftrightarrow -570 \text{ kJ}$$

That is, we can now add an energy amount to the equivalences—the enthalpy change of a balanced chemical reaction. This equivalence can also be used to construct conversion factors so that we can relate enthalpy change to amounts of substances reacted or produced.

Note that these equivalences address a concern. When an amount of energy is listed for a balanced chemical reaction, what amount(s) of reactants or products does it refer to? The answer is that relates to the number of moles of the sub-

stance as indicated by its coefficient in the balanced chemical reaction.Thus, 2 mol of H2 are related to −570 kJ, while 1 mol of O2 is related to −570 kJ. This is why the unit on the energy change is kJ, not kJ/mol.

For example, consider the thermochemical equation

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g) \; \Delta H = -184.6 \text{ kJ}$$

The equivalences for this thermochemical equation are

$$1 \text{ mol } H_2 \Leftrightarrow 1 \text{ mol } Cl_2 \Leftrightarrow 2 \text{ mol } HCl \Leftrightarrow -184.6 \text{ kJ}$$
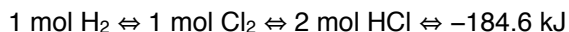
Suppose we asked how much energy is given off when 8.22 mol of H2 react. We would construct a conversion factor between the number of moles of H2 and the energy given off, −184.6 kJ:

The negative sign means that this much energy is given off.

EXAMPLE 8

Given the thermochemical equation

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \; \Delta H = -91.8 \text{ kJ}$$
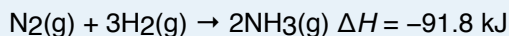
how much energy is given off when 222.4 g of N2 reacts?

Solution

The balanced thermochemical equation relates the energy change to moles, not grams, so we first convert the amount of N2 to moles and then use the thermochemical equation to determine the energy change:

Test Yourself

Given the thermochemical equation

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \; \Delta H = -91.8 \text{ kJ}$$
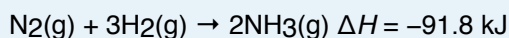
how much heat is given off when 1.00 g of H2 reacts?

Answer

−15.1 kJ

Like any stoichiometric quantity, we can start with energy and determine an amount, rather than the other way around.

Test Yourself

How many grams of N2 will react if 100.0 kJ of energy are supplied?

$$N_2(g) + O_2(g) \rightarrow 2NO(g) \; \Delta H = 180.6 \text{ kJ}$$
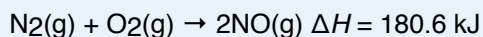
Answer

15.5 g

Chemistry Is Everywhere: Welding with Chemical Reactions

One very energetic reaction is called the *thermite reaction*. Its classic reactants are aluminum metal and iron(III) oxide; the reaction produces iron metal and aluminum oxide:

$$2Al(s) + Fe_2O_3(s) \rightarrow Al_2O_3(s) + 2Fe(s) \ \Delta H = -850.2 \text{ kJ}$$
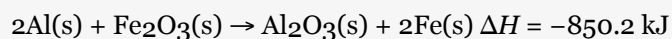
When properly done, the reaction gives off so much energy that the iron product comes off as a *liquid*. (Iron normally melts at 1,536°C.) If carefully directed, the liquid iron can fill spaces between two or more metal parts and, after it quickly cools, can weld the metal parts together.

Thermite reactions are used for this purpose even today. For civilian purposes, they are used to reweld broken locomotive axles that cannot be easily removed for repair. They are used to weld railroad tracks together. Thermite reactions can also be used to separate thin pieces of metal if, for whatever reason, a torch doesn't work.

A small clay pot contains a thermite mixture. It is reacting at high temperature in the photo and will eventually produce molten metal to join the railroad tracks below it.

Source: Photo courtesy of Skatebiker,http://commons.wikimedia.org/wiki/File:Velp- thermitewelding-1.jpg.

Thermite reactions are also used for military purposes. Thermite mixtures are frequently used with additional components as incendiary devices—devices that start fires. Thermite reactions are also useful in disabling enemy weapons: a piece of artillery doesn't work so well when it has a hole melted into its barrel because of a thermite reaction!

KEY TAKEAWAY

- ❖ The energy change of a chemical reaction can be used in stoichiometry calculations.

EXERCISES

1. Write the equivalences that this balanced thermochemical equation implies. $PCl_3(g) + Cl_2(g) \rightarrow PCl_5(g)$ $\Delta H = -87.9$ kJ

2. Write the equivalences that this balanced thermochemical equation implies. $2SO_3(g) \rightarrow 2SO_2(g) + O_2(g)$ $\Delta H = 197.9$ kJ

3. How many kilojoules are given off when 17.8 mol of $CH_4(g)$ react? $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell)$ $\Delta H = -890.1$ kJ

4. How many kilojoules are absorbed when 0.772 mol of $N_2(g)$ reacts? $N_2(g) + 2NO(g) \rightarrow 2N_2O(g)$ $\Delta H = 73.8$ kJ

5. How many kilojoules are absorbed when 23.09 mol of $C_6H_6(\ell)$ are formed? $6C(s) + 3H_2(g) \rightarrow C_6H_6(\ell)$ $\Delta H = 49.0$ kJ

6. How many kilojoules are given off when 8.32 mol of Mg react? $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$ $\Delta H = -1,213$ kJ

7. Glucose is the main fuel metabolized in animal cells: $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$ $\Delta H = -2,799$ kJ

    How much energy is given off when 100.0 g of $C_6H_{12}O_6$ react?

8. Given the thermochemical equation $2Al(s) + Fe_2O_3(s) \rightarrow Al_2O_3(s) + 2Fe(s)$ $\Delta H = -850.2$ kJ, how much energy is given off when 288 g of Fe are produced?

9. Given the thermochemical equation $2CO_2(g) \rightarrow 2CO(g) + O_2(g)$ $\Delta H = 566$ kJ, how much energy is absorbed when 85.2 g of CO_2 are reacted?

10. Given the thermochemical equation $2Na^+(aq) + SO_4(aq) \rightarrow Na_2SO_4(s)$ $\Delta H = 819.8$ kJ, how much energy is absorbed when 55.9 g of Na^+ (aq) are reacted?

11. $NaHCO_3$ decomposes when exposed to heat: $2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(\ell)$ $\Delta H = 91.5$ kJ What mass of $NaHCO_3$ is decomposed by 256 kJ?

12. HgO decomposes when exposed to heat: $2HgO(s) \rightarrow 2Hg(\ell) + O_2(g)$ $\Delta H = 181.6$ kJ . What mass of O_2 can be made with 100.0 kJ?

13. For the thermochemical equation $Fe_2O_3(s) + 3SO_3(g) \rightarrow Fe_2(SO_4)_3$ (s) $\Delta H = -570.2$ kJ, what mass of SO_3 is needed to generate 1,566 kJ?

14. For the thermochemical equation $H_2(g) + Br_2(\ell) \rightarrow 2HBr(g)$ $\Delta H = -72.6$ kJ, what mass of HBr will be formed when 553 kJ of energy are given off?

15. $2Na^+(aq) + SO_4(aq) \rightarrow Na_2SO_4(s)$ $\Delta H = 819.8$ kJ, how much energy is absorbed when 55.9 g of $Na^+(aq)$ are reacted?

16. $NaHCO_3$ decomposes when exposed to heat: $2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(\ell)$ $\Delta H = 91.5$ kJ What mass of $NaHCO_3$ is decomposed by 256 kJ?

17. HgO decomposes when exposed to heat: $2HgO(s) \rightarrow 2Hg(\ell) + O_2(g)$ $\Delta H = 181.6$ kJ What mass of O_2 can be made with 100.0 kJ?

18. For the thermochemical equation $Fe_2O_3(s) + 3SO_3(g) \rightarrow Fe_2(SO_4)_3$ (s) $\Delta H = -570.2$ kJ, what mass of SO_3 is needed to generate 1,566 kJ?

19. For the thermochemical equation $H2(g) + Br2(\ell) \rightarrow 2HBr(g)$ $\Delta H = -72.6$ kJ, what mass of HBr will be formed when 553 kJ of energy are given off?

5. HESS'S LAW

LEARNING OBJECTIVE

1. Learn how to combine chemical equations and their enthalpy changes.

Now that we understand that chemical reactions occur with a simultaneous change in energy, we can apply the concept more broadly. To start, remember that some chemical reactions are rather difficult to perform. For example, consider the combustion of carbon to make carbon monoxide:

$$2C(s) + O_2(g) \rightarrow 2CO(g) \ \Delta H = ?$$
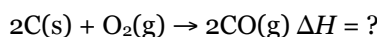
In reality, this is extremely difficult to do; given the opportunity, carbon will react to make another compound, carbon dioxide:

$$2C(s) + O_2(g) \rightarrow 2CO_2(g) \ \Delta H = -393.5 \text{ kJ}$$
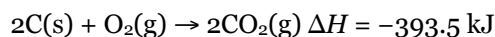
Is there a way around this? Yes. It comes from the understanding that chemical equations can be treated like algebraic equations, with the arrow acting like the equals sign. Like algebraic equations, chemical equations can be combined, and if the same substance appears on both sides of the arrow, it can be canceled out (much like a spectator ion in ionic equations). For example, consider these two reactions:

$$2C(s) + 2O_2(g) \rightarrow 2CO_2(g) 2CO_2(g) \rightarrow 2CO(g) + O_2(g)$$
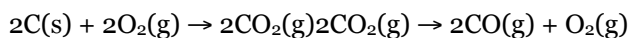
If we added these two equations by combining all the reactants together and all the products together, we would get

$$2C(s) + 2O_2(g) + 2CO_2(g) \rightarrow 2CO_2(g) + 2CO(g) + O_2(g)$$
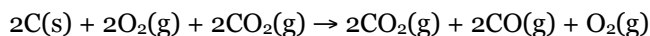
We note that $2CO_2(g)$ appears on both sides of the arrow, so they cancel:

$$2\,C(s) + \tfrac{1}{2}O_2(g) + \cancel{2\,CO_2(g)} \rightarrow \cancel{2\,CO_2(g)} + 2\,CO(g) + O_2(g)$$
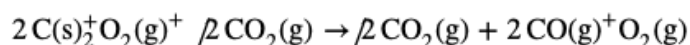
We also note that there are 2 mol of O_2 on the reactant side, and 1 mol of O_2 on the product side. We can cancel 1 mol of O_2 from both sides:

$$2\,C(s) + \tfrac{1}{2}O_2(g) \rightarrow 2\,CO(g) + O_2(g)$$

215
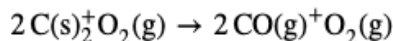
What do we have left?

$$2C(s) + O_2(g) \rightarrow 2CO(g)$$
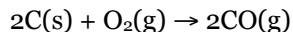
This is the reaction we are looking for! So by algebraically combining chemical equations, we can generate new chemical equations that may not be feasible to perform.

What about the enthalpy changes? Hess's law states that when chemical equations are combined algebraically, their enthalpies can be combined in exactly the same way. Two corollaries immediately present themselves:

1. If a chemical reaction is reversed, the sign on ΔH is changed.

2. If a multiple of a chemical reaction is taken, the same multiple of the ΔH is taken as well.

What are the equations being combined? The first chemical equation is the combustion of C, which produces CO2:

$$2C(s) + 2O_2(g) \rightarrow 2CO_2(g)$$
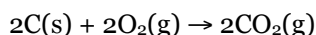
This reaction is two times the reaction to make CO2 from C(s) and O2(g), whose enthalpy change is known:

$$C(s) + O_2(g) \rightarrow CO_2(g) \; \Delta H = -393.5 \text{ kJ}$$
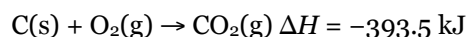
According to the first corollary, the first reaction has an energy change of two times −393.5 kJ, or −787.0 kJ:

$$2C(s) + 2O_2(g) \rightarrow 2CO_2(g) \; \Delta H = -787.0 \text{ kJ}$$

The second reaction in the combination is related to the combustion of CO(g):

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g) \; \Delta H = -566.0 \text{ kJ}$$

The second reaction in our combination is the *reverse* of the combustion of CO. When we reverse the reaction, we change the sign on the ΔH:

$$2CO_2(g) \rightarrow 2CO(g) + O_2(g) \; \Delta H = +566.0 \text{ kJ}$$
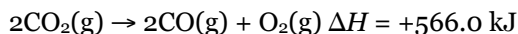
Now that we have identified the enthalpy changes of the two component chemical equations, we can combine the ΔH values and add them:

$$
\begin{cases}
2C(s) + 2O_2(g) \rightarrow 2CO_2(g) & \Delta H = -787.0 kJ \\
\cancel{2CO_2(g)} \rightarrow 2CO(g)) + \cancel{O_2(g)} & \Delta H = +566.0 kJ \\
\text{------------------------------} \\
2C(s) + O_2(g) \rightarrow 2CO(g) & \Delta H = -787.0 + 566.0 = -221.0 kJ
\end{cases}
$$
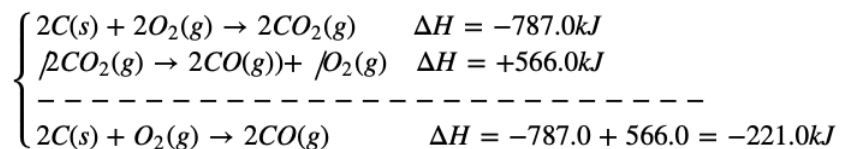
Hess's law is very powerful. It allows us to combine equations to generate new chemical reactions whose enthalpy changes can be calculated, rather than directly measured.

EXAMPLE 10

Determine the enthalpy change of C2H4 + 3O2 → 2CO2 + 2H2O ΔH = ?

from these reactions:

C2H2 + H2 → C2H4 ΔH = −174.5 kJ2C2H2 + 5O2 → 4CO2 + 2H2O ΔH = −1,692.2

kJ2CO2 + H2 → 2O2 + C2H2 ΔH = −167.5 kJ
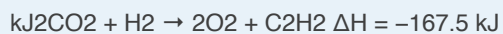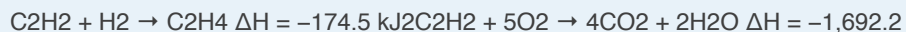
Solution

We will start by writing chemical reactions that put the correct number of moles of the correct substance on the proper side. For example, our desired reaction has C2H4 as a reactant, and only one reaction from our data has C2H4. However, it has C2H4 as a product. To make it a reactant, we need to reverse the reaction, changing the sign on the ΔH:

C2H4 → C2H2 + H2 ΔH = +174.5 kJ
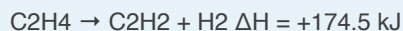
We need CO2 and H2O as products. The second reaction has them on the proper side, so let us include one of these reactions (with the hope that the coefficients will work out when all our reactions are added):

$$2C_2H_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O \quad \Delta H = -1{,}692.2 \text{ kJ}$$
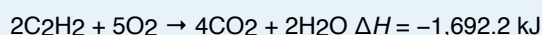
We note that we now have 4 mol of CO2 as products; we need to get rid of 2 mol of CO2. The last reaction has 2CO2 as a reactant. Let us use it as written:

$$2CO_2 + H_2 \rightarrow 2O_2 + C_2H_2 \quad \Delta H = -167.5 \text{ kJ}$$
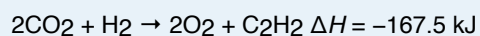
We combine these three reactions, modified as stated:

$$
\begin{array}{ll}
C_2H_4 \rightarrow C_2H_2 + H_2 & \Delta H = +174.5 \text{ kJ} \\
2C_2H_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O & \Delta H = -1{,}692.2 \text{ kJ} \\
2CO_2 + H_2 \rightarrow 2O_2 + C_2H_2 & \Delta H = -167.5 \text{ kJ} \\
\hline
C_2H_4 + 2C_2H_2 + 5O_2 + 2CO_2 + H_2 \rightarrow C_2H_2 + H_2 + 4CO_2 + 2H_2O + 2O_2 + C_2H_2 &
\end{array}
$$
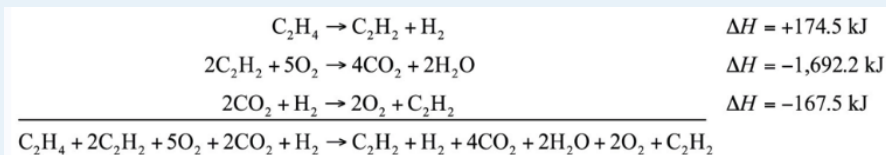
What cancels? 2C2H2, H2, 2O2, and 2CO2. What is left is

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$$
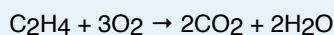
which is the reaction we are looking for. The ΔH of this reaction is the sum of the three ΔH values:

$$\Delta H = +174.5 - 1{,}692.2 - 167.5 = -1{,}685.2 \text{ kJ}$$

Test Yourself

Given the thermochemical equations

$$Pb + Cl_2 \rightarrow PbCl_2 \quad \Delta H = -223 \text{ kJ} \qquad PbCl_2 + Cl_2 \rightarrow PbCl_4 \quad \Delta H = -87 \text{ kJ}$$

determine ΔH for

$$2PbCl_2 \rightarrow Pb + PbCl_4$$
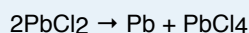
Answer

+136 kJ

❖   Hess's law allows us to combine reactions algebraically and then combine their enthalpy changes the same way.

EXERCISES

1   Define *Hess's law*.

2   What does Hess's law require us to do to the ΔH of a thermochemical equation if we reverse the equation?

3   If the ΔH for $C_2H_4 + H_2 \rightarrow C_2H_6$ is –65.6 kJ, what is the ΔH for this reaction? $C_2H_6 \rightarrow C_2H_4 + H_2$

4   If the ΔH for $2Na + Cl_2 \rightarrow 2NaCl$ is –772 kJ, what is the ΔH for this reaction: $2NaCl \rightarrow 2Na + Cl_2$

5   If the ΔH for $C_2H_4 + H_2 \rightarrow C_2H_6$ is –65.6 kJ, what is the ΔH for this reaction? $2C_2H_4 + 2H_2 \rightarrow 2C_2H_6$

6   If the ΔH for $2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$ is –2,650 kJ, what is the ΔH for this reaction? $6C_2H_6 + 21O_2 \rightarrow 12\text{-}CO_2 + 18H_2O$

7   The ΔH for $C_2H_4 + H_2O \rightarrow C_2H_5OH$ is –44 kJ. What is the ΔH for this reaction? $2C_2H_5OH \rightarrow 2C_2H_4 + 2H_2O$

8   The ΔH for $N_2 + O_2 \rightarrow 2NO$ is 181 kJ. What is the ΔH for this reaction? $NO \rightarrow 1/2N_2 + 1/2O_2$

9   Determine the ΔH for the reaction $Cu + Cl_2 \rightarrow CuCl_2$ given these data:

   $2Cu + Cl_2 \rightarrow 2CuCl$ $\Delta H = -274$ kJ $2CuCl + Cl_2 \rightarrow 2CuCl_2$ $\Delta H = -166$ kJ

10. Determine ΔH for the reaction $2CH_4 \rightarrow 2H_2 + C_2H_4$ given these data:

   $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ $\Delta H = -891$ kJ $C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$ $\Delta H = -1,411$ kJ $2H_2 + O_2 \rightarrow 2H_2O$

   $\Delta H = -571$ kJ

11. Determine ΔH for the reaction $Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3SO_3$ given these data:

   $4Fe + 3O_2 \rightarrow 2Fe_2O_3$ $\Delta H = -1,650$ kJ $2S + 3O_2 \rightarrow 2SO_3$ $\Delta H = -792$ kJ $2Fe + 3S$

   $+ 6O_2 \rightarrow Fe_2(SO_4)_3$ $\Delta H = -2,583$ kJ

12. Determine ΔH for the reaction $CaCO_3 \rightarrow CaO + CO_2$ given these data:

   $2Ca + 2C + 3O_2 \rightarrow 2CaCO_3$ $\Delta H = -2,414$ kJ $C + O_2 \rightarrow CO_2$ $\Delta H = -393.5$ kJ $2Ca + O_2 \rightarrow 2CaO$
   $\Delta H = -1,270$ kJ

6. FORMATION REACTIONS

LEARNING OBJECTIVES

1. Define a *formation reaction* and be able to recognize one.

2. Use enthalpies of formation to determine the enthalpy of reaction.

Hess's law allows us to construct new chemical reactions and predict what their enthalpies of reaction will be. This is a very useful tool because now we don't have to measure the enthalpy changes of every possible reaction. We need measure only the enthalpy changes of certain benchmark reactions and then use these reactions to algebraically construct any possible reaction and combine the enthalpies of the benchmark reactions accordingly.

But what are the benchmark reactions? We need to have some agreed-on sets of reactions that provide the central data for any thermochemical equation.

Formation reactions are chemical reactions that form one mole of a substance from its constituent elements in their standard states. By *standard states* we mean as a diatomic molecule if that is how the element exists and the proper phase at normal temperatures (typically room temperature). The product is one mole of substance, which may require that coefficients on the reactant side be fractional (a change from our normal insistence that all coefficients be whole numbers). For example, the formation reaction for methane (CH_4) is

$$C(s) + 2H_2(g) \rightarrow CH_4(g)$$
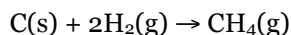
The formation reaction for carbon dioxide (CO_2) is

$$C(s) + O_2(g) \rightarrow CO_2(g)$$
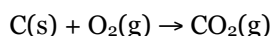
In both cases, one of the elements is a diatomic molecule because that is the standard state for that particular element. The formation reaction for H_2O:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(\ell)$$
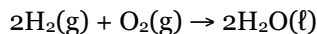
is *not* in a standard state because the coefficient on the product is 2; for a proper formation reaction, only one mole of product is formed. Thus, we have to divide all coefficients by 2:

$$H_2(g) + 1/2 O_2(g) \rightarrow H_2O(\ell)$$
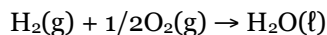
On a molecular scale, we are using half of an oxygen molecule, which may be problematic to visualize. However, on a molar level, it implies that we are reacting only half of a mole of oxygen molecules, which should be an easy concept for us to understand.

Given the formula of any substance, you should be able to write the proper formation reaction for that substance.
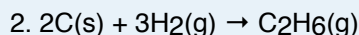
The enthalpy change for a formation reaction is called the **enthalpy of formation** and is given the symbol ΔH_f. The subscript f is the clue that the reaction of interest is a formation reaction. Thus, for the formation of FeO(s),

$$Fe(s) + \frac{1}{2}O_2(g) \rightarrow FeO(s) \quad \Delta H = \Delta H_f = -272 kJ/mol$$
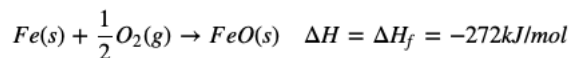
Note that now we are using kJ/mol as the unit because it is understood that the enthalpy change is for one mole of substance. Note, too, by definition, that the enthalpy of formation of an element is exactly zero because making an element from an element is no change. For example,

$$H_2(g) \rightarrow H_2(g) \; \Delta H_f = 0$$
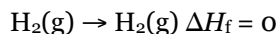
Formation reactions and their enthalpies are important because *these are the thermochemical data that are tabulated for any chemical reaction.* Table 7.2 "Enthalpies of Formation for Various Substances" lists some enthalpies of formation for a variety of substances; in some cases, however, phases can be important (e.g., for H_2O).

It is easy to show that any general chemical equation can be written in terms of the formation reactions of its reactants and products, some of them reversed (which means the sign must change in accordance with Hess's law). For example, consider

$$2NO_2(g) \rightarrow N_2O_4(g)$$
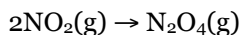
We can write it in terms of the (reverse) formation reaction of NO2 and the formation reaction of N2O4:

$$
\begin{array}{ll}
2 \times \left[NO_2(g) \rightarrow \frac{1}{2}N_2(g) + O_2(g) \right] & \Delta H = -2 \times \Delta H_r\,[NO_2] = -2(33.1 kJ) \\
N_2(g) + 2O_2(g) \rightarrow N_2O_4(g) & \Delta H = \Delta H_r\,[N_2O_4] \quad = 9.1 kJ \\
\hline
\quad\quad 2NO_2(g) \rightarrow N_2O_4 & \quad\quad\quad \Delta H = -57.1 kJ
\end{array}
$$
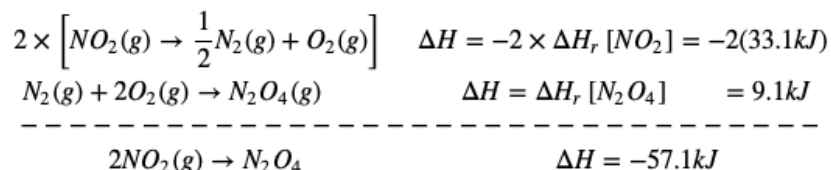
We must multiply the first reaction by 2 to get the correct overall balanced equation. We are simply using Hess's law in combining the ΔH_f values of the formation reactions.

Table 7.2 Enthalpies of Formation for Various Substances

Compound	ΔH_f(kJ/mol)	Compound	ΔH_f(kJ/mol)	Compound	ΔH_f(kJ/mol)	Compound	ΔH_f(kJ/mol)
Ag(s)	0	Ca(s)	0	Hg2Cl2(s)	-265.37	NaHCO3(s)	-950.81
AgBr(s)	-100.37	CaCl2(s)	-795.80	I2(s)	0	NaN3(s)	21.71
AgCl(s)	-127.01	CaCO3(s, arag)	-1,207.1	K(s)	0	Na2CO3(s)	-1,130.77
Al(s)	0	CaCO3(s, calc)	-1,206.9	KBr(s)	-393.8	Na2O(s)	-417.98
Al2O3(s)	-1,675.7	Cl2(g)	0	KCl(s)	-436.5	Na2SO4(s)	-331.64
Ar(g)	0	Cr(s)	0	KF(s)	-567.3	Ne(g)	0
Au(s)	0	Cr2O3(s)	-1,134.70	KI(s)	-327.9	Ni(s)	0
BaSO4(s)	-1,473.19	Cs(s)	0	Li(s)	0	O2(g)	0
Br2(ℓ)	0	Cu(s)	0	LiBr(s)	-351.2	O3(g)	142.67
C(s, dia)	1.897	F2(g)	0	LiCl(s)	-408.27	PH3(g)	22.89
C(s, gra)	0	Fe(s)	0	LiF(s)	-616.0	Pb(s)	0
CCl4(ℓ)	-128.4	Fe2(SO4)3(s)	-2,583.00	LiI(s)	-270.4	PbCl2(s)	-359.41
CH2O(g)	-115.90	Fe2O3(s)	-825.5	Mg(s)	0	PbO2(s)	-274.47
CH3COOH(ℓ)	-483.52	Ga(s)	0	MgO(s)	-601.60	PbSO4(s)	-919.97
CH3OH(ℓ)	-238.4	HBr(g)	-36.29	NH3(g)	-45.94	Pt(s)	0
CH4(g)	-74.87	HCl(g)	-92.31	NO(g)	90.29	S(s)	0
CO(g)	-110.5	HF(g)	-273.30	NO2(g)	33.10	SO2(g)	-296.81
CO2(g)	-393.51	HI(g)	26.5	N2(g)	0	SO3(g)	-395.77
C2H5OH(ℓ)	-277.0	HNO2(g)	-76.73	N2O(g)	82.05	SO3(ℓ)	-438
C2H6(g)	-83.8	HNO3(g)	-134.31	N2O4(g)	9.08	Si(s)	0
C6H12(ℓ)	-157.7	H2(g)	0	N2O5(g)	11.30	U(s)	0
C6H12O6(s)	-1277	H2O(g)	-241.8	Na(s)	0	UF6(s)	-2,197.0
C6H14(ℓ)	-198.7	H2O(ℓ)	-285.83	NaBr(s)	-361.1	UO2(s)	-1,085.0
C6H5CH3(ℓ)	12.0	H2O(s)	-292.72	NaCl(s)	-385.9	Xe(g)	0
C6H6(ℓ)	48.95	He(g)	0	NaF(s)	-576.6	Zn(s)	0
C10H8(s)	77.0	Hg(ℓ)	0	NaI(s)	-287.8	ZnCl2(s)	-415.05
C12H22O11(s)	-2,221.2						

Sources: National Institute of Standards and Technology's Chemistry WebBook ,http://webbook.nist.gov/chemistry; D. R. Lide, ed., *CRC Handbook of Chemistry and Physics*, 89th ed. (Boca Raton, FL: CRC Press, 2008); J. A. Dean, ed., *Lange's Handbook of Chemistry*, 14th ed. (New York: McGraw-Hill, 1992).

EXAMPLE 13

Show that the reaction

Fe2O3(s) + 3SO3(g) → Fe2(SO4)3(s)
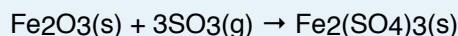
can be written as a combination of formation reactions.

Solution

There will be three formation reactions. The one for the products will be written as a formation reaction, while the ones for the reactants will be written in reverse. Furthermore, the formation reaction for SO3 will be multiplied by 3 because there are three moles of SO3 in the balanced chemical equation. The formation reactions are as follows:

$$Fe_2O_3(s) \rightarrow 2Fe(s) + \frac{3}{2}O_2(g)$$

$$3 \times \left[SO_3(g) \rightarrow S(s) + \frac{3}{2}O_2(g) \right]$$

2Fe(s) + 3S(s) + 6O2(g) → Fe2(SO4)3(s)
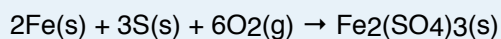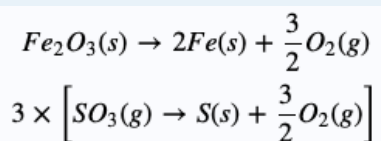
When these three equations are combined and simplified, the overall reaction is

Fe2O3(s) + 3SO3(s) → Fe2(SO4)3(s)
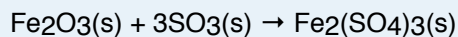
Test Yourself

Write the formation reactions that will yield

2SO2(g) + O2(g) → 2SO3(g).
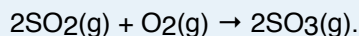
Answer

Now that we have established formation reactions as the major type of thermochemical reaction we will be interested in, do we always need to write all the formation reactions when we want to determine the enthalpy change of any random chemical reaction? No. There is an easier way. You may have noticed in all our examples that we change the signs on all the enthalpies of formation of the reactants, and we don't change the signs on the enthalpies of formation of the products. We also multiply the enthalpies of formation of any substance by its coefficient—technically, even when it is just 1. This allows us to make the following statement: the enthalpy change of any chemical reaction is equal to the sum of the enthalpies of formation of the products minus the sum of the enthalpies of formation of the reactants. In mathematical terms,

$$\Delta H_{rxn} = \sum n_p \Delta H_{f,p} - \sum n_r \Delta H_{f,r}$$

where n_p and n_r are the number of moles of products and reactants, respectively (even if they are just 1 mol), and $\Delta H_{f,p}$ and $\Delta H_{f,r}$ are the enthalpies of formation of the product and reactant species, respectively. This *products-minus-reactants* scheme is very useful in determining the enthalpy change of any chemical reaction, if the enthalpy of formation data are available. Because the mol units cancel when multiplying the amount by the enthalpy of formation, the enthalpy change of the chemical reaction has units of energy (joules or kilojoules) only.

Food and Drink App: Calories and Nutrition

Section 7.1 "Energy" mentioned the connection between the calorie unit and nutrition: the calorie is the common unit of energy used in nutrition, but we really consider the kilocalorie (spelled Calorie with a capital C). A daily diet of 2,000 Cal is actually 2,000,000 cal, or over 8,000,000 J, of energy.

Nutritionists typically generalize the Calorie content of foods by separating it into the three main

food types: proteins, carbohydrates, and fats. The general rule of thumb is as follows:

If the food is	It has this energy content
protein	4 Cal/g
carbohydrate	4 Cal/g
fat	9 Cal/g

This table is very useful. Assuming a 2,000 Cal daily diet, if our diet consists solely of proteins and carbohydrates, we need only about 500 g of food for sustenance—a little more than a pound. If our diet consists solely of fats, we need only about 220 g of food—less than a half pound. Of course, most of us have a mixture of proteins, carbohydrates, and fats in our diets. Water has no caloric value in the diet, so any water in the diet is calorically useless. (However, it is important for hydration; also, many forms of water in our diet are highly flavored and sweetened, which bring other nutritional issues to bear.)

When your body works, it uses calories provided by the diet as its energy source. If we eat more calories than our body uses, we gain weight—about 1 lb of weight for every additional 3,500 Cal we ingest. Similarly, if we want to lose weight, we need to expend an extra 3,500 Cal than we ingest to lose 1 lb of weight. No fancy or fad diets are needed; maintaining an ideal body weight is a straightforward matter of thermochemistry—pure and simple.

KEY TAKEAWAYS

- ❖ A formation reaction is the formation of one mole of a substance from its constituent elements.
- ❖ Enthalpies of formation are used to determine the enthalpy change of any given reaction.

EXERCISES

1 Define *formation reaction* and give an example.

2 Explain the importance of formation reactions in thermochemical equations.

3

    1. $H_2(g) + S(s) \rightarrow H_2S(g)$

    2. $2HBr(g) + Cl_2(g) \rightarrow 2HCl(g) + Br_2(\ell)$

4

    1. $Fe(g) + 1/2O_2(g) \rightarrow FeO(s)$

    2. $Hg(\ell) + 1/2O_2(g) \rightarrow HgO(s)$

5 Which of the following reactions is a formation reaction? If it is not a formation reaction, explain why.

1. $H_2(g) + S(s) + 2O_2(g) \rightarrow H_2SO_4(\ell)$

2. $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(\ell)$

6. Which of the following reactions is a formation reaction? If it is not a formation reaction, explain why.

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

   2. b. $2Na(s) + C(s) + 3/2O_2(g) \rightarrow Na_2CO_3(s)$

7. Write a proper formation reaction for each substance.

   1. $H_3PO_4(s)$

   2. $Na_2O(s)$

   3. $C_3H_7OH(\ell)$

8. Write a proper formation reaction for each substance.

   1. $N_2O_5(g)$

   2. $BaSO_4(s)$

   3. $Fe(OH)_3(s)$

9. Write a proper formation reaction for each substance.

   1. a. $C_{12}H_{22}O_{11}(s)$

   2. $Zn(NO_3)_2(s)$

   3. $Al(OH)_3(s)$

10. Write a proper formation reaction for each substance.
    1. $O_3(g)$

    2. $Na_2O_2(s)$

    3. $PCl_5(g)$

11. Write this reaction in terms of formation reactions. $MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$

12. Write this reaction in terms of formation reactions. $2NO + 4NO_2 \rightarrow 2N_2O_5 + N_2$

13. Write this reaction in terms of formation reactions. $2CuCl(s) \rightarrow Cu(s) + CuCl_2(s)$

14. Write this reaction in terms of formation reactions. $SiH_4 + 4F_2 \rightarrow SiF_4 + 4HF$

15. Determine the enthalpy change of this reaction. Data can be found in Table 7.2 "Enthalpies of Formation for Various Substances". $CH_2O(g) + O_2 \rightarrow CO_2(g) + H_2O(\ell)$

16. Determine the enthalpy change of this reaction. Data can be found in Table 7.2 "Enthalpies of Formation for Various Substances". $2AgBr(s) + Cl_2(g) \rightarrow 2AgCl(s) + Br_2(\ell)$

17. Determine the enthalpy change of this reaction. Data can be found in Table 7.2 "Enthalpies of Formation for Various Substances". $Mg(s) + N_2O_5(g) \rightarrow MgO(s) + 2NO_2(g)$

ANSWERS

1. A formation reaction is a reaction that produces one mole of a substance from its elements. Example: $C(s) + O_2(g) \rightarrow CO_2(g)$

3. a. formation reaction

   b. It is not the formation of a single substance, so it is not a formation reaction.

5. a. formation reaction

   b. It is not the formation of a single substance, so it is not a formation reaction.

7. a. $3/2H_2(g) + P(s) + 2O_2(g) \rightarrow H_3PO_4(s)$

   b. $2Na(s) + 1/2O_2(g) \rightarrow Na_2O(s)$

   c. $3C(s) + 1/2O_2(g) + 4H_2(g) \rightarrow C_3H_7OH(\ell)$

9. a. $12C(s) + 11H_2(g) + 11/2O_2(g) \rightarrow C_{12}H_{22}O_{11}(s)$ b. $Zn(s) + N_2(g) + 3O_2(g) \rightarrow Zn(NO_3)_2$

   c. $Al(s) + 3/2O_2(g) + 3/2H_2(g) \rightarrow Al(OH)_3(s)$

11. a. $MgCO_3(s) \rightarrow Mg(s) + C(s) + 3/2O_2(g)$

    b. $Mg(s) + 1/2O_2(g) \rightarrow MgO(s)$

    c. $C(s) + O_2(g) \rightarrow CO_2(g)$

13. a. $2 \times [CuCl(s) \rightarrow Cu(s) + 1/2Cl_2(g)]$

    b. $Cu(s) \rightarrow Cu(s)$

    b. $Cu(s) + Cl_2(g) \rightarrow CuCl_2(s)$

15. $\Delta H = -563.44$ kJ

17. $\Delta H = -546.7$ kJ

7. END-OF-CHAPTER MATERIAL

1. What is the work when 124 mL of gas contract to 72.0 mL under an external pressure of 822 torr.

2. What is the work when 2,345 mL of gas contract to 887 mL under an external pressure of 348 torr?

3. A 3.77 L volume of gas is exposed to an external pressure of 1.67 atm. As the gas contracts, 156 J of work are added to the gas. What is the final volume of the gas?

4. A 457 mL volume of gas contracts when 773 torr of external pressure act on it. If 27.4 J of work are added to the gas, what is its final volume?

5. What is the heat when 1,744 g of Hg increase in temperature by 334°C? Express your final answer in kJ.

6. What is the heat when 13.66 kg of Fe cool by 622°C? Express your final answer in kJ.

7. What is final temperature when a 45.6 g sample of Al at 87.3°C gains 188 J of heat?

8. What is final temperature when 967 g of Au at 557°C lose 559 J of heat?

9. Plants take CO_2 and H_2O and make glucose ($C_6H_{12}O_6$) and O_2. Write a balanced thermochemical equation for this process. Use data in Table 7.2 "Enthalpies of Formation for Various Substances".

10. Exercise 9 described the formation of glucose in plants, which take in CO_2 and H_2O and give off O_2. Is this process exothermic or endothermic? If exothermic, where does the energy go? If endothermic, where does the energy come from?

11. The basic reaction in the refining of aluminum is to take $Al_2O_3(s)$ and turn it into $Al(s)$ and $O_2(g)$. Write the balanced thermochemical equation for this process. Use data in Table 7.2 "Enthalpies of Formation for Various Substances".

12. Is the enthalpy change of the reaction $H_2O(\ell) \rightarrow H_2O(g)$ zero or nonzero? Use data in Table 7.2 "Enthalpies of Formation for Various Substances" to determine the answer.

13. What mass of H_2O can be heated from 22°C to 80°C in the combustion of 1 mol of CH_4? You will need the balanced thermochemical equation for the combustion of CH_4. Use data in Table 7.2 "Enthalpies of Formation for Various Substances".

14. What mass of H_2O can be heated from 22°C to 80°C in the combustion of 1 mol of C_2H_6? You will need the balanced thermochemical equation for the combustion of C_2H_6. Use data in Table 7.2 "Enthalpies of Formation for Various Substances". Compare your answer to Exercise 13.

15. What is the enthalpy change for the unknown reaction?
    $Pb(s) + Cl_2(g) \rightarrow PbCl_2(s)$ $\Delta H = -359$ kJ
    $PbCl_2(s) + Cl_2(g) \rightarrow PbCl_4(\ell)$ $\Delta H = ?$
    $Pb(s) + 2Cl_2(g) \rightarrow PbCl_4(\ell)$ $\Delta H = -329$ kJ

1 What is the enthalpy change for the unknown reaction?

$P(s) + 3/2Br_2(\ell) \rightarrow PBr_3(\ell) \ \Delta H = -185 \ kJPI_3(s) \rightarrow P(s) + 3/2I_2(s) \ \Delta H = ?PI_3(s) + 3/2Br_2(\ell) \rightarrow PBr_3(\ell)$

$+ 3/2I_2(s) \ \Delta H = -139 \ kJ$
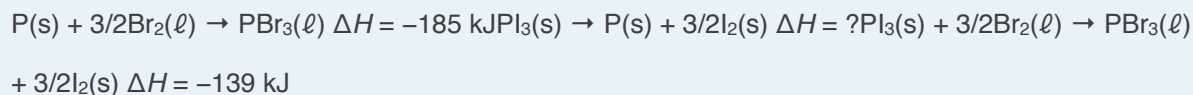
1 What is the ΔH for this reaction? The label *gra* means graphite, and the label *dia* means diamond. What does your answer mean?

$C(s, gra) \rightarrow C(s, dia)$
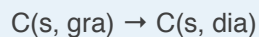
1 Without consulting any tables, determine the ΔH for this reaction. Explain your answer. $H_2O(\ell, 25°C) \rightarrow$

$H_2O(\ell, 25°C)$

ANSWERS

1. 5.70 J

3. 4.69 L

5. 80.97 kJ

7. 91.9°C

9. $6CO_2(g) + 6H_2O(\ell) \rightarrow C_6H_{12}O_6(s) + 6O_2(g) \ \Delta H = 2,799 \ kJ$

11. $2Al_2O_3(s) \rightarrow 4Al(s) + 3O_2(g) \ \Delta H = 3351.4 \ kJ$

13. 3,668 g

15. $\Delta H = 30 \ kJ$

17. $\Delta H = 1.897 \ kJ$; the reaction is endothermic.

CHAPTER 8: ELECTRONIC STRUCTURE

Opening Essay

Normal light microscopes can magnify objects up to about 1,500 times. Electron microscopes can magnify objects up to 1,000,000 times. Why can electron microscopes magnify images so much?

A microscope's resolution depends on the wavelength of light used. The smaller the wavelength, the more a microscope can magnify. Light is a wave, and, as such, it has a wavelength associated with it. The wavelength of visible light, which is detected by the eyes, varies from about 700 nm to about 400 nm.

One of the startling conclusions about modern science is that electrons also act as waves. However, the wavelength of electrons is much, much shorter—about 0.5 to 1 nm. This allows electron microscopes to magnify 600–700 times more than light microscopes. This allows us to see even smaller features in a world that is invisible to the naked eye.

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.

1. LIGHT

LEARNING OBJECTIVES
1. Describe light with its frequency and wavelength.
2. Describe light as a particle of energy.

What we know 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 8.1 "Characteristics of Light Waves" shows how these two characteristics are defined.

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

$$\text{speed} = \lambda \nu$$

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

$$c = \lambda \nu$$
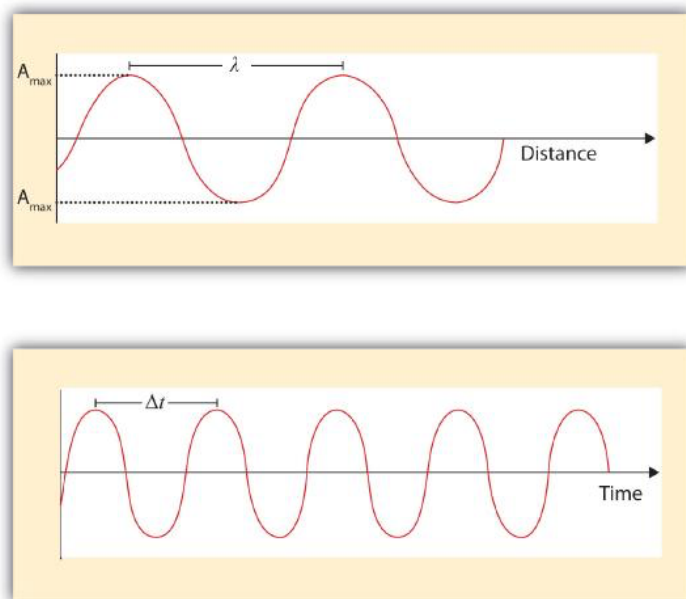
Figure 8.1: Characteristics of Light - Light acts as a wave and can be described by a wavelength λ and a frequency v.

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 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

$$3.00 \times 10^8 m/s = (5.55 \times 10^{-7} m) \, v$$

We divide both sides of the equation by 5.55 × 10–7 m and get

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

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."

Test Yourself

What is the wavelength of light if its frequency is 1.55 × 1010 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 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

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

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

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

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

Test Yourself

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 8.2 "The Electromagnetic Spectrum" 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.

Electromagnetic Spectrum
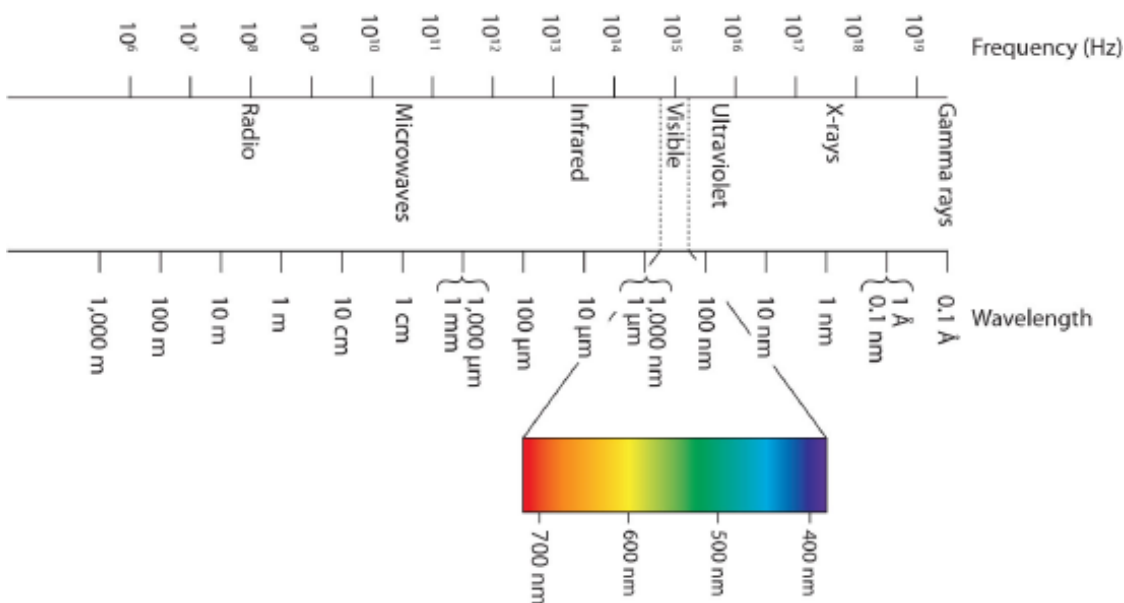
Figure 8.2: *The Electromagnetic Spectrum - The electromagnetic spectrum, with its various regions labeled. The borders of each region are approximate.*

EXERCISES

1. Describe the characteristics of a light wave.

2. What is a a characteristic of a particle of light?

3. What is the frequency of light if its wavelength is 733 x 10^{-5} n?

4. What is the frequency of light if its wavelength is 733 nm?

5. What is the frequency of light if its wavelength is 8.528 cm?

6. What is the wavelength of light if its frequency is 8.19×10^{14} s^{-1}?

7. What is the wavelength of light if its frequency is 3.66×10^{6} s^{-1}?

8. What is the wavelength of light if its frequency is 1.009×10^{6} Hz?

9. What is the wavelength of light if its frequency is 3.79×10^{-3} Hz?

10. What is the energy of a photon if its frequency is 5.55×10^{13} s^{-1}?

11. What is the energy of a photon if its frequency is 2.06×10^{18} s^{-1}?

12. What is the energy of a photon if its wavelength is 5.88×10^{-4} m?

13. What is the energy of a photon if its wavelength is 1.888×10^{2} m?

ANSWERS

1. Light has a wavelength and a frequency.

3. 4.09×10^{12} s^{-1}

5. 4.09×10^{14} s^{-1}

7. 3.66×10^{-7} m

9. 297 m

11. 3.68×10^{-20} J

13. 3.38×10^{-22} J

2. QUANTUM NUMBERS FOR ELECTRONS

LEARNING OBJECTIVES

1. Explain what spectra are.
2. 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 8.3 "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 8.3 "Prisms and Light"). This image is called a **line spectrum**. It turns out that every element has its own unique, characteristic line spectrum.

(a)

(b)
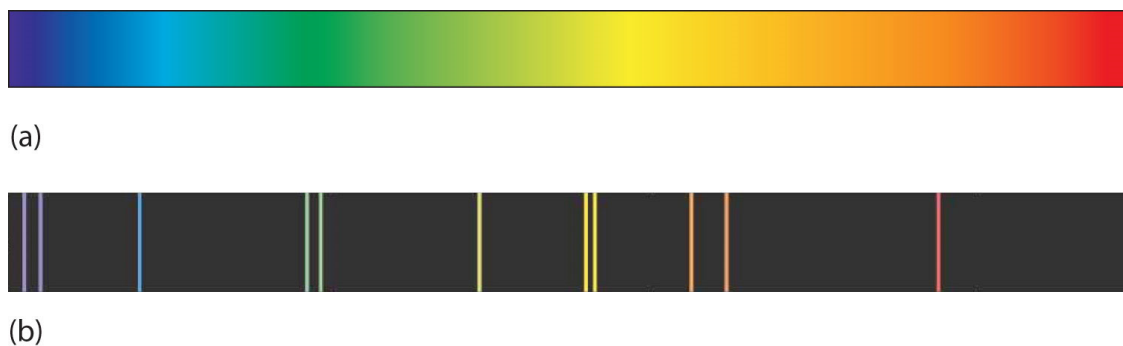
Figure 8.3: *Prisms and Light (a) A glowing object gives off a full rainbow of colors, which are noticed only when light is passed through a prism to make a continuous spectrum. (b) However, when electricity is passed through a gas, only certain colors of light are emitted. Here are the colors of light 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 8.4 "Hydrogen Spectrum"). Late-nineteenth-century scientists found that the positions of the lines obeyed a pattern given by the equation

$$\frac{1}{\lambda} = (109,700 cm^{-1})\left(\frac{1}{4} - \frac{1}{n^2}\right)$$

where n = 3, 4, 5, 6,..., but they could not explain why this was so.
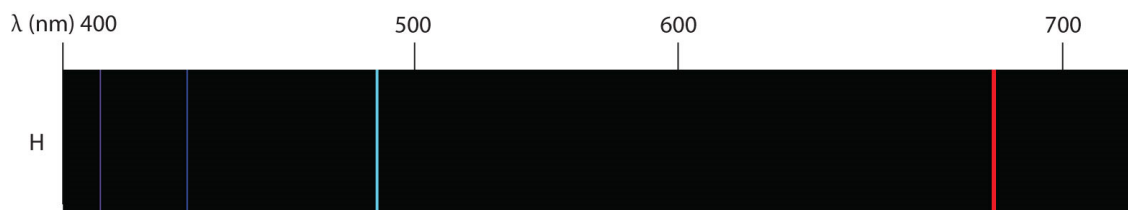
Figure 8.4: *Hydrogen Spectrum - The spectrum of hydrogen was particularly simple and could be predicted by a simple mathematical expression.*

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 same n in the equation above and now called a **quantum number**). Quantities that have certain specific values are called **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:

$$E_{light} = h\nu = \Delta E_{electron}$$

This means that only certain frequencies (and thus, certain wavelengths) of light are emitted. Figure 8.5 "Bohr's Model of the Hydrogen Atom" shows a model of the hydrogen atom based on Bohr's ideas.
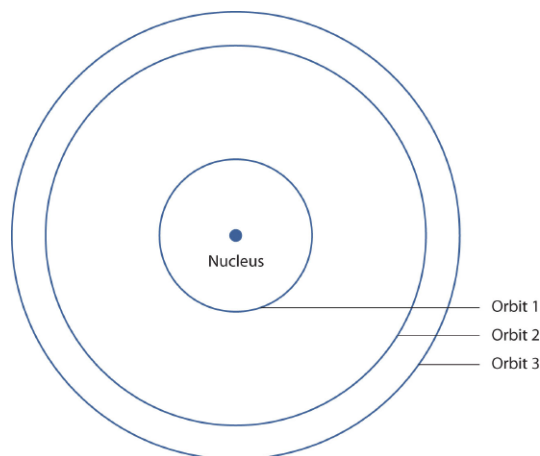
Figure 8.5: *Bohr's Model of the Hydrogen Atom - Bohr's description of the hydrogen atom had specific orbits for the electron, which had quantized energies.*

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 random-

ly 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 $n - 1$:

$$\ell = 0, 1, 2,..., n - 1$$

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:

$$-\ell \leq m_\ell \leq \ell$$

or

$$|m\ell| \leq \ell$$

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

If ℓ equals	The $m\ell$ 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 8.6 "Electron Orbitals"). Any s orbital is spherically symmetric (part (a) in Figure 8.6 "Electron Orbitals"), and there is only one orbital in any s sub-shell. Any p orbital has a two-lobed, dumbbell-like shape (part (b) in Figure 8.6 "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 (part (c) in Figure 8.6 "Electron Orbitals"); they are oriented differently in space (the one labeled $dz2$ 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 8.6 "Electron Orbitals" are estimates of the electron distribution in space, not surfaces electrons are fixed on.

Figure 8.6: *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 dz2 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).*
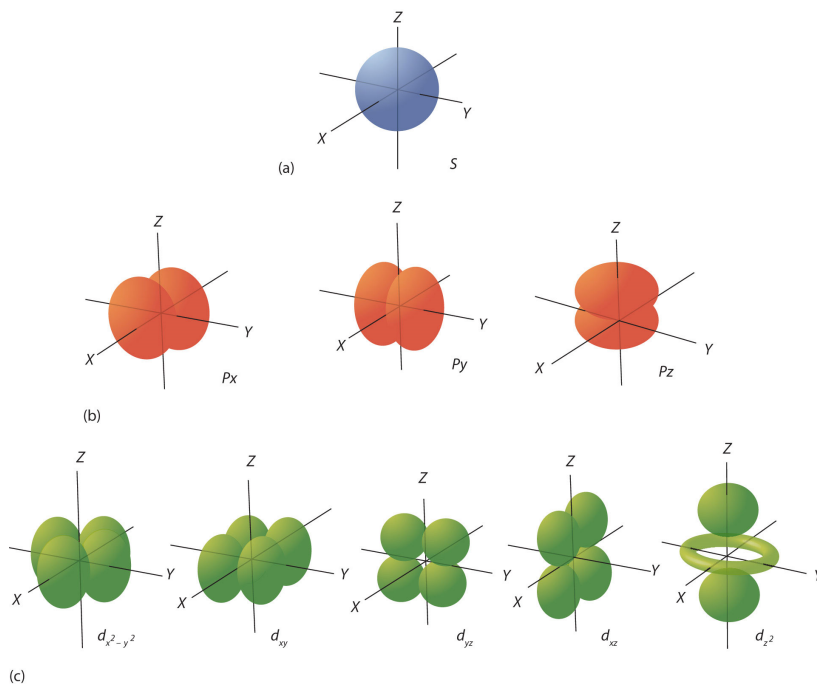
Electrons themselves have two possible spin states, and because of mathematics, they are assigned the quantum numbers +1/2 and −1/2. These are the only two possible choices for the spin quantum number of an electron.

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.

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

EXERCISES

1. Differentiate between a continuous spectrum and a line spectrum.

2. Under what circumstances is a continuous spectrum formed? Under what circumstances is a line spectrum formed?

3. What is the wavelength of light from the hydrogen atom spectrum when $n = 3$?

4. What is the wavelength of light from the hydrogen atom spectrum when $n = 5$?

5. What are the restrictions on the principal quantum number?

6. What are the restrictions on the angular momentum quantum number?

7. What are the restrictions on the magnetic quantum number?

8. What are the restrictions on the spin quantum number?

9. What are the possible values for ℓ when $n = 5$?

10. What are the possible values for ℓ when $n = 1$?

11. What are the possible values for m_ℓ when $\ell = 3$?

12. What are the possible values for m_ℓ when $\ell = 6$?

13. Describe the shape of an s orbital.

14. Describe the shape of a p orbital.

15. Which of these sets of quantum numbers is allowed? If it is not, explain why.
    1. {4, 1, −2, +1/2}
    2. {2, 0, 0, −1/2}

16. Which of these sets of quantum numbers is allowed? If it is not, explain why.
    1. {5, 2, −1, −1/2}
    2. {3, −1, −1, −1/2}

ANSWERS

1. A continuous spectrum is a range of light frequencies or wavelengths; a line spectrum shows only certain frequencies or wavelengths.

3. 6.56×10^{-7} m, or 656 nm

5. The principal quantum number is restricted to being a positive whole number.

7. The absolute value of m_ℓ must be less than or equal to ℓ: $|m_\ell| \leq \ell$.

9. ℓ can be 0, 1, 2, 3, or 4.

11. m_ℓ can be -3, -2, -1, 0, 1, 2, or 3.

13. An s orbital is spherical in shape.

15. a. Because $|m_\ell|$ must be less than ℓ, this set of quantum numbers is not allowed.

    b. allowed

3. ORGANIZATION OF ELECTRONS IN ATOMS

LEARNING OBJECTIVES

1. Learn how electrons are organized in atoms.

2. 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 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.

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 anelectron 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

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

He 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

$$\text{Li: } 1s^2 2s^1$$
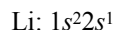
Be has four electrons, two in the 1s subshell and two in the 2s subshell. Its electron configuration is

$$\text{Be: } 1s^2 2s^2$$
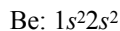
Now that the 2s subshell is filled, electrons in larger atoms must go into the 2p subshell, which can hold a maximum of six electrons. The next six elements progressively fill up the 2p subshell:

$$\text{B: } 1s^2 2s^2 2p^1$$

$$\text{C: } 1s^2 2s^2 2p^2$$

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

$$\text{O: } 1s^2 2s^2 2p^4$$

$$\text{F: } 1s^2 2s^2 2p^5$$

$$\text{Ne: } 1s^2 2s^2 2p^6$$
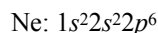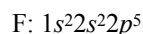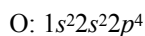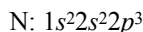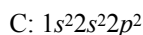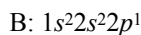
Now that the 2p subshell is filled (all possible subshells in the $n = 2$ shell), the next electron for the next-larger atom must go into the $n = 3$ shell, s subshell.

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

Answer

$$1s^2 2s^2 2p^6 3s^2$$
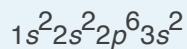
For larger atoms, the electron arrangement becomes more complicated. This is because after the 3p subshell is filled, filling the 4s subshell first actually leads to a lesser overall energy than filling the 3d subshell. Recall that while the principal quantum number largely dictates the energy of an 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:

$$\text{K: } 1s^2 2s^2 2p^6 3s^2 3p^6 4s^1, \text{ not } 1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$$
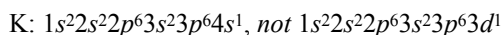
For larger and larger atoms, the order of filling the shells and subshells seems to become even more complicated. There are some useful ways to remember the order, like that shown in Figure 8.7 "Electron Shell Filling Order". If you follow the arrows in order, they pass through the subshells in the order 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 8.7 "Electron Shell Filling Order" gives a valid ordering of filling subshells with electrons for most atoms.

Figure 8.7: *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.*
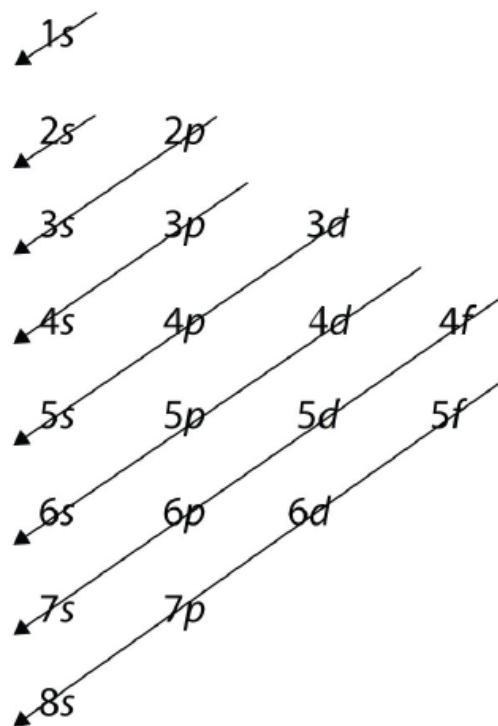
EXAMPLE 6

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

Solution

We will follow the chart in Figure 8.7 "Electron Shell Filling Order" until we can accommodate 50 electrons in the subshells in the proper order:

Sn: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^2$
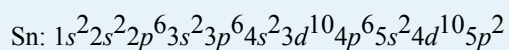
Verify by adding the superscripts, which indicate the number of electrons: 2 + 2 + 6 + 2 + 6 + 2 + 10 + 6 + 2 + 10 + 2 = 50, so we have placed all 50 electrons in subshells in the proper order.

Test Yourself

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

Answer

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2$
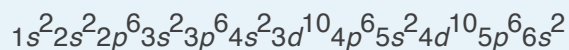
As the previous example demonstrated, electron configurations can get fairly long. An **abbreviated electron configuration** uses one of the elements from the last column of the periodic table, which contains what are called the *noble gases*, to represent the core of electrons up to that element. Then the remaining electrons are listed explicitly. For example, the abbreviated electron configuration for Li, which has three electrons, would be

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

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:

$$\text{W: } [\text{Xe}]6s^2 4f^{14} 5d^4$$
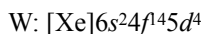
This is a significant simplification over an explicit listing of all 74 electrons. So for larger elements, the abbreviated electron configuration can be a very useful shorthand.

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

$$\text{Ag: } [\text{Kr}]5s^2 4d^9$$
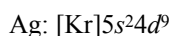
However, experiments have shown that the electron configuration is actually

$$\text{Ag: } [\text{Kr}]5s^1 4d^{10}$$
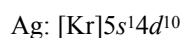
This, then, qualifies as an exception to our expectations. At this point, you do not need to memorize the exceptions; but if you come across one, understand that it is an exception to the normal rules of filling subshells with electrons, which can happen.

EXERCISES

1. What is the maximum number of electrons in the entire $n = 4$ shell?

2. Write the complete electron configuration for each atom.

   1. Si, 14 electrons
   2. Sc, 21 electrons

3. Write the complete electron configuration for each atom.

   1. Br, 35 electrons
   2. Be, 4 electrons

3. Write the complete electron configuration for each atom.

   1. Cd, 48 electrons
   2. Mg, 12 electrons

3. Write the complete electron configuration for each atom.

   1. Cs, 55 electrons
   2. Ar, 18 electrons

4. Write the abbreviated electron configuration for each atom in Exercise 7.

5. Write the abbreviated electron configuration for each atom in Exercise 8.

6. Write the abbreviated electron configuration for each atom in Exercise 9.

7. Write the abbreviated electron configuration for each atom in Exercise 10.

4. ELECTRONIC STRUCTURE AND THE PERIODIC TABLE

LEARNING OBJECTIVES

1. Relate the electron configurations of the elements to the shape of the periodic table.

2. Determine the expected electron configuration of an element by its place on the periodic table.

In Chapter 3 "Atoms, Molecules, and Ions", we introduced the periodic table as a tool for organizing the known chemical elements. A periodic table is shown in Figure 8.8 "The Periodic Table". 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.

Figure 8.8: *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.* 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 (see Figure 8.9 "The 1").

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) |
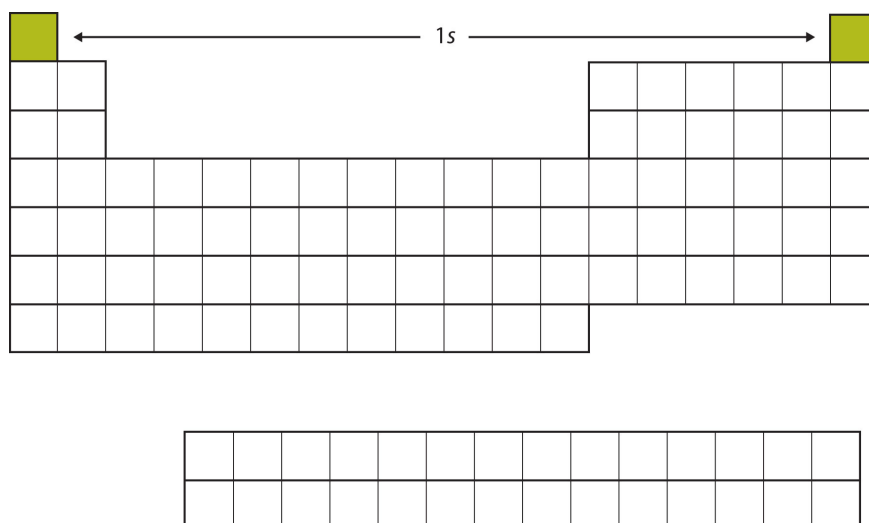
Figure 8.9: *The 1s Subshell - H and He represent the filling of the 1s subshell.*

The next two electrons, for Li and Be, would go into the 2*s* subshell. Figure 8.10 "The 2" shows that these two elements are adjacent on the periodic table.
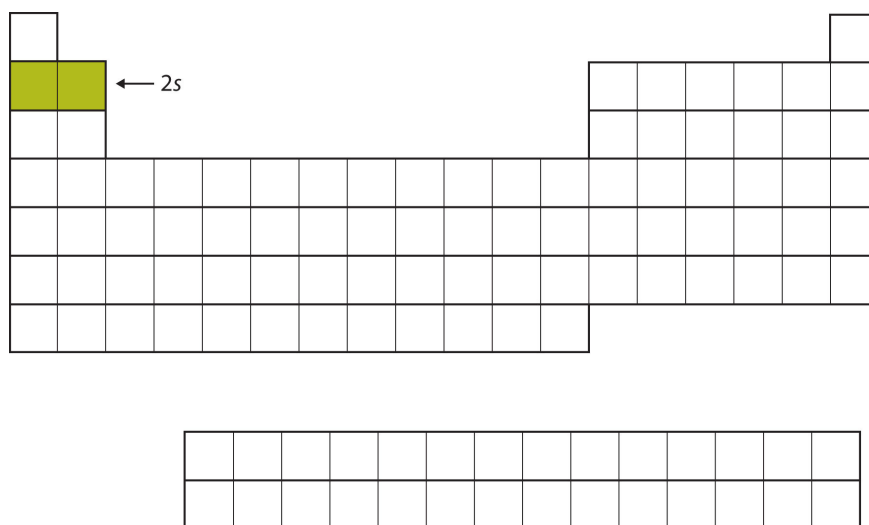
Figure 8.10: *The 2s Subshell - In Li and Be, the 2s subshell is being filled.*

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 8.11 "The 2").
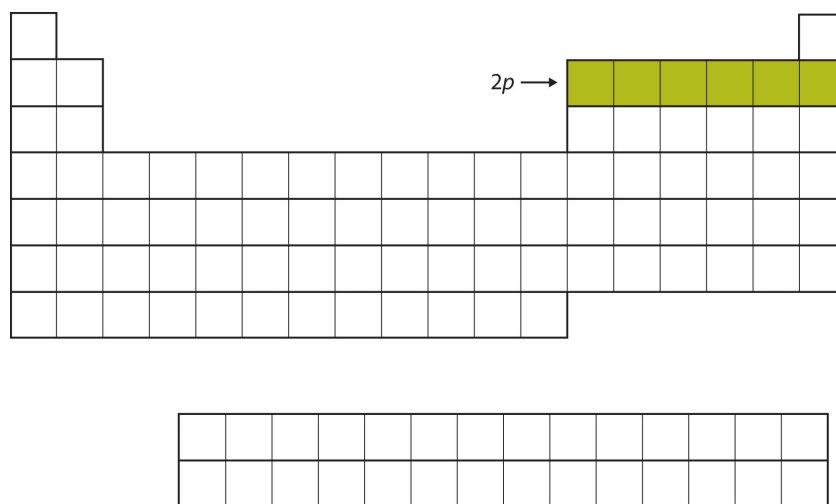
Figure 8.11: *The 2p Subshell - For B through Ne, the 2p subshell is being occupied.*

The next subshell to be filled is the 3s subshell. The elements when this subshell is being filled, Na and Mg, are back on the left side of the periodic table (Figure 8.12 "The 3").
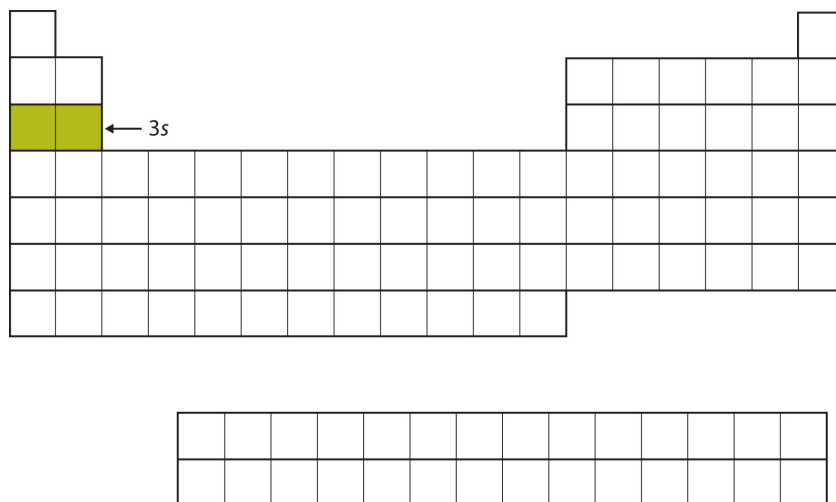
Figure 8.12: *The 3s Subshell - Now the 3s subshell is being occupied.*

Next, the 3*p* subshell is filled with the next six elements (Figure 8.13 "The 3").
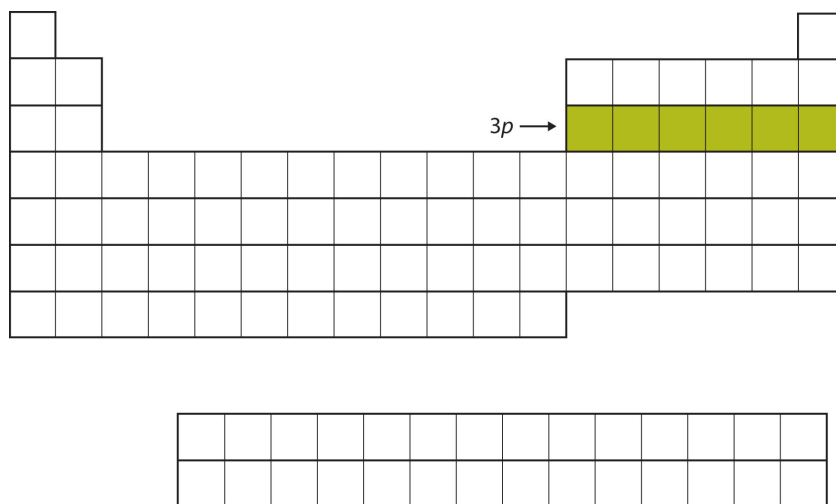
Figure 8.13: *The 3p Subshell - Next, the 3p subshell is filled with electrons.*

Instead of filling the 3*d* subshell next, electrons go into the 4*s* subshell (Figure 8.14 "The 4").
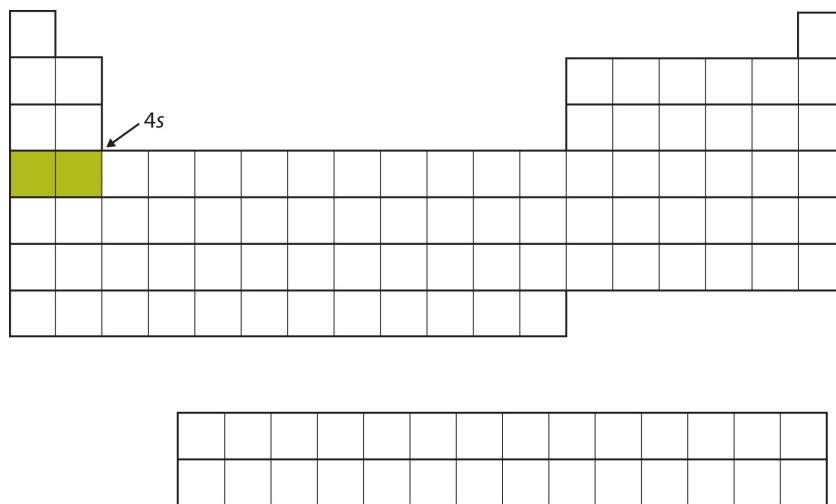
Figure 8.14: *The 4s Subshell - The 4s subshell is filled before the 3d subshell. This is reflected in the structure of the periodic table.*

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 8.15 "The 3").
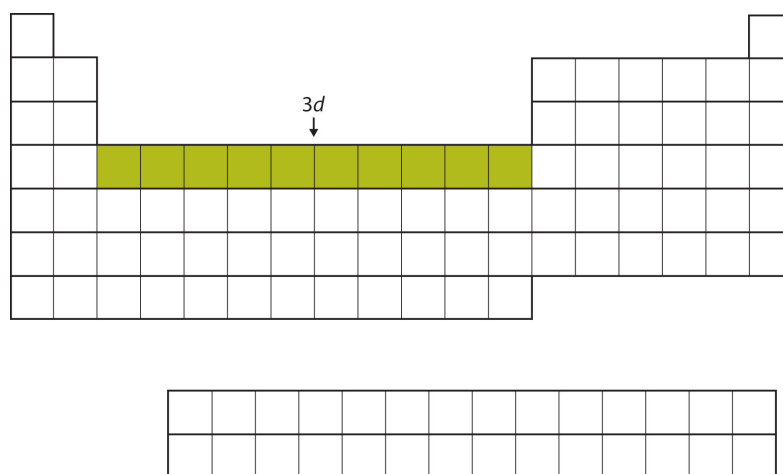
Figure 8.15: *The 3d Subshell - The 3d subshell is filled in the middle section of the periodic table.*

And so forth. As we go across the rows 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** are 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 8.16 "Blocks on the Periodic Table" shows the blocks of the periodic table.
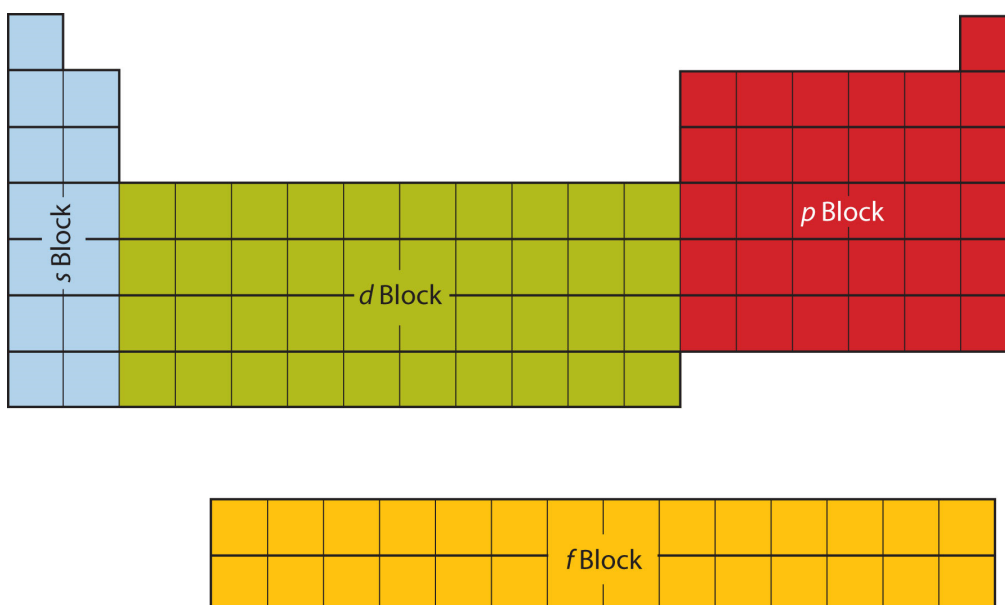
Figure 8.16: *Blocks on the Periodic Table - The periodic table is separated into blocks depending on which subshell is being filled for the atoms that belong in that section.*

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:

H:	$1s^1$
Li:	$1s^2 2s^1$
Na:	$[Ne]3s^1$
K:	$[Ar]4s^1$
Rb:	$[Kr]5s^1$
Cs:	$[Xe]6s^1$

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 8.17 "Selenium on the Periodic Table". 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 8.17: *Selenium on the Periodic Table*

EXAMPLE 7

From the element's position on the periodic table, predict the valence shell electron configuration for each atom.

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 $[Kr]5s^2 4d^{10} 5p^2$.

Test Yourself

From the element's position on the periodic table, predict the valence shell electron configuration for each atom. See Figure 8.18 "Various Elements on the Periodic Table".

1   Ti

1   Cl

Answer

1. $[Ar]4s^2 3d^2$

2. $[Ne]3s^2 3p^5$

Food and Drink App: 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. Despite this, most people continue to enjoy processed foods with artificial coloring (like those shown in the accompanying figure).

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, although it's likely that the animal doesn't care!

Source: Photo courtesy of Matthew Bland, http://www.flickr.com/photos/matthewbland/3111904731.

KEY TAKEAWAYS

1. The arrangement of electrons in atoms is responsible for the shape of the periodic table.

2. Electron configurations can be predicted by the position of an atom on the periodic table.

EXERCISES

1. Where on the periodic table are *s* subshells being occupied by electrons?

2. Where on the periodic table are *d* subshells being occupied by electrons?

3. In what block is Ra found?

4. In what block is Br found?

5. What are the valence shell electron configurations of the elements in the second column of the periodic table?

6. What are the valence shell electron configurations of the elements in the next-to-last column of the periodic table?

7. What are the valence shell electron configurations of the elements in the first column of the *p* block?

8. What are the valence shell electron configurations of the elements in the last column of the *p* block?

9. From the element's position on the periodic table, predict the electron configuration of each atom.
    1. Sr
    2. S

10. From the element's position on the periodic table, predict the electron configuration of each atom.
    1. Fe
    2. Ba

11. From the element's position on the periodic table, predict the electron configuration of each atom.
    1. V
    2. Ar

12. From the element's position on the periodic table, predict the electron configuration of each atom.
    1. Cl
    2. K

13. From the element's position on the periodic table, predict the electron configuration of each atom.
    1. Ge
    2. C

14. From the element's position on the periodic table, predict the electron configuration of each atom.
    1. Mg
    2. I

5. PERIODIC TRENDS

LEARNING OBJECTIVE

1. Be able to state how certain properties of atoms vary based on their relative position on the periodic table.

One of the reasons the periodic table is so useful is because its structure allows us to qualitatively determine how some properties of the elements vary versus their position on the periodic table. The variation of properties versus position on the periodic table is 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 a whole 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:

$$\text{as} \downarrow \text{PT, atomic radius} \uparrow$$

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:

$$\text{as} \rightarrow \text{PT, atomic radius} \downarrow$$

Figure 8.19 "Atomic Radii Trends on the Periodic Table" 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.
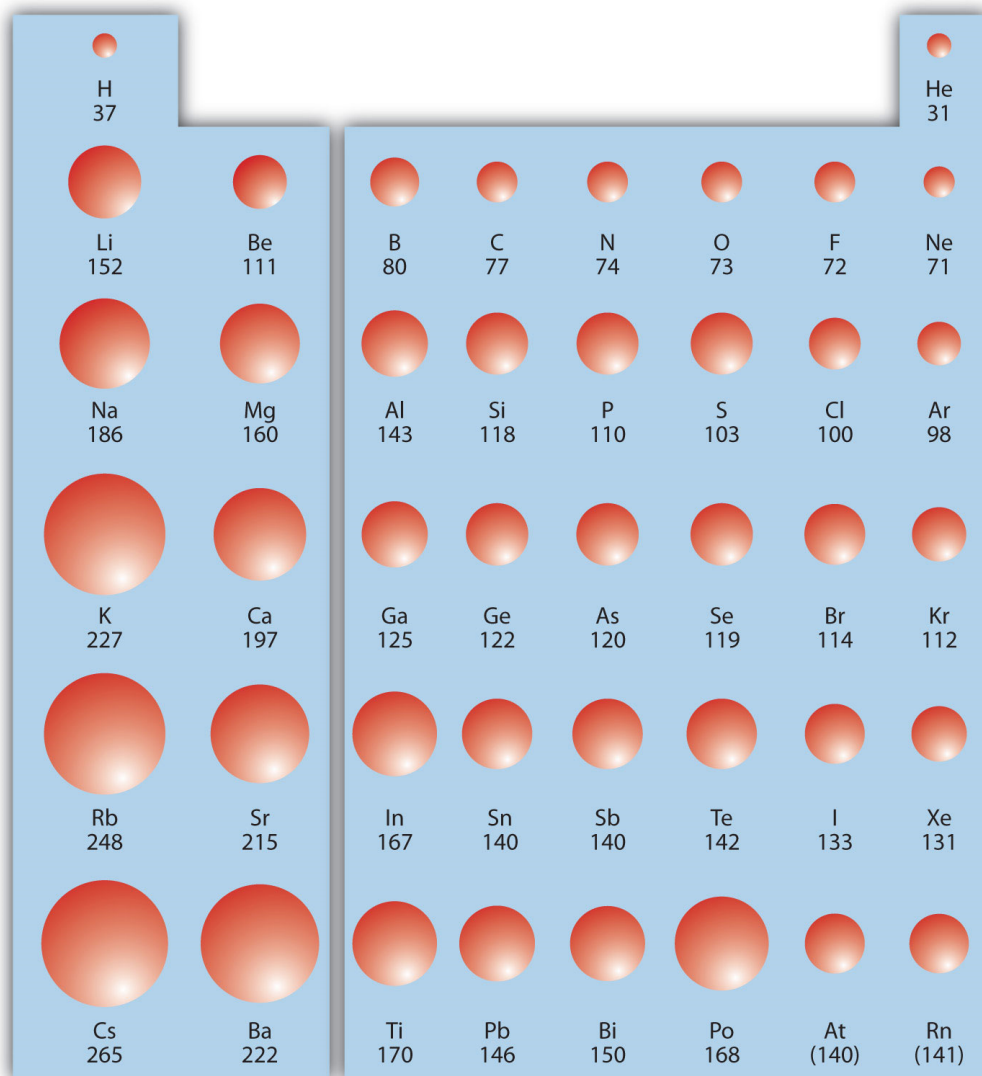
Figure 8.19: *Atomic Radii Trends on the Periodic Table - Although there are some reversals in the trend (e.g., see Po in the bottom row), atoms generally get smaller as you go across the periodic table and larger as you go down any one column. Numbers are the radii in pm.*

Ionization energy (IE) is the amount of energy required to remove an electron from an atom in the gas phase:

$$A(g) \rightarrow A^+(g) + e^- \quad \Delta H \equiv IE$$
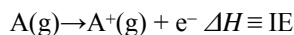
IE is usually expressed in kJ/mol of atoms. It is always positive because the removal of an electron always requires that energy be put in (i.e., it is endothermic). IE also shows periodic trends. As you go down the periodic table, it becomes easier to remove an electron from an atom (i.e., IE decreases) because the valence electron is farther away from the nucleus. Thus,

$$\text{as} \downarrow \text{PT, IE} \downarrow$$

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:

$$\text{as} \rightarrow \text{PT, IE} \uparrow$$

Figure 8.20 "Ionization Energy on the Periodic Table" 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.
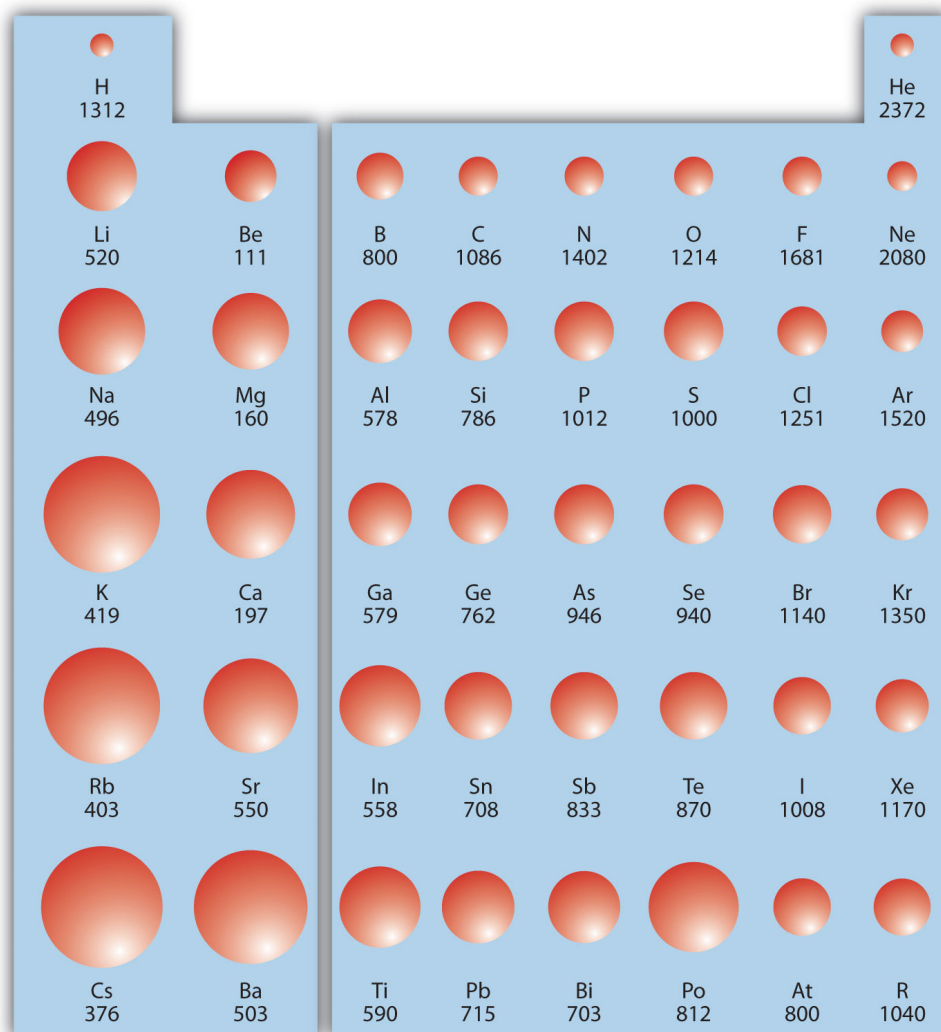
Figure 8.20: *Ionization Energy on the Periodic Table Values are in kJ/mol.*

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):

$$A(g) \rightarrow A^+(g) + e^- \ IE_1$$

$$A^+(g) \rightarrow A^{2+}(g) + e^- \ IE_2$$

$$A^{2+}(g) \rightarrow A^{3+}(g) + e^- \ IE_3$$
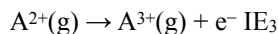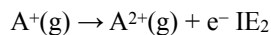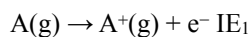
and so forth.

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

$$Mg(g) \rightarrow Mg^+(g) + e^- \ IE_1 = 738 \ kJ/mol$$

$$Mg^+(g) \rightarrow Mg^{2+}(g) + e^- \ IE_2 = 1{,}450 \ kJ/mol$$

$$Mg^{2+}(g) \rightarrow Mg^{3+}(g) + e^- \ IE_3 = 7{,}734 \ kJ/mol$$
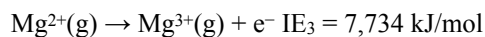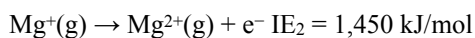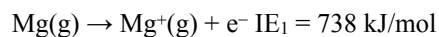
The second IE is twice the first, which is not a surprise: the first IE involves removing an electron from a neutral atom, while the second one involves removing an electron from a positive ion. The third IE, however, is over *five times* the previous one. Why is it so much larger? Because the first 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. It is trends like this that demonstrate that electrons are organized in atoms in groups.

The opposite of IE is described by electron affinity (EA), which is the energy change when a gas-phase atom accepts an electron:

$$A(g) + e^- \rightarrow A^-(g) \; \Delta H \equiv EA$$
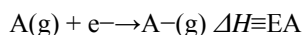
EA is also usually expressed in kJ/mol. EA also demonstrates some periodic trends, although they are less obvious than the other periodic trends discussed previously. Generally, as you go across the periodic table, EA increases its magnitude:

$$as \rightarrow PT, EA \uparrow$$

There is not a definitive trend as you go down the periodic table; sometimes EA increases, sometimes it decreases. Figure 8.21 "Electron Affinity on the Periodic Table" 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.
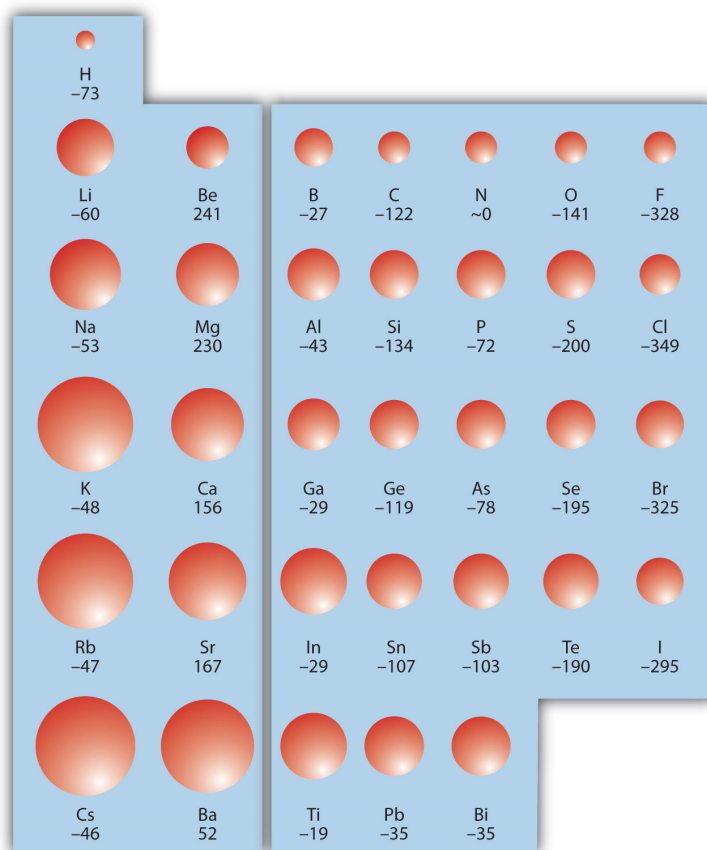
Figure 8.21: *Electron Affinity on the Periodic Table - Values are in kJ/mol.*

EXAMPLE 10

Predict which atom in each pair will have the highest magnitude of EA.

a   C or F

a   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.

a   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.

Test Yourself

Predict which atom will have the highest magnitude of EA, As or Br.

Answer

Br

KEY TAKEAWAY

1. Certain properties—notably atomic radius, IE, and EA—can be qualitatively understood by the positions of the elements on the periodic table.

6. END-OF-CHAPTER MATERIAL

1. What is the frequency of light if its wavelength is 1.00 m?

2. What is the wavelength of light if its frequency is 1.00 s^{-1}?

3. What is the energy of a photon if its wavelength is 1.00 meter?

4. What is the energy of a photon if its frequency is 1.00 s^{-1}?

5. If visible light is defined by the wavelength limits of 400 nm and 700 nm, what is the energy range for visible light photons?

6. Domestic microwave ovens use microwaves that have a wavelength of 122 mm. What is the energy of one photon of this microwave?

7. Use the equation for the wavelengths of the lines of light in the H atom spectrum to calculate the wavelength of light emitted when n is 7 and 8.

8. Use the equation for the wavelengths of the lines of light in the H atom spectrum to calculate the wavelengths of light emitted when n is 5 and 6.

9. Make a table of all the possible values of the four quantum numbers when the principal quantum number $n = 5$.

10. Make a table of all the possible values of m_ℓ and m_s when $\ell = 4$. What is the lowest value of the principal quantum number for this to occur?

11. Predict the electron configurations of Sc through Zn.

12. From a source of actual electron configurations, determine how many exceptions there are from your predictions in part a.

13. Predict the electron configurations of Ga through Kr.

14. From a source of actual electron configurations, determine how many exceptions there are from your predictions in part a.

15. Recently, Russian chemists reported experimental evidence of element 117. Use the periodic table to predict its valence shell electron configuration.

16. Bi (atomic number 83) is used in some stomach discomfort relievers. Using its place on the periodic table, predict its valence shell electron configuration.

17. Which atom has a higher ionization energy (IE), O or P?

18. Which atom has a higher IE, F or As?

19. Which atom has a smaller radius, As or Cl?

20. Which atom has a smaller radius, K or F?

21. How many IEs does an H atom have? Write the chemical reactions for the successive ionizations.

22. How many IEs does a Be atom have? Write the chemical reactions for the successive ionizations.

23. Based on what you know of electrical charges, do you expect Na^+ to be larger or smaller than Na?

24. Based on what you know of electrical charges, do you expect Cl^- to be larger or smaller than Cl?

ANSWERS

1. $3.00 \times 10^8 \ s^{-1}$

3. $1.99 \times 10^{-22} \ J$

5. $4.97 \times 10^{-19} \ J$ to $2.84 \times 10^{-19} \ J$

7. $3.97 \times 10^{-7} \ m$ and $3.89 \times 10^{-7} \ m$, respectively

11. a. The electron configurations are predicted to end in $3d^1$, $3d^2$, $3d^3$, $3d^4$, $3d^5$, $3d^6$, $3d^7$, $3d^8$, $3d^9$, and $3d^{10}$.

   b. Cr and Cu are exceptions.

13. Element 117's valence shell electron configuration should be $7s^2 7p^5$.

15. O

17. Cl

19. H has only one IE: $H \rightarrow H^+ + e^-$

21. smaller

CHAPTER 9: CHEMICAL BONDS

Opening Essay

Diamond is the hardest natural material known on Earth. Yet diamond is just pure carbon. What is special about this element that makes diamond so hard?

Bonds. Chemical bonds.

In a perfect diamond crystal, each C atom makes four connections—bonds—to four other C atoms in a three-dimensional matrix. Four is the greatest number of bonds that is commonly made by atoms, so C atoms maximize their interactions with other atoms. This three- dimensional array of connections extends throughout the diamond crystal, making it essentially one large molecule. Breaking a diamond means breaking every bond at once.

Also, the bonds are moderately strong. There are stronger interactions known, but the carbon- carbon connection is fairly strong itself. Not only does a person have to break many connections at once, but also the bonds are strong connections from the start.

There are other substances that have similar bonding arrangements as diamond does. Silicon dioxide and boron nitride have some similarities, but neither of them comes close to the ultimate hardness of diamond.

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.

1. LEWIS ELECTRON DOT DIAGRAMS

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

$$\text{H·}$$

Because the side is not important, the Lewis electron dot diagram could also be drawn as follows:

$$\dot{\text{H}} \quad or \quad \text{·H} \quad or \quad \underset{\cdot}{\text{H}}$$
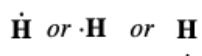
The electron dot diagram for helium, with two valence electrons, is as follows:

$$He:$$

By putting the two electrons together on the same side, we emphasize the fact that these two electrons are both in the $1s$ 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:

$$Li\cdot$$

Beryllium has two valence electrons in its $2s$ shell, so its electron dot diagram is like that of helium:

$$Be:$$

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:

$$\cdot B:$$

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 $2s$ subshell and two in the $2p$ subshell. As usual, we will draw two dots together on one side, to represent the $2s$ 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:

$$\cdot \dot{C}:$$

With N, which has three p electrons, we put a single dot on each of the three remaining sides:

$$\cdot \dot{N}:$$

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.

Fluorine and neon have seven and eight dots, respectively:

$$:\ddot{F}:$$

$$:\ddot{Ne}:$$

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.

What is the Lewis electron dot diagram for each element?

1. aluminum
2. selenium

Solution

1. The valence electron configuration for aluminum is $3s^23p^1$. So it would have three dots around the symbol for aluminum, two of them paired to represent the $3s$ electrons:

$$\cdot\text{AL :}$$

2. The valence electron configuration for selenium is $4s^24p^4$. In the highest-numbered shell, the $n = 4$ shell, there are six electrons. Its electron dot diagram is as follows:

$$\cdot\dot{\text{Se}}\text{:}$$

Test Yourself

What is the Lewis electron dot diagram for each element?

1. phosphorus
2. argon

Answer

1. $\cdot\dot{\text{P}}\text{:}$

2. $\text{:}\ddot{\text{Ar}}\text{:}$
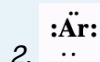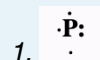
For atoms with partially filled d or f subshells, these electrons are typically omitted from Lewis electron dot diagrams. For example, the electron dot diagram for iron (valence shell configuration $4s^23d^6$) is as follows:

Fe:

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:

H· Li· Na· K· Rb· Cs·

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:

Lewis dot diagram: Na· *Na+*

Electron configuration: [Ne]3s¹ *[Ne]*

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 $4s$ electrons first, not its $3d$ electrons, despite the fact that the $3d$ subshell is the last subshell being filled. Thus we have

Lewis dot diagram: Fe : *Fe²⁺*

Electron configuration: [Ar]4s²3d⁶ *[Ar]3d⁶*

Anions have extra electrons when compared to the original atom. Here is a comparison of the Cl atom with the Cl⁻ ion:

Lewis dot diagram : $:\ddot{\text{C}}\text{l}\cdot$ $:\ddot{\text{C}}\text{l}:^-$

Electron configuration : $[Ne]\,3s^2 3p^5$ $[Ne]\,3s^2 3p^6$

EXAMPLE 2

What is the Lewis electron dot diagram for each ion?

1. Ca^{2+}

2. O^{2-}

Solution

1. Having lost its two original valence electrons, the Lewis electron dot diagram is just Ca^{2+}.

$$Ca^{2+}$$

2. The O^{2-} ion has gained two electrons in its valence shell, so its Lewis electron dot diagram is as follows:

$$:\ddot{\text{O}}:^{2-}$$

Test Yourself

The valence electron configuration of thallium, whose symbol is Tl, is $6s^2 5d^{10} 6p^1$. What is the Lewis electron dot diagram for the Tl^+ ion?

Answer

$$Tl :^+$$

KEY TAKEAWAYS

1. Lewis electron dot diagrams use dots to represent valence electrons around an atomic symbol.

2. Lewis electron dot diagrams for ions have less (for cations) or more (for anions) dots than the corresponding atom.

1. Explain why the first two dots in a Lewis electron dot diagram are drawn on the same side of the atomic symbol.

2. Is it necessary for the first dot around the atomic symbol to go on a particular side of the symbol?

3. What column of the periodic table has Lewis electron dot diagrams with two electrons?

4. Draw the Lewis electron dot diagram for each element.

   1. strontium

   2. silicon

5. Draw the Lewis electron dot diagram for each element.

   1. krypton

   2. sulfur

6. Draw the Lewis electron dot diagram for each element.

   1. titanium

   2. phosphorus

7. Draw the Lewis electron dot diagram for each element.

   1. bromine

   2. gallium

8. Draw the Lewis electron dot diagram for each ion.

   1. Mg^{2+}

   2. S^{2-}

9. Draw the Lewis electron dot diagram for each ion.

   1. In^+

   2. Br^-

10. Draw the Lewis electron dot diagram for each ion.

   1. Fe^{2+}

   2. N^{3-}

11. Draw the Lewis electron dot diagram for each ion.
   1. H^+

   2. H^-

ANSWERS

1. The first two electrons in a valence shell are *s* electrons, which are paired.

3. the second column of the periodic table

2. ELECTRON TRANSFER: IONIC BONDS

LEARNING OBJECTIVES
1. State the octet rule.
2. Define *ionic bond*.
3. Demonstrate electron transfer between atoms to form ionic bonds.

In Section 9.1 "Lewis Electron Dot Diagrams", 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:

$$\text{Na} \cdot \qquad \cdot \ddot{\text{Cl}} :$$

$$[Ne]\, 3s^1 \qquad [Ne]\, 3s^2 3p^5$$
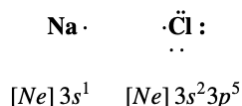
For the Na atom to obtain an octet, it must lose an electron; for the Cl atom to gain an octet, it must gain an electron. An electron transfers from the Na atom to the Cl atom:

$$\text{Na} \cdot \curvearrowright \cdot \ddot{\text{Cl}} :$$
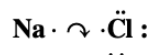
resulting in two ions—the Na^+ ion and the Cl^- ion:

$$\text{Na} \cdot^+ \qquad :\ddot{\text{Cl}} :^-$$

$$[Ne] \qquad [Ne]\, 3s^2 3p^6$$
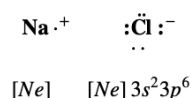
Both species now have complete octets, and the electron shells are energetically stable. From basic physics, we know that opposite charges attract. This is what happens to the Na^+ and Cl^- ions:

$$\mathbf{Na}\cdot^+ \ + \ \mathbf{:\ddot{C}l:}^- \rightarrow Na^+Cl^- \ \ or \ \ NaCl$$
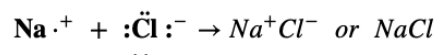
where we have written the final formula (the formula for sodium chloride) as per the convention for ionic compounds, without listing the charges explicitly. The attraction between oppositely charged ions is called an **ionic bond**, and it is one of the main types of chemical bonds in chemistry. Ionic 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:

$$\mathbf{Mg}^{2+} \ + \ \mathbf{:\ddot{O}:}^{2-} \ \ Mg^{2+}O^{2-} \ \ or \ \ MgO$$
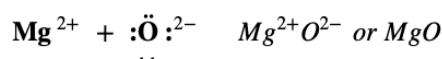
Remember, in the final formula for the ionic compound, we do not write the charges on the ions.

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:

$$\mathbf{Na}\cdot \curvearrowright \cdot\ddot{\mathbf{O}}\mathbf{:}$$
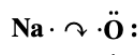
The O atom still does not have an octet of electrons. What we need is a second Na atom to donate a second electron to the O atom:

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 3

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:
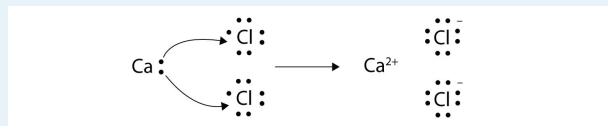
The oppositely charged ions attract each other to make CaCl$_2$.

Test Yourself

With arrows, illustrate the transfer of electrons to form potassium sulfide from K atoms and S atoms.

Answer
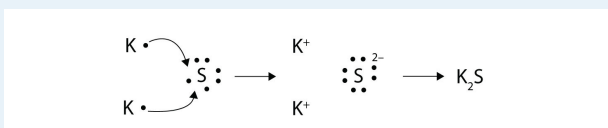
The strength of ionic bonding depends on two major characteristics: the magnitude of the charges and the size of the ion. The greater the magnitude of the charge, the stronger the ionic bond. The smaller the ion, the stronger the ionic bond (because a smaller ion size allows the ions to get closer together). The measured strength of ionic bonding is called the **lattice energy**. Some lattice energies are given in Table 9.1 "Lattice Energies of Some Ionic Compounds".

Table 9.1 Lattice Energies of Some Ionic Compounds

Compound	Lattice Energy (kJ/mol)
LiF	1,036
LiCl	853
NaCl	786
NaBr	747
MgF$_2$	2,957
Na$_2$O	2,481
MgO	3,791

KEY TAKEAWAYS

❖ 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.

3. COVALENT BONDS

LEARNING OBJECTIVES

1. Define *covalent bond*.

2. 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 another atom to gain one or more electrons. However, some atoms won't 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 make a bond called 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 1s subshell. Each H atom starts with a single electron in its valence shell:

H· ·H

The two H atoms can share their electrons:

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:
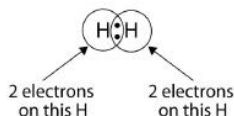
Because each H atom has a filled valence shell, this bond is stable, and we have made a diatomic hydrogen molecule. (This explains why hydrogen is one of the diatomic elements.) For simplicity's sake, it is not unusual to represent the covalent bond with a dash, instead of with two dots:

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:
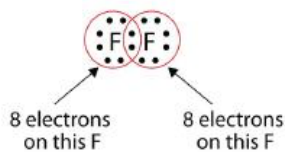
We can also write this using a dash to represent the shared electron pair:
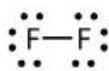
There are two different types of electrons in the fluorine diatomic molecule. The **bonding electron pair** makes the covalent bond. Each F atom has three other pairs of electrons that do not participate in the bonding; they are called **lone electron pairs**. Each F atom has one bonding pair and three 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:

$$H:\ddot{\underset{..}{F}}: \quad \text{or} \quad H-\ddot{\underset{..}{F}}:$$
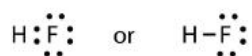
We note that the H atom has a full valence shell with two electrons, while the F atom has a complete octet of electrons.

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:

$$H\cdot \quad \cdot\ddot{\underset{.}{O}}:$$

The H and O atoms can share an electron to form a covalent bond:

$$H:\ddot{\underset{.}{O}}:$$

The H atom has a complete valence shell. However, the O atom has only seven electrons around it, which is not a complete octet. We fix this by including a second H atom, whose single electron will make a second covalent bond with the O atom:

$$H:\ddot{\underset{.}{O}}: \quad \cdot H \longrightarrow \begin{array}{c} H:\ddot{\underset{.}{O}}: \\ H \end{array}$$
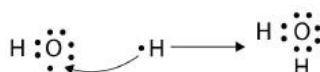
(It does not matter on what side the second H atom is positioned.) Now the O atom has a complete octet around it, and each H atom has two electrons, filling its valence shell. This is how a water molecule, H_2O, is made.

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.**

$$
\begin{array}{c}
\text{F} \\
\text{F B F} \\
\text{F}
\end{array}
$$

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.

$$
\begin{array}{c}
\text{F} \\
\text{F:B:F} \\
\text{F}
\end{array}
$$
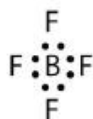
4 **Complete the octets around the surrounding atoms (except for H).** This uses up 24 more electrons, leaving $24 - 24 = 0$ electrons left.

$$
\begin{array}{c}
\text{:F:} \\
\text{:F:B:F:} \\
\text{:F:}
\end{array}
$$
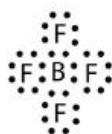
5 **Put remaining electrons, if any, around the central atom.** There are no additional electrons to add to the central atom.

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 don't work. If we were to follow these steps for the compound formaldehyde (CH_2O), we would get the following:

$$
\begin{array}{c}
\text{:O:} \\
\text{H:C:H}
\end{array}
$$

The H and O atoms have the proper number of electrons, but the C atom has only 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:

$$:\!O\!:$$
$$H:C:H$$
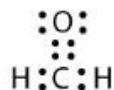
By circling the electrons around each atom, we can now see that the O and C atoms have octets, while each H atom has two electrons:

$$:\!O\!:$$
$$H:C:H$$
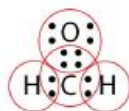
Each valence shell is full, so this is an acceptable Lewis electron dot diagram. If we were to use lines to represent the bonds, we would use two lines between the C and O atoms:

$$:\!O\!:$$
$$\|$$
$$H-C-H$$
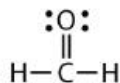
The bond between the C and O atoms is a **double bond** and represents two bonding pairs of electrons between the atoms. If using the rules for drawing Lewis electron dot diagrams don't work as written, a double bond may be required.

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):

$$:N:::N:\quad \text{or}\quad :N\equiv N:\qquad\qquad H:C:::C:H\quad \text{or}\quad H:C\equiv C:H$$

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 App: 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	

Every entry down through pantothenic acid is a vitamin, and everything from calcium and below is a mineral.

KEY TAKEAWAYS

1. Covalent bonds are formed when atoms share electrons.

2. Lewis electron dot diagrams can be drawn to illustrate covalent bond formation.

3. Double bonds or triple bonds between atoms may be necessary to properly illustrate the bonding in some molecules.

EXERCISES

1. How many electrons will be in the valence shell of H atoms when it makes a covalent bond?

2. How many electrons will be in the valence shell of non-H atoms when they make covalent bonds?

3. What is the Lewis electron dot diagram of I_2? Circle the electrons around each atom to verify that each valence shell is filled.

4. What is the Lewis electron dot diagram of H_2S? Circle the electrons around each atom to verify that each valence shell is filled.

5. What is the Lewis electron dot diagram of NCl_3? Circle the electrons around each atom to verify that each valence shell is filled.

6. What is the Lewis electron dot diagram of SiF_4? Circle the electrons around each atom to verify that each valence shell is filled.

7. Draw the Lewis electron dot diagram for each substance.

    1. SF_2
    2. BH_4^-

8. Draw the Lewis electron dot diagram for each substance.

    1. PI_3

    2. OH^-

9. Draw the Lewis electron dot diagram for each substance.

    1. GeH_4

    2. ClF

10. Draw the Lewis electron dot diagram for each substance.

    1. AsF_3
    2. NH_4

11. Draw the Lewis electron dot diagram for each substance. Double or triple bonds may be needed.
    1. SiO_2

    2. C_2H_4 (assume two central atoms)

12. Draw the Lewis electron dot diagram for each substance. Double or triple bonds may be needed.

    1. CN^-

    2. C_2Cl_2 (assume two central atoms)

13. Draw the Lewis electron dot diagram for each substance. Double or triple bonds may be needed.

    1. CS_2

    2. NH_2CONH_2 (assume that the N and C atoms are the central atoms)

14. Draw the Lewis electron dot diagram for each substance. Double or triple bonds may be needed.

    1. POCl

    2. HCOOH (assume that the C atom and one O atom are the central atoms)

4. OTHER ASPECTS OF COVALENT BONDS

Consider the H2 molecule:

$$H:H$$

Because the nuclei of each H atom contain protons, the electrons in the bond are attracted to the nuclei (opposite charges attract). But because the two atoms involved in the covalent bond are both H atoms, each nucleus attracts the electrons by the same amount. Thus the electron pair is equally shared by the two atoms. The equal sharing of electrons in a covalent bond is called a **nonpolar covalent bond**.

Now consider the HF molecule:

There are two different atoms involved in the covalent bond. The H atom has one proton in its nucleus that is attracting the bonding pair of electrons. However, the F atom has nine protons in its nucleus, with nine times the attraction of the H atom. The F atom attracts the electrons so much more strongly that the electrons remain closer to the F atom than to the H atom; the electrons are no longer equally balanced between the two nuclei. Instead of representing the HF molecule as
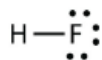
it may be more appropriate to draw the covalent bond as
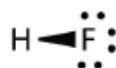
with the electrons in the bond being nearer to the F atom than the H atom. Because the electrons in the bond are nearer to the F atom, this side of the molecule takes on a partial negative charge, which is represented by δ– (δ is the lowercase Greek letter delta). The other side of the molecule, the H atom, adopts a partial positive charge, which is represented by δ+:

A covalent bond between different atoms that attract the shared electrons by different amounts and cause an imbalance of electron distribution is called a **polar covalent bond**.

Technically, any covalent bond between two different elements is polar. However, the degree of polarity is important. A covalent bond between two different elements may be so slightly imbalanced that the bond is, essentially, nonpolar. A bond may be so polar that an electron actually transfers from one atom to another, forming a true ionic bond. How do we judge the degree of polarity?

Scientists have devised a scale called **electronegativity**, a scale for judging how much atoms of any element attract electrons. Electronegativity is a unitless number; the higher the number, the more an atom attracts electrons. A common scale for electronegativity is shown in Figure 9.2 "Electronegativities of the Elements".

H 2.1																	
Li 1.0	Be 1.5											B 1.5	C 2.5	N 3.0	D 3.5	F 4.0	
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 3.5	Cl 3.0	
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.9	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	
Cs 0.7	Ba 0.9		Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 2.0	At 2.2	
Fr 0.7	Ra 0.9																

Figure 9.2: *Electronegativities of the Elements - Electronegativities are used to determine the polarity of covalent bonds.*

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

What is the polarity of each bond?
1. C–H
2. O–H

Solution

Using Figure 9.2 "Electronegativities of the Elements", we can calculate the difference of the electronegativities of the atoms involved in the bond.

1. For the C–H bond, the difference in the electronegativities is 2.5 – 2.1 = 0.4. Thus we predict that this bond will be slightly polar covalent.

2. For the O–H bond, the difference in electronegativities is 3.5 – 2.1 = 1.4, so we predict that this bond will be definitely polar covalent.

Test Yourself

What is the polarity of each bond?
1. Rb-F
2. P-Cl

Answers
1. likely ionic

2. polar covalent

The polarity of a covalent bond can have significant influence on the properties of the substance. If the overall molecule is polar, the substance may have a higher melting point and boiling point than expected; also, it may or may not be soluble in various other substances, such as water or hexane.

It should be obvious that covalent bonds are stable because molecules exist. However, they can be broken if enough energy is supplied to a molecule. For most covalent bonds between any two given atoms, a certain amount of energy must be supplied. Although the exact amount of energy depends on the molecule, the approximate amount of energy to be supplied is similar if the atoms in the bond are the same. The approximate amount of energy needed to break a covalent bond is called the **bond energy** of the covalent bond. Table 9.2 "Bond Energies of Covalent Bonds" lists the bond energies of some covalent bonds.

Table 9.2 Bond Energies of Covalent Bonds

Bond	Energy (kJ/mol)		Bond	Energy (kJ/mol)
C–C	348		N–N	163
C=C	611		N=N	418

C≡C	837		N≡N	946
C–O	351		N–H	389
C=O	799		O–O	146
C–Cl	328		O=O	498
C–H	414		O–H	463
F–F	159		S–H	339
H–Cl	431		S=O	523
H–F	569		Si–H	293
H–H	436		Si–O	368

A few trends are obvious from Table 9.2 "Bond Energies of Covalent Bonds". For bonds that involve the same two elements, a double bond is stronger than a single bond, and a triple bond is stronger than a double bond. The energies of multiple bonds are not exact multiples of the single bond energy; for carbon- carbon bonds, the energy increases somewhat less than double or triple the C–C bond energy, while for nitrogen-nitrogen bonds the bond energy increases at a rate greater than the multiple of the N–N single bond energy. The bond energies in Table 9.2 "Bond Energies of Covalent Bonds" are average values; the exact value of the covalent bond energy will vary slightly among molecules with these bonds but should be close to these values. To be broken, covalent bonds always require energy; that is, covalent bond breaking is always an *endothermic* process. Thus the ΔH for this process is positive:

$$\text{Molecule–O–H} \rightarrow \text{Molecule–O + H } \Delta H \approx +463 \text{ kJ/mol}$$

However, when making a covalent bond, energy is always given off; covalent bond making is always an *exothermic* process. Thus ΔH for this process is negative:

$$\text{Molecule–S + H} \rightarrow \text{Molecule–S–H } \Delta H \approx -339 \text{ kJ/mol}$$
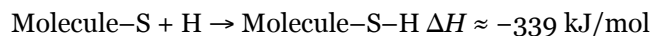
Bond energies can be used to estimate the energy change of a chemical reaction. When bonds are broken in the reactants, the energy change for this process is endothermic. When bonds are formed in the products, the energy change for this process is exothermic. We combine the positive energy change with the negative energy change to estimate the overall energy change of the reaction. For example, in

$$2H_2 + O_2 \rightarrow 2H_2O$$
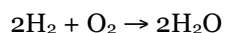
we can draw Lewis electron dot diagrams for each substance to see what bonds are broken and what bonds are formed:
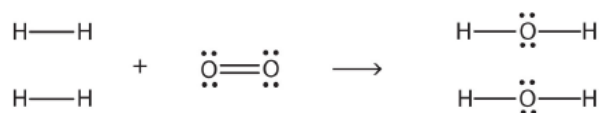
(The lone electron pairs on the O atoms are omitted for clarity.) We are breaking two H–H bonds and one O–O double bond and forming four O–H single bonds. The energy required for breaking the bonds is as follows:

2 H–H bonds:	2(+436 kJ/mol)
1 O=O bond:	+498 kJ/mol
Total:	+1,370 kJ/

The energy given off when the four O–H bonds are made is as follows:

4 O–H bonds:	4(−463 kJ/mol)
Total:	−1,852 kJ/mol

Combining these two numbers:

Net Change:	−482 kJ/mol ≈ ΔH

The actual ΔH is −572 kJ/mol; we are off by about 16%—although not ideal, a 16% difference is reasonable because we used estimated, not exact, bond energies.

KEY TAKEAWAYS

❖ Covalent bonds can be nonpolar or polar, depending on the electronegativities of the atoms involved.

❖ Covalent bonds can be broken if energy is added to a molecule.

❖ The formation of covalent bonds is accompanied by energy given off.

❖ Covalent bond energies can be used to estimate the enthalpy changes of chemical reactions.

EXERCISES

1. Give an example of a nonpolar covalent bond. How do you know it is nonpolar?

2. Give an example of a polar covalent bond. How do you know it is polar?

3. How do you know which side of a polar bond has the partial negative charge? Identify the negatively charged side of each polar bond.

    1. H–Cl

    2. H–S

4. How do you know which side of a polar bond has the partial positive charge? Identify the positively charged side of each polar bond.

   1. H–Cl
   2. N-F

5. Label the bond between the given atoms as nonpolar covalent, slightly polar covalent, definitely polar covalent, or likely ionic.

   1. H and C
   2. C and F
   3. K and F

6. Label the bond between the given atoms as nonpolar covalent, slightly polar covalent, definitely polar covalent, or likely ionic.

   1. S and Cl
   2. P and O
   3. Cs and O

7. Which covalent bond is stronger—a C–C bond or a C–H bond?

8. Which covalent bond is stronger—an O–O double bond or an N–N double bond?

9. Estimate the enthalpy change for this reaction. Start by drawing the Lewis electron dot diagrams for each substance.
$$N_2 + 3H_2 \rightarrow 2NH_3$$
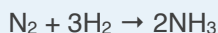
10. Estimate the enthalpy change for this reaction. Start by drawing the Lewis electron dot diagrams for each substance.
$$HN{=}NH + 2H_2 \rightarrow 2NH_3$$

11. Estimate the enthalpy change for this reaction. Start by drawing the Lewis electron dot diagrams for each substance.
$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$
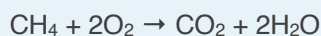
12. Estimate the enthalpy change for this reaction. Start by drawing the Lewis electron dot diagrams for each substance.
$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$$
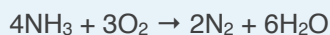
5. VIOLATIONS OF THE OCTET RULE

LEARNING OBJECTIVE

1. 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** represent 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, NO_2, and ClO_2. The Lewis electron dot diagram for NO is as follows:

$$.\ddot{N}::\ddot{O}.$$

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 represent 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:

$$:\ddot{Cl}\!-\!Be\!-\!\ddot{Cl}:$$
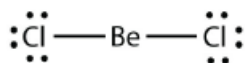
Boron commonly makes only three covalent bonds, resulting in only six valence electrons around the B atom. A well-known example is BF_3:

285
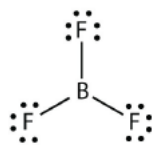
The third violation to the octet rule is found in those compounds with more than eight electrons assigned to their valence shell. These are called **expanded valence shell molecules**. Such compounds are formed only by central atoms in the third row of the periodic table or beyond that have empty d orbitals in their valence shells that can participate in covalent bonding. One such compound is PF_5. The only reasonable Lewis electron dot diagram for this compound has the P atom making five covalent bonds:
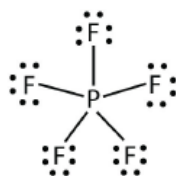
Formally, the P atom has 10 electrons in its valence shell.

EXAMPLE 9

Identify each violation to the octet rule by drawing a Lewis electron dot diagram.

1. ClO

2. SF_6

Solution

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:'

In 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:

Test Yourself

Identify the violation to the octet rule in 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.

EXERCISES

1.   Why can an odd-electron molecule not satisfy the octet rule?

2.   Why can an atom in the second row of the periodic table not form expanded valence shell molecules?

3.   Draw an acceptable Lewis electron dot diagram for these molecules that violate the octet rule.

   1. NO_2

   2. XeF_4

4.   Draw an acceptable Lewis electron dot diagram for these molecules that violate the octet rule.

   1. BCl_3

   2. ClO_2

5.   Draw an acceptable Lewis electron dot diagram for these molecules that violate the octet rule.

   1. POF_3

   2. ClF_3

6.   Draw an acceptable Lewis electron dot diagram for these molecules that violate the octet rule.

   1. SF_4

   2. BeH_2

ANSWERS

1. There is no way all electrons can be paired if there are an odd number of them.

6. MOLECULAR SHAPES

LEARNING OBJECTIVE

1.   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:

H — Be — H
180°

$\ddot{O} = C = \ddot{O}$
180°

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:

:F:
| 120°
B
:F   F:
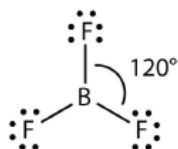
Some substances have a trigonal planar electron group distribution but have atoms bonded to only two of the three electron groups. An example is GeF_2:

Ge
:F   F:
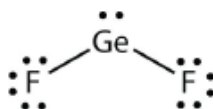
From an electron group geometry perspective, GeF_2 has a trigonal planar shape, but its real shape is dictated by the positions of the atoms. This shape is called *bent* or *angular*.

A molecule with four electron groups about the central atom orients the four groups in the direction of a tetrahedron, as shown in Figure 9.3 "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 9.3: *Tetrahedral Geometry Four electron groups orient themselves in the shape of a tetrahedron.*
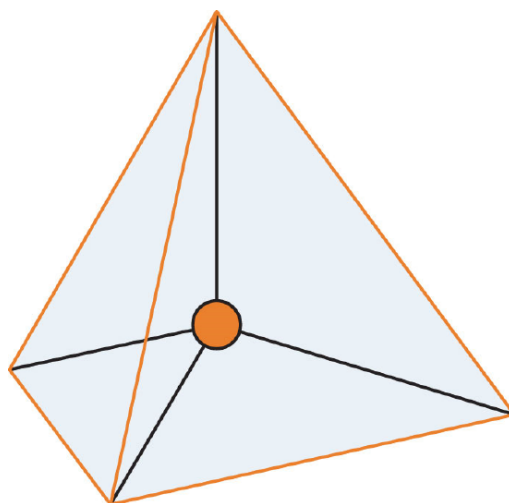
This diagram of CH_4 illustrates the standard convention of displaying a three-dimensional molecule on a two-dimensional surface. The straight lines are in the plane of the page, the solid wedged line is coming out of the plane toward the reader, and the dashed wedged line is going out of the plane away from the reader.
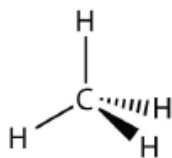
NH_3 is an example of a molecule whose central atom has four electron groups but only three of them are bonded to surrounding atoms.
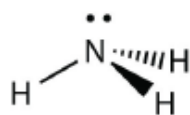
Although the electron groups are oriented in the shape of a tetrahedron, from a molecular geometry perspective, the shape of NH_3 is *trigonal pyramidal*.

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.
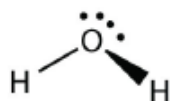
Although the electron groups are oriented in the shape of a tetrahedron, the shape of the molecule is *bent* or *angular*. A molecule with four electron groups about the central atom but only one electron group bonded to another atom is linear because there are only two atoms in the molecule.

Double or triple bonds count as a single electron group. CH_2O has the following Lewis electron dot diagram.
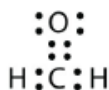
The central C atom has three electron groups around it because the double bond counts as one electron group. The three electron groups repel each other to adopt a trigonal planar shape:
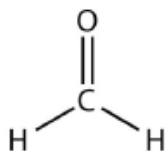
(The lone electron pairs on the O atom are omitted for clarity.) The molecule will not be a perfect equilateral triangle because the C–O double bond is different from the two C–H bonds, but both planar and triangular describe the appropriate approximate shape of this molecule.

EXAMPLE 10

What is the approximate shape of each molecule?

1. PCl_3

2. 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:
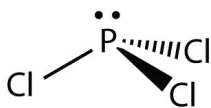
The lone electron pairs on the Cl atoms are omitted for clarity. The P atom has four electron groups with three of them bonded to surrounding atoms, so the molecular shape is trigonal pyramidal.

2. The electron dot diagram for NOF is as follows:
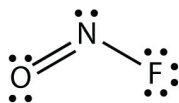
The N atom has three electron groups on it, two of which are bonded to other atoms. The molecular shape is bent.

Test Yourself

What is the approximate molecular shape of CH_2Cl_2?

Answer

Tetrahedral

Table 9.3 "Summary of Molecular Shapes" summarizes the shapes of molecules based on their number of electron groups and surrounding atoms.

Table 9.3 Summary of Molecular Shapes

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

KEY TAKEAWAY

1. The approximate shape of a molecule can be predicted from the number of electron groups and the number of surrounding atoms.

1. What is the basic premise behind VSEPR?

2. What is the difference between the electron group geometry and the molecular geometry?

3. Identify the electron group geometry and the molecular geometry of each molecule.

    1. H_2S

    2. $POCl_3$

4. Identify the electron group geometry and the molecular geometry of each molecule.

    1. CS_2

    2. H_2S

5. Identify the electron group geometry and the molecular geometry of each molecule.

    1. HCN

    2. CCl_4

6. Identify the electron group geometry and the molecular geometry of each molecule.

    1. BI_3

    2. PH_3

7. What is the geometry of each species?

    1. CN^-

    2. PO_4

8. What is the geometry of each species?
    1. PO_3-

    2. NO_3

9. What is the geometry of each species?

    1. COF_2

    2. C_2Cl_2 (both C atoms are central atoms and are bonded to each other)

10. What is the geometry of each species?
    1. CO_3

    2. N_2H_4 (both N atoms are central atoms and are bonded to each other)

1. Electron pairs repel each other.

3.
1. electron group geometry: tetrahedral; molecular geometry: bent

2. electron group geometry: tetrahedral; molecular geometry: tetrahedral

5.
1. electron group geometry: linear; molecular geometry: linear

2. electron group geometry: tetrahedral; molecular geometry: tetrahedral

7.
1. linear

2. tetrahedral

9.

1. trigonal planar
2. linear and linear about each central atom

7. END-OF-CHAPTER MATERIAL

1. Explain why iron and copper have the same Lewis electron dot diagram when they have different numbers of electrons.

2. Name two ions with the same Lewis electron dot diagram as the Cl^- ion.

3. Based on the known trends, what ionic compound from the first column of the periodic table and the next-to-last column of the periodic table should have the highest lattice energy?

4. Based on the known trends, what ionic compound from the first column of the periodic table and the next-to-last column of the periodic table should have the lowest lattice energy?

5. P_2 is not a stable form of phosphorus, but if it were, what would be its likely Lewis electron dot diagram?

6. Se_2 is not a stable form of selenium, but if it were, what would be its likely Lewis electron dot diagram?

7. What are the Lewis electron dot diagrams of SO_2, SO_3, and SO_4 ?

8. What are the Lewis electron dot diagrams of PO_3 and PO_4 ?

9. Which bond do you expect to be more polar—an O–H bond or an N–H bond?

10. Which bond do you expect to be more polar—an O–F bond or an S–O bond?

11. Use bond energies to estimate the energy change of this reaction. $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$

12. Use bond energies to estimate the energy change of this reaction. $N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$

13. Ethylene (C_2H_4) has two central atoms. Determine the geometry around each central atom and the shape of the overall molecule.

14. Hydrogen peroxide (H_2O_2) has two central atoms. Determine the geometry around each central atom and the shape of the overall molecule.

\

ANSWERS

1. Iron has d electrons that typically are not shown on Lewis electron dot diagrams.

3. LiF

5. It would be like N_2:

9. an O–H bond

11. –2,000 kJ

13. trigonal planar about both central C atoms

CHAPTER 10: SOLIDS AND LIQUIDS

> **Opening Essay**
>
> 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.
>
> Liquids flow when a small force is placed on them, even if only very slowly. Solids, however, 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.
>
> Glass is a solid at room temperature. Don't let anyone tell you otherwise!

In Chapter 6 "Gases", we discussed the properties of gases. Here, we consider some properties of liquids and solids. As a review, Table 10.1 "Properties of the Three Phases of Matter" lists some general properties of the three phases of matter.

Table 10.1 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

1. INTERMOLECULAR FORCES

LEARNING OBJECTIVE

1. Relate phase to intermolecular forces.

Why does a substance have the phase 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 10.1 "Dipole-Dipole Interactions"). Thus a polar molecule such 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 10.1: *Dipole-Dipole Interactions - Oppositely charged ends of polar molecules attract each other.*

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 10.2 "Hydrogen Bonding").

Figure 10.2 *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.*
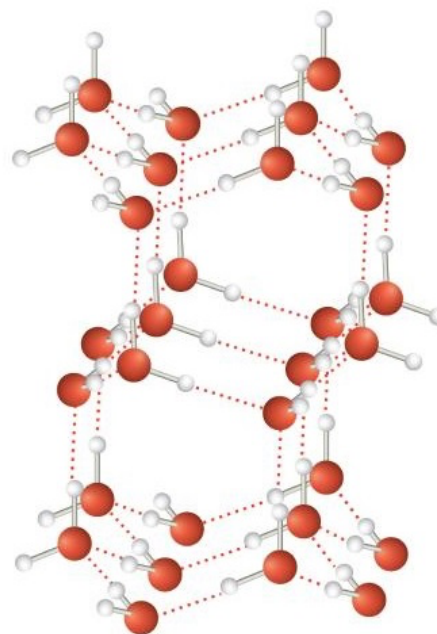
EXAMPLE 1

Identify the most significant intermolecular force in each substance.

1. C_3H_8
2. CH_3OH
3. 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.

Test Yourself

Identify the most significant intermolecular force in each substance.

1. HF
2. HCL

Answers

1. hydrogen bonding
2. 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 10.2 "Phase Transitions: Melting, Boiling, and Subliming"). 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 is it 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.

2. PHASE TRANSITIONS: MELTING, BOILING, AND SUBLIMING

LEARNING OBJECTIVES

1. Describe what happens during a phase change.

2. 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 10.2 "Enthalpies of Fusion for Various Substances"; 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 as long as you keep in mind that melting is always endothermic (so ΔH will be positive), while solidification is always exothermic (so ΔH will be negative).

Table 10.2 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

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 any 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.

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 10.3 "Enthalpies of Vaporization for Various Substances"; 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 10.3 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 3

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.

Because the process is exothermic, the actual value will be negative:

$$\Delta H = -6.43 \text{ kJ.}$$

Test Yourself

What is the energy change when 822 g of C_2H_5OH(ℓ) 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 10.3 "Liquids and Gases"). It is this property of gases that explains why they can be compressed, a fact that is considered in Chapter 6 "Gases".

(a)   (b)

Figure 10.3: *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.*

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.

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:

$$H_2O(s) \rightarrow H_2O(\ell)$$
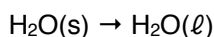
No chemical change is taking place; however, a physical change is taking place.

EXERCISES

1. What is the difference between *melting* and *solidification*?

2. What is the difference between *boiling* and *condensation*?

3. Describe the molecular changes when a solid becomes a liquid.

4. Describe the molecular changes when a liquid becomes a gas.

5. What is the energy change when 78.0 g of Hg melt at −38.8°C?

6. What is the energy change when 30.8 g of Al solidify at 660°C?

7. What is the energy change when 111 g of Br_2 boil at 59.5°C?

8. What is the energy change when 98.6 g of H_2O condense at 100°C?

9. Each of the following statements is incorrect. Rewrite them so they are correct.

    1. Temperature changes during a phase change.

    2. The process of a liquid becoming a gas is called sublimation.

10. Each of the following statements is incorrect. Rewrite them so they are correct.

    1. The volume of a gas contains only about 10% matter, with the rest being empty space.

    2. ΔH_{sub} is equal to ΔH_{vap}.

11. Write the chemical equation for the melting of elemental sodium.

12. Write the chemical equation for the solidification of benzene (C_6H_6).

13. Write the chemical equation for the sublimation of CO_2.

14. Write the chemical equation for the boiling of propanol (C_3H_7OH).

15. What is the ΔH_{sub} of H_2O? (Hint: see Table 10.2 "Enthalpies of Fusion for Various Substances" and Table 10.3 "Enthalpies of Vaporization for Various Substances".)

16. The ΔH_{sub} of I_2 is 60.46 kJ/mol, while its ΔH_{vap} is 41.71 kJ/mol. What is the ΔH_{fus} of I_2?

3. PROPERTIES OF LIQUIDS

LEARNING OBJECTIVES

1. Define the vapor pressure of liquids.

2. Explain the origin of both surface tension and capillary action.

There are some properties that all liquids have. The liquid that we are most familiar with is probably water, and it has these properties. Other liquids have them as well, which is something to keep in mind. All liquids have a certain portion of their particles having enough energy to enter the gas phase, and if these particles are at the surface of the liquid, they do so (- ball-ch10_s03_f01). 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.

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 (- ball- ch10_s03_f02). 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*.
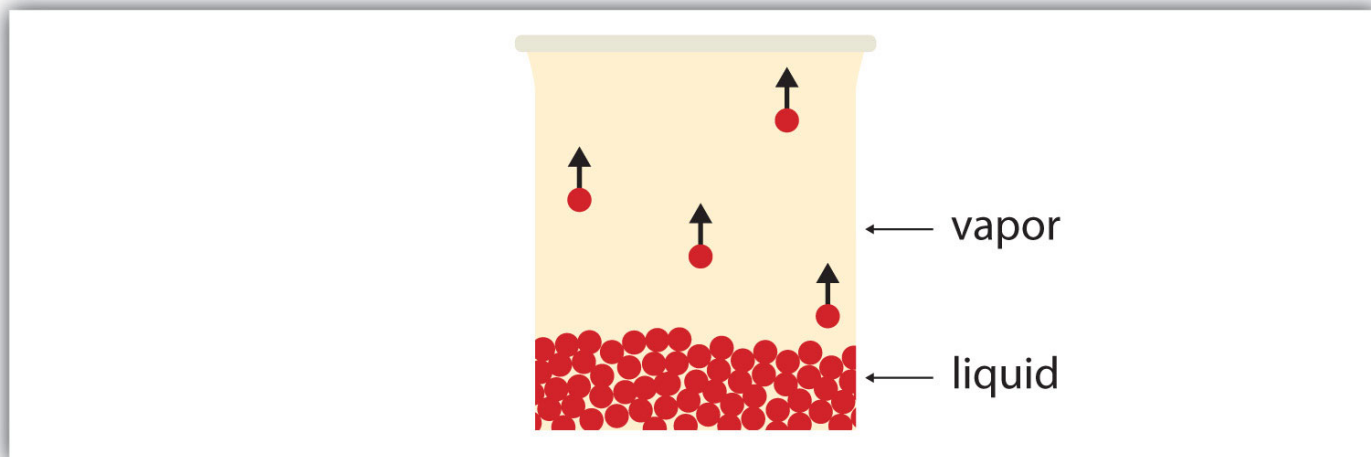
Figure 10.4: *Evaporation - Some particles of a liquid have enough energy to escape the liquid phase to become a vapor.*
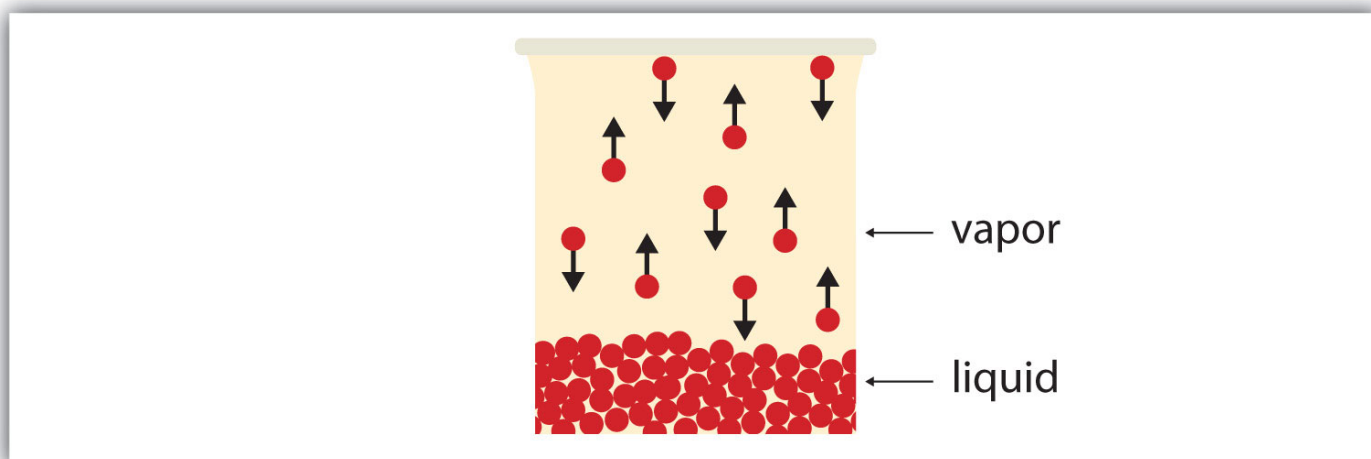
Figure 10.6: *Equilibrium - At some point, the number of particles entering the vapor phase will be balanced by the number of particles returning to the liquid. This point is called equilibrium.*

Understand that the liquid has not stopped evaporating. The reverse process—condensation—is occurring as fast as evaporation is, 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 10.7 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.
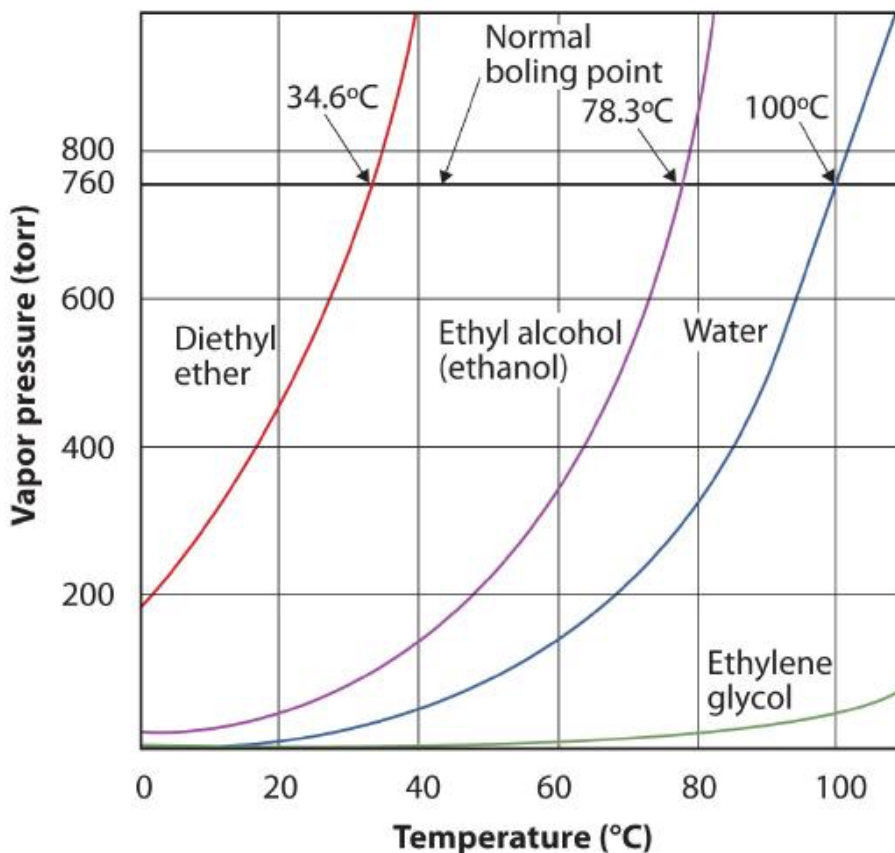
Figure 10.7: *Plots of Vapor Pressure versus Temperature for Several Liquids - The vapor pressure of a liquid depends on the identity of the liquid and the temperature, as this plot shows.*

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. The blue particle in the bulk of the liquid in Figure 10.8 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 that we call surface tension.

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. Surface tension causes liquids to form spheres in free fall or zero gravity (see : the "floating" water isn't in the shape of a sphere by accident; it is the result of surface tension). 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. Carefully done, this phenomenon can also be illustrated with a thin razor blade or a paper clip.
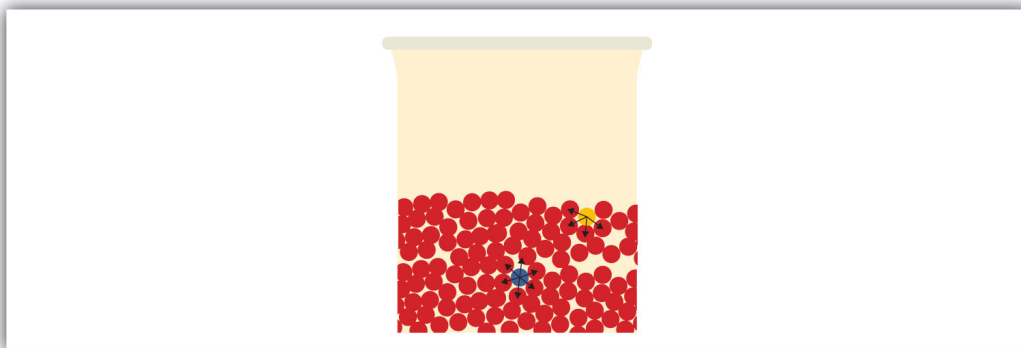
Figure 10.9*: Surface Tension Surface tension comes from the fact that particles at the surface of a liquid do not experience interactions from all directions, leading to an imbalance of forces on the surface.*

Fig. 10.10: *Walking on Water © Thinkstock. Small insects can actually walk on top of water because of surface tension effects.*

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. We say 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 moves 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.

Water **Mercury**

Figure 10.10 *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.*

KEY TAKEAWAYS

- ❖ 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.

1. What is the difference between evaporation and boiling?

2. What is the difference between a gas and vapor?

3. Define *normal boiling point* in terms of vapor pressure.

4. Is the boiling point higher or lower at higher environmental pressures? Explain your answer.

5. Referring to Figure 10.7, if the pressure is 400 torr, which liquid boils at the lowest temperature?

6. Referring to Figure 10.7, if the pressure is 100 torr, which liquid boils at the highest temperature?

7. Referring to Figure 10.7, estimate the boiling point of ethanol at 200 torr.

8. Referring to Figure 10.7, at approximately what pressure is the boiling point of water 40°C?

9. Explain how surface tension works.

10. From what you know of intermolecular forces, which substance do you think might have a higher surface tension—ethyl alcohol or mercury? Why?

11. Under what conditions would a liquid demonstrate a capillary rise?

12. Under what conditions would a liquid demonstrate a capillary depression?

ANSWERS

1. Evaporation occurs when a liquid becomes a gas at temperatures below that liquid's boiling point, whereas boiling is the conversion of a liquid to a gas at the liquid's boiling point.

3. the temperature at which the vapor pressure of a liquid is 760 torr

5. diethyl ether

7. 48°C

9. Surface tension is an imbalance of attractive forces between liquid molecules at the surface of a liquid.

11. Adhesion must be greater than cohesion.

4. END-OF-CHAPTER MATERIAL

ADDITIONAL EXERCISES

1. All other things being equal, rank the intermolecular forces in order of increasing strength.

2. Which subatomic particles (protons, neutrons, electrons) are most responsible for intermolecular forces? Explain your answer.

3. Can a molecule experience more than one intermolecular force at the same time? Why or why not?

4. Of the properties boiling point, structure of the solid phase, and molar mass, which are influenced by hydrogen bonding? Explain your answer.

5. How many grams of solid water can be melted with 1.55 kJ of energy?

6. How many grams of Hg can be vaporized using 29,330 J of energy?

7. Another way to minimize freezer burn is to wrap food tightly before freezing. Why would this minimize freezer burn?

8. The ΔH_{sub} of naphthalene ($C_{10}H_8$) is 72.6 kJ/mol. What energy is needed to sublime 100.0 g of $C_{10}H_8$?

9. Which do you think would have a higher surface tension—liquid neon or liquid krypton? Explain your answer.

10. Under what condition would a liquid not show either capillary rise or capillary depression?

ANSWERS

1. dispersion forces < dipole-dipole interactions < hydrogen bonding < ionic bonding

3. Yes, but one intermolecular force usually dominates.

5. 4.64 g

7. Water in the vapor phase has no space to evaporate into.

9. liquid krypton because it would have stronger dispersion forces

CHAPTER 11: HEALTH, FOOD, AND NUTRITION

1. FATS

Fats and oils are organic compounds that, like carbohydrates, are composed of the elements carbon (C), hydrogen (H), and oxygen (O), arranged to form molecules. There are many types of fats and oils and a number of terms and concepts associated with them, which are detailed further here.

Lipids

In baking, lipids are generally a synonym for fats. Baking books may talk about the "lipid content of eggs," for example.

Triglycerides

Triglycerides is another chemical name for the most common type of fats found in the body, indicating that they are usually made up of three (tri) fatty acids and one molecule of glycerol (glycerine is another name) as shown in Figure 3. (The mono and diglycerides that are used as emulsifiers have one and two fatty acids respectively.)

Figure 1: Composition of fats (triglycerides) Fatty Acids

Each kind of fat or oil has a different combination of fatty acids. The nature of the fatty acid will determine the consistency of the fat or oil. For example, stearic acid is the major fatty acid in beef fat, and linoleic acid is dominant in seed oils. Fatty acids are defined as short, medium, or long chain, depending on the number of atoms in the molecule.

The reason that some fat melts gradually is that as the temperature rises, each fatty acid will, in turn, soften, as its melting point is reached. Fats that melt all of a sudden mean that the fatty acids are of the same or similar type and have melting points within a narrow range. An example of such a fat is coconut fat: one second it is solid, the next, liquid.

Table 1 shows the characteristics of three fatty acids.

Type of Fatty Acid	Melting Point	Physical State (at room temperature)
Stearic	69°C (157°F)	Solid
Oleic	16°C (61°F)	Liquid
Linoleic	-12°C (9°F)	Liquid

Rancid

Rancid is a term used to indicate that fat has spoiled. The fat takes on an unpleasant flavor when exposed to air and heat. Unsalted butter, for example, will go rancid quickly if left outside the refrigerator, especially in warm climates.

Oxidation/Antioxidants

Oxidation (exposure to air) causes rancidity in fats over time. This is made worse by combination with certain metals, such as copper. This is why doughnuts are never fried in copper pans!

Some oils contain natural antioxidants, such as tocopherols (vitamin E is one kind), but these are often destroyed during the processing. As a result, manufacturers add synthetic antioxidants to retard rancidity. BHA and BHT are synthetic antioxidants commonly used by fat manufacturers.

Saturated/Unsaturated

Saturated and unsaturated refer to the extent to which the carbon atoms in the molecule of fatty acid are linked or bonded (saturated) to hydrogen atoms. One system of fatty acid classification is based on the number of double bonds.

0 double bonds: saturated fatty acids. Stearic acid is a typical long-chain saturated fatty acid.

Stearic acid, a saturated fatty acid
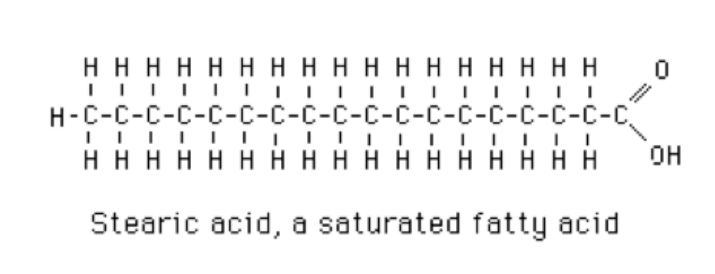
Figure 2: Stearic Acid

1 double bond: monounsaturated fatty acids. Oleic acid is a typical monounsaturated fatty acid.

Oleic acid, a monounsaturated fatty acid.
Note that the double bond is *cis*; this is
the common natural configuration.
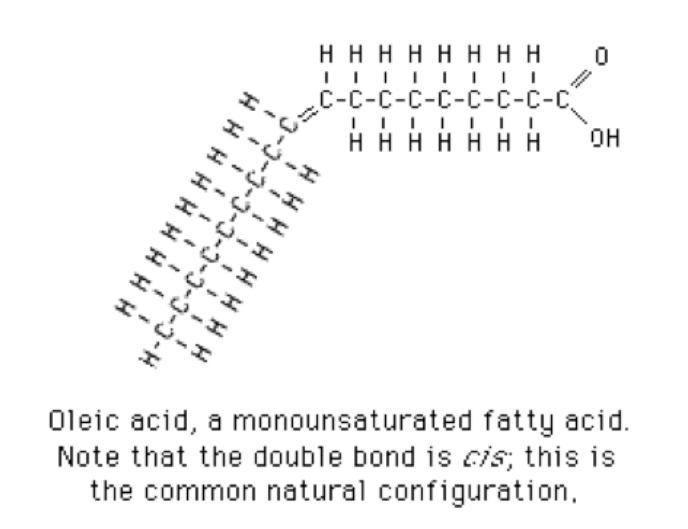
Figure 3: Oleic Acid

312

2 or more double bonds: polyunsaturated fatty acids. Linoleic acid is a typical polyunsaturated fatty acid (Figure 4).

Linoleic acid, a polyunsaturated fatty acid.
Both double bonds are *cis*.
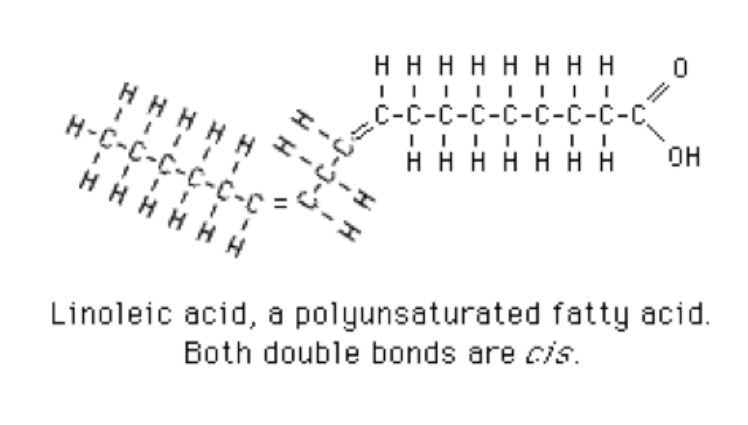
Figure 4: Linoleic Acid

Saturated fat is a type of fat found in food. For many years, there has been a concern that saturated fats may lead to an increased risk of heart disease; however, there have been studies to the contrary and the literature is far from conclusive. The general assumption is that the less saturated fat the better as far as health is concerned. For the fat manufacturer, however, low saturated fat levels make it difficult to produce oils that will stand up to the high temperatures necessary for processes such as deep-frying. Hydrogenation has been technology's solution. Hydrogenation will be discussed later in the chapter.

Saturated fat is found in many foods:

- Animal foods (like beef, chicken, lamb, pork, and veal)
- Coconut, palm, and palm kernel oils
- Dairy products (like butter, cheese, and whole milk)
- Lard

Shortening

Unsaturated fat is also in the foods you eat. Replacing saturated and trans fats (see below) with unsaturated fats has been shown to help lower cholesterol levels and may reduce the risk of heart disease. Unsaturated fat is also a source of omega-3 and omega-6 fatty acids, which are generally referred to as "healthy" fats. Choose foods with unsaturated fat as part of a balanced diet using the U.S. Department of Health and Human Service's Dietary Guidelines.

Even though unsaturated fat is a "good fat," having too much in your diet may lead to having too many calories, which can increase your risk of developingobesity, type 2 diabetes, heart disease, and certain types of cancer.

There are two main types of unsaturated fats:

Monounsaturated fat, which can be found in:

- Avocados
- Nuts and seeds (like cashews, pecans, almonds, and peanuts)
- Vegetable oils (like canola, olive, peanut, safflower, sesame, and sunflower)

Polyunsaturated fat, which can be found in:

- Fatty fish (like herring, mackerel, salmon, trout and smelt)

  Fish oils

  Nuts and seeds (like cashews, pecans, almonds and peanuts)
- Vegetable oils (like canola, corn, flaxseed, soybean and sunflower)

Hydrogenation

Simply put, hydrogenation is a process of adding hydrogen gas to alter the melting point of the oil or fat.
The injected hydrogen bonds with the available carbon, which changes liquid oil into solid fat. This is practical, in that it makes fats versatile. Think of the different temperature conditions within a bakery during which fat must be workable; think of the different climatic conditions encountered in bakeries.

Trans Fat

Trans fat is made from a chemical process known as "partial hydrogenation." This is when liquid oil is made into a solid fat. Like saturated fat, trans fat has been shown to raise LDL or "bad" cholesterol levels, which may in turn increase your risk for heart disease. Unlike saturated fat, trans fat also lowers HDL or "good" cholesterol. A low level of HDL-cholesterol is also a risk factor for heart disease.

Until recently, most of the trans fat found in a typical American diet came from:

- Fried foods (like doughnuts)
- baked goods including cakes, pie crusts, biscuits, frozen pizza, cookies, and crackers
- stick margarine and other spreads

The US Food and Drug Administration (FDA) specifically prescribe what information must be displayed on a label. The trans fat content of food is one piece of core nutrition information that is required to be declared in a nutrition facts table.

Emulsification (Emulsified Shortenings)

Emulsification is the process by which normally unmixable ingredients (such as oil and water) can be combined into a stable substance. Emulsifiers are substances that can aid in this process. There are natural emulsifiers such as lecithin, found in egg yolks. Emulsifiers are generally made up of monoglycerides and diglycerides and have been added to many hydrogenated fats, improving the fat's ability to:

- Develop a uniformly fine structure
- Absorb a high percentage of sugar
- Hold in suspension a high percentage of liquid

Emulsified shortenings are ideal for cakes and icings, but they are not suitable for deep-frying.

Stability

Stability refers to the ability of a shortening to have an extended shelf life. It refers especially to deep-frying fats, where a smoke point (see below) of 220°C to 230°C (428°F to 446°F) indicates a fat of high stability.

Smoke Point

The smoke point is the temperature reached when fat first starts to smoke. The smoke point will decline over time as the fat breaks down (see below).

Fat Breakdown

The technical term for fat breakdown is hydrolysis, which is the chemical reaction of a substance with water. In this process, fatty acids are separated from their glycerol molecules and accumulate over time in the fat. When their concentration reaches a certain point, the fat takes on an unpleasant taste, and continued use of the fat will yield a nasty flavor. The moisture, which is at the root of this problem, comes from the product being fried. This is why it is a good reason to turn off the fryer or turn it to "standby" between batches of frying foods such as doughnuts. Another cause of fat breakdown is excessive flour on the product or particles breaking off the product.

Sources of Bakery Fats and Oils

Edible fats and oils are obtained from both animal and vegetable sources. Animal sources include:

- Beef

- Pork

- Sheep

- Fish

In North America, the first two are the prime sources.

Vegetable sources include canola, coconut, corn, cotton, olive, palm fruit and palm kernel, peanut, soya bean, safflower, and sunflower.

Refining of Fats and Oils

The major steps in refining fats and oils are as follows:

1. Free fatty acids are neutralized and treated with an alkali.

2. Color is removed.

3. The fat is hydrogenated.

4. The fat is deodorized.

5. The fat is chilled and beaten to make it softer and whiter. This is done by a votator (a machine that cools and kneads liquid margarine).

6. Fat is stored to facilitate the correct crystallization (tempering).

Major Fats and Oils Used in Bakeries

Lard

Lard is obtained from the fatty tissues of pigs, with a water content of 12% to 18%. Due to dietary concerns, lard has gradually lost much of its former popularity. It is still extensively used, however, for:

- Yeast dough additions

- Pie pastry

- Pan greasing

Lard has a good plastic range, which enables it to be worked in a pie dough at fairly low temperatures (try the same thing with butter!). It has a fibrous texture and does not cream well. It is therefore not suitable for cake making. Some grades of lard also have a distinctive flavor, which is another reason it is unsuitable for cake making.

Butter

Butter is made from sweet, neutralized, or ripened creams pasteurized and standardized to a fat content of 30% to 40%. When cream is churned or overwhipped, the fat particles separate from the watery liquid known as buttermilk. The separated fat is washed and kneaded in a water wheel to give it plasticity and consistency. Color is added during this process to make it look richer, and salt is added to improve its keeping quality.

In Canada, the following regulations apply to butter:

- Minimum 80% milk fat by weight

- Permitted ingredients: milk solids, salt, air or inert gas, permitted food color, permitted bacterial culture

- The grade and grade name for butter and butter products is Canada 1.

Sweet (or unsalted) butter is made from a cream that has a very low acid content and no salt is added to it. It is used in some baking products like French butter cream, where butter should be the only fat used in the recipe. Keep sweet butter in the refrigerator.

From the standpoint of flavor, butter is the most desirable fat used in baking. Its main drawback is its relatively high cost. It has moderate but satisfactory shortening and creaming qualities. When used in cake mixing, additional time, up to five minutes more, should be allowed in the creaming stage to give maximum volume. Adding an emulsifier (about 2% based on flour weight) will also help in cake success, as butter has a poor plastic range of 18°C to 20°C (64°F to 68°F).

Butter and butter products may also be designated as "whipped" where they have had air or inert gas uniformly incorporated into them as a result of whipping. Whipped butter may contain up to 1% added edible casein or edible caseinates. Butter and butter products may also be designated as "cultured" where they have been produced from cream to which a permitted bacterial culture has been added.

Margarine

Margarines are made primarily from vegetable oils (to some extent hydrogenated) with a small fraction of milk powder and bacterial culture to give a butter-like flavor. Margarines are very versatile and include:

- General purpose margarine with a low melting point, suitable for blending in dough and general baking

- Cake margarine with excellent creaming qualities

- Roll-in margarine, which is plastic and suitable for Danish pastries

- Puff pastry roll-in, which is the most waxy and has the highest melting point

Margarine may be obtained white, but is generally colored. Margarine has a fat content ranging from 80% to 85%, with the balance pretty much the same as butter.

Oil content claims on margarine

The claim that margarine contains a certain percentage of a specific oil in advertisements should always be based on the percentage of oil by weight of the total product. All the oils used in making the margarine should be named. For example, if a margarine is made from a mixture of corn oil, cottonseed oil, and soybean oil, it would be considered misleading to refer only to the corn oil content in an advertisement for the margarine. On the other hand, the mixture of oils could be correctly referred to as vegetable oils.

It used to be that you could only buy margarines in solid form full of saturated and trans fat. The majority of today's margarines come in tubs, are soft and spreadable, and are non-hydrogenated, which means they have low levels of saturated and trans fat. Great care must be taken when attempting to substitute spreadable margarine for solid margarine in recipes.

Shortenings

Since the invention of hydrogenated vegetable oil in the early 20th century, shortening has come almost exclusively to mean hydrogenated vegetable oil. Vegetable shortening shares many properties with lard: both are semi-solid fats with a higher smoke point than butter and margarine. They contain less water and are thus less prone to splattering, making them safer for frying. Lard and shortening have a higher fat content (close to 100%) compared to about 80% for butter and margarine. Cake margarines and shortenings tend to contain a bit higher percentage of monoglycerides than margarines. Such "high-ratio shortenings" blend better with hydrophilic (attracts water) ingredients such as starches and sugar.

Health concerns and reformulation

Early in this century, vegetable shortening became the subject of some health concerns due to its traditional formulation from partially hydrogenated vegetable oils that contain trans fats, which have been linked to a number of adverse health effects. Consequently, a low trans-fat variant of Crisco brand shortening was introduced in 2004. In January 2007, all Crisco products were reformulated to contain less than one gram of trans fat per serving, and the separately marketed trans-fat free version introduced in 2004 was consequently discontinued. Since 2006, many other brands of shortening have also been reformulated to remove trans fats. Non-hydrogenated vegetable shortening can be made from palm oil.

Hydrogenated vegetable shortenings

Hydrogenated shortenings are the biggest group of fats used in the commercial baking industry. They feature the following characteristics:

- They are made from much the same oils as margarine.

- They are versatile fats with good creaming ability.

- Their hydrogenation differs according to the specific use for which the fat is designed.

- They are 100% fat – no water.

- They keep well for six to nine months.

Variations on these shortenings are: emulsified vegetable shortenings, roll-in pastry shortenings, and deep- frying

Emulsified vegetable shortenings

Emulsified vegetable shortenings are also termed high-ratio fats. The added emulsifiers (mono- and diglycerides) increase fat dispersion and give added fineness to the baked product. They are ideal for high- ratio cakes, where relatively large amounts of sugar and liquid are incorporated. The result is a cake:

- Fine in texture

- Light in weight and of excellent volume

- Superior in moisture retention (good shelf life)

- Tender to eat

This is also the fat of choice for many white cake icings.

Roll-in pastry shortenings

This type of shortening is also called special pastry shortening (SPS). These fats have a semi-waxy consistency and offer:

- Large plastic range

- Excellent extensibility

- Excellent lifting ability

They are primarily used in puff pastry and Danish pastry products where lamination is required. They come in various specialized forms, with varying qualities and melting points. It is all a matter of compromise between cost, palatability, and leavening power. A roll-in that does not have "palate cling" may have a melting point too low to guarantee maximum lift in a puff pastry product.

Deep-Frying Fats

Deep-frying fats are special hydrogenated fats that have the following features:

- High smoke point of up to 250°C (480°F)

- High heat stability and resistance to fat breakdown

- No undesirable flavor on finished products

- No greasiness when cold

These fats contain an anti-foaming agent.

Vegetable Oils

Vegetable oil is an acceptable common name for an oil that contains more than one type of vegetable oil. Generally, when such a vegetable oil blend is used as an ingredient in another food, it may be listed in the ingredients as "vegetable oil."

There are two exceptions: if the vegetable oils are ingredients of a cooking oil, salad oil, or table oil, the oils must be specifically named in the ingredient list (e.g., canola oil, corn oil, safflower oil), and using the general term vegetable oil is not acceptable. As well, if any of the oils are coconut oil, palm oil, palm kernel oil, peanut oil, or cocoa butter, the oils must be specifically named in the ingredient list.

When two or more vegetable oils are present and one or more of them has been modified or hydrogenated, the common name on the principal display panel and in the list of ingredients must include the word "modified" or "hydrogenated," as appropriate (e.g., modified vegetable oil, hydrogenated vegetable oil, modified palm kernel oil).

Vegetable oils are used in:

- Chemically leavened batters (e.g., muffin mixes)

- Dough additives (to replace the fat)

- Short sponges (to replace the butter or fat)

Coconut Fat

Coconut fat is often used to stabilize butter creams as it has a very small plastic range. It has a quite low melting point and its hardness is due to other factors. It can be modified to melt at different temperatures, generally between 32°C and 36°C (90°F and 96°F).

The Importance of Melting Points

As mentioned above, all fats become oils and vice versa, depending on temperature. Physically, fats consist of minute solid fat particles enclosing a microscopic liquid oil fraction. The consistency of fat is very important to the baker. It is very difficult to work with butter (relatively low melting point) in hot weather, for example. At the other extreme, fats with a very high melting point are not very palatable, since they tend to stick to the palate. Fat manufacturers have therefore attempted to customize fats to accommodate the various needs of the baker.

Fats with a melting range between 40°C and 44°C (104°F and 112°F) are considered to be a good compromise between convenience in handling and palatability. New techniques allow fats with quite high melting points without unpleasant palate-cling.

Table 1 shows the melting points of some fats.

Type of Fat	Melting Point
Coconut fat	32.5°C-34.5°C (90.5°F-4.1°F)
Regular margarine	34°C (93°F)
Butter	38°C (100°F)
Regular shortenings	44°C-47°C (111°F-116°F)
Roll-in shortenings	40°C-50°C (104°F-122°F)
Roll-in margarine	44°C-54°C (111°F-130°F)

Blending

It is probably safe to say that most fats are combinations or blends of different oils and/or fats.

They may be all vegetable sources. They may be combined vegetable and animal sources. A typical ratio is 90% vegetable source to 10% animal (this is not a hard and fast rule). Formerly, blends of vegetable and animal oils and fats were termed compound fats. Nowadays, this term, if used at all, may refer also to combinations of purely vegetable origin.

Functions of Fat in Baking

The following summarize the various functions of fat in baking.

Tenderizing Agents

Used in sufficient quantity, fats tend to "shorten" the gluten strands in flour; hence their nam shortenings. Traditionally, the best example of such fat was lard.

Creaming Ability

This refers to the extent to which fat, when beaten with a paddle, will build up a structure of air pockets. This aeration, or creaming ability, is especially important for cake baking; the better the creaming ability, the lighter the cake.

Plastic Range

Plastic range relates to the temperature at which the fatty acid component melts and over which shortening will stay workable and will "stretch" without either cracking (too cold) or softening (too warm). A fat that stays "plastic" over a temperature range of 4°C to 32°C (39°F to 90°F) would be rated as excellent.

A dough made with such a fat could be taken from the walk-in cooler to the bench in a hot bakeshop and handled interchangeably. Butter, on the other hand, does not have a good plastic range; it is almost too hard to work at 10°C (50°F) and too soft at 27°C (80°F).

Lubrication

In dough making, the fat portion makes it easier for the gluten network to expand. The dough is also easier to mix and to handle. This characteristic is known as lubrication.

Moistening Ability

Whether in dough or in a cake batter, fat retards drying out. For this purpose, a 100% fat shortening will be superior to either butter or margarine.

Nutrition

As one of the three major food categories, fats provide a very concentrated source of energy. They contain many of the fatty acids essential for health.

2. SUGAR

Sugar Chemistry

Chemically, sugar consists of carbon (C), oxygen (O), and hydrogen (H) atoms, and is classified as a carbohydrate.

There are three main groups of sugars, classified according to the way the atoms are arranged together in the molecular structure. These groups are the following:

- Monosaccharides or simple sugars. Dextrose (glucose) is the major monosaccharide. Others are levulose or fructose (found in honey and many fruits), and galactose, which is a milk sugar. Such sugars do not readily crystallize. (Mono means one, indicating that the sugar consists of only one molecule.)
- Disaccharides or complex sugars. Sucrose (common sugar) is the primary example of a disaccharide. Maltose, found in cereals, and lactose, found in milk, are others.
- Polysaccharides. Examples are starches, dextrins, and cellulose.

Bakers are not concerned with polysaccharides but rather with the monosaccharides and disaccharides. The latter two both sweeten, but they cannot be used interchangeably because they have different effects on the end product. These differences are touched on later in the book.

Sugar Names

It is helpful to understand some of the conventions of the names of different sugars. Note that sugar names often end in "ose": sucrose, dextrose, maltose, lactose, etc. Sucrose is the chemical name for sugar that comes from the cane and beet sugar plants.

Note that glucose is the chemical name for a particular type of sugar. What is sometimes confusing is that glucose occurs naturally, as a sugar molecule in substances such as honey, but it is also produced industrially from the maize plant (corn).

The Canadian Food and Drug Regulations (FDR) govern the following definitions:

- Sugars: All monosaccharides and disaccharides. Used for nutrition labelling purposes.

- Sweetening agent: Any food for which a standard is provided in Division 18 of the Food and Drug Regulation, or any combination of these. Includes sugar (sucrose), sugar syrups, and molasses derived from sugar cane or sugar beet, dextrose, glucose and syrups, honey and lactose. Excludes sweeteners considered to be food additives.

- Sweetening ingredient: Any sugar, invert sugar, honey, dextrose, glucose, or glucose solids, or any combination of these in dry or liquid form. Designed for sweetening fruits, vegetables, and their products and substitutes.

- Maple syrup: The syrup obtained by the concentration of maple sap or by the dilution or solution of a maple product, other than maple sap, in potable water.

- Sweetener: Any food additive listed as a sweetener. Includes both sugar alcohols and high intensity- sweeteners such as acesulfame-potassium, aspartame, and sucralose.

- Sugar alcohols: Food additives that may be used as sweeteners. Includes isomalt, lactitol, maltitol, maltitol syrup, mannitol, sorbitol, sorbitol syrup, xylitol, and erythritol.

Sugar Refining

While some refining usually occurs at source, most occurs in the recipient country. The raw sugar that arrives at the ports is not legally edible, being full of impurities.

At the refinery, the raw brown sugar goes through many stages:

1. Washing and boiling

2. Filtering to remove impurities

3. Evaporation to the desired crystal size under vacuum to avoid caramelization

4. Centrifuging, in which the fluid is spun off leaving the crystals

5. Drying in a rotating drum with hot air

6. Packaging in various sizes, depending on the intended market

Sugar beet undergoes identical steps after the initial processing, which involves:

1. Slicing the beets and extracting the sugar with hot water

2. Removing impurities

3. Filtration

4. Concentration in evaporators

From here, the process is identical to the final steps in cane processing. See Figure 2 which illustrates the process.

Some of the sugar passes through a machine that presses the moist sugar into cubes and wraps and packages them; still other sugar is made into icing sugar. The sugar refining process is completely mechanical, and machine operators' hands never touch the sugar.

Brown and yellow sugars are produced only in cane sugar refineries. When sugar syrup flows from the centrifuge machine, it passes through further filtration and purification stages and is re-boiled in vacuum pans such as the two illustrated in Figure 2. The sugar crystals are then centrifuged but not washed, so the sugar crystals still retain some of the syrup that gives the product its special flavour and colour.

During the whole refining process almost 100 scientific checks for quality control are made, while workers in research laboratories at the refineries constantly carry out experiments to improve the refining process and the final product. Sugar is carefully checked at the mills and is guaranteed to have a high purity. Government standards both in the United States and Canada require a purity of at least 99.5% sucrose.

Are animal ingredients included in white sugar?

Bone char — often referred to as natural carbon — is widely used by the sugar industry as a decolourizing filter, which allows the sugar cane to achieve its desirable white colour. Other types of filters involve granular carbon or an ion-exchange system rather than bone char.

Bone char is made from the bones of cattle, and it is heavily regulated by the European Union and the USDA. Only countries that are deemed BSE-free can sell the bones of their cattle for this process.

Bone char is also used in other types of sugar. Brown sugar is created by adding molasses to refined sugar, so companies that use bone char in the production of their regular sugar also use it in the production of their brown sugar. Confectioner's sugar — refined sugar mixed with cornstarch — made by these companies also involves the use of bone char. Fructose may, but does not typically, involve a bone-char filter.

Bone char is not used at the sugar beet factory in Taber, Alberta, or in Montreal's cane refinery. Bone char is used only at the Vancouver cane refinery. All products under the Lantic trademark are free of bone char. For the products under the Rogers trademark, all Taber sugar beet products are also free of bone char. In order to differentiate the Rogers Taber beet products from the Vancouver cane products, you can verify the inked-jet code printed on the product. Products with the code starting with the number "22" are from Taber, Alberta, while products with the code starting with the number "10" are from Vancouver.

If you want to avoid all refined sugars, there are alternatives such as sucanat and turbinado sugar, which are not filtered with bone char. Additionally, beet sugar — though normally refined — never involves the use of bone char.

The Application of Sugar

Sugar is the third most used ingredient in the bakeshop. Sugar has several functions in baking. The most recognized purpose is, of course, to sweeten food, but there are many other reasons sugar is used in cooking and baking:

It can be used for browning effect, both caramelization and the Maillard reaction, on everything from breads to cookies to cakes. Browning gives a pleasant color and flavor to the finished product. Caramelization results from the action of heat on sugars. At high temperatures, the chemical changes associated with melting sugars result in a deep brown color and new flavors. The Maillard reaction results from chemical interactions between sugars and proteins at high heat. An amino group from a protein combines with a reducing sugar to produce a brown color in a variety of foods (e.g., brewed coffee, fried foods, and breads).

It acts as the most important tenderizing agent in all baked goods, and one of the factors responsible for the spread in cookies. It helps delay the formation of gluten, which is essential for maintaining a soft or tender product.
It makes an important contribution to the way we perceive the texture of food. For example, adding sugar to ice cream provides body and texture, which is perceived as smoothness. This addition helps prevent lactose crystallization and thus reduces sugar crystal formation that otherwise causes a grainy texture sometimes associated with frozen dairy products.

- It preserves food when used in sufficient quantity.

- In baking, it increases the effectiveness of yeast by providing an immediate and more usable source of nourishment for the yeast's growth. This hastens the leavening process by producing more carbon dioxide, which allows the dough to rise at a quicker and more consistent rate.

Just as there are many functions of sugar in the bakeshop, there are different uses for the various types of sugar as well:

Fine granulated sugar is most used by bakers. It generally dissolves easily in mixes and is pure enough for sugar crafters to boil for "pulled" sugar decorations.

Coarse granulated sugar may be used for a topping on sugar cookies, puff pastry, and Danish pastries as it doesn't liquefy or caramelize so readily. In some European countries, an extra coarse sugar (called hail — a literal translation) is used for this purpose.

Icing or powdered sugar is used in icings and fillings and in sifted form as a top decoration on many baked goods. Brown or yellow sugars are used where their unique flavour is important, or in bakeries where an old-fashioned or rustic image is projected. Brown sugar can usually be substituted for white sugar without technical problems in sugar/batter mixes such as cakes and muffins, and in bread dough.

Agave

Agave has gained popularity in the food industry due to some of its nutritional properties. The agave nectar is obtained from the sap of the heart of the agave plant, a desert succulent, which is also used to produce tequila. The syrup/sugar production process of agave is similar to that of sugar. See more about the nutritional properties and application of agave in the chapter Special Diets, Allergies, Intolerances, Emerging Issues, and Trends in the open textbook Nutrition and Labelling for the Canadian Baker.

Glucose/Dextrose

The sugar known as glucose has two origins:

- In a natural form in most fruits

- In a processed form from corn (corn syrup)

In baking, we usually refer to industrially made glucose. It is made from corn and the resulting product, a thick syrup, is then adjusted to a uniform viscosity or consistency. The particular form of the syrup is defined by what is known as the dextrose equivalent, or DE for short. Corn syrup is the most familiar form of glucose.

In plant baking, high-fructose corn syrup (HFCS) is the major sweetening agent in bread and buns. It consists of roughly half fructose and half dextrose. Dextrose (chemically identical to glucose) is available in crystalline form and has certain advantages over sucrose:

- It is easily fermentable.

- It contributes to browning in bread and bun making.

- In crystalline form, it is often used in doughnut sugars as it is more inclined to stay dry and non- greasy.

- It is hygroscopic and valued as a moisture-retaining ingredient.

- It retards crystallization in syrups, candies, and fondant.

Corn syrup is made from the starch of maize (corn) and contains varying amounts of glucose and maltose, depending on the processing methods. Corn syrup is used in foods to soften texture, add volume, prevent crystallization of sugar, and enhance flavor.

Glucose/dextrose has a sweetening level of approximately three-quarters that of sugar. Table 1 shows the amount of corn syrup or HFCS needed to replace sugar in a formula.

Glucose, HFCS, and corn syrup are not appropriate substitutions for sucrose in all bakery products. Certain types of cakes, such as white layer cakes, will brown too much if glucose or HFCS is used in place of sugar.

Type of Sugar	Solids	Replacement Factor
Granulated sugar	100%	1.0
Regular corn syrup	80%	1.25
High-fructose corn syrup	71%	1.41

Honey

Honey is a natural food, essentially an invert sugar. Bees gather nectar and, through the enzyme invertase, change it into honey. Honey varies in composition and flavor depending on the source of the nectar. The average composition of honey is about 40% levulose, 35% dextrose, and 15% water, with the remainder being ash, waxes, and gum.

Blended honey is a mixture of pure honey and manufactured invert sugar, or a blend of different types of honey mixed together to produce a good consistency, color, and aroma. Dehydrated honey is available in a granular form.

Store honey in a tightly covered container in a dry place and at room temperature because it is hygroscopic, meaning it absorbs and retains moisture. Refrigeration or freezing won't harm the color or flavor but it may hasten granulation. Liquid honey crystallizes during storage and is re-liquefied by warming
in a double boiler not exceeding a temperature of 58°C (136°F).

Honey is used in baking:

- As a sweetener
- To add unique flavor
- In gingerbread and special cookies where a certain moistness is characteristic of the product
- To improve keeping qualities

There are several types of honey available:

- Comb honey is "packed by the bees" directly from the hive. Liquid honey is extracted from the comb and strained. It is the type used by most bakers.
- Creamed honey has a certain amount of crystallized honey added to liquid honey to give body to the final product.
- Chunk honey consists of pieces of comb honey as well as liquid.
- Granulated honey has been crystallized.

In the United States, honey categories are based on color, from white to dark amber. Honey from orange blossom is an example of white honey. Clover honey is an amber honey, and sage and buckwheat honeys are dark amber honeys.

Malt

Malt is the name given to a sweetening agent made primarily from barley. The enzymes from the germ of the seeds become active, changing much of the starch into maltose, a complex sugar. Maltose has a distinct flavor and is used for making yeast products such as bread and rolls. Malt is considered to be relatively nutritious compared to other sweeteners.

Malt is available as:

- Flour

- Malt syrup

- Malt extract

- Dried malt

The flour is not recommended since it can lead to problems if not scaled precisely. Malt syrup is inconvenient to work with, as it is sticky, heavy, and bulky. Dried malt is the most practical, though it must be kept protected from humidity.

There are two distinct types of malt. Diastatic malt flour is dried at low temperature, thus retaining the activity of the diastatic enzymes. Non-diastatic malt flour is darker in color. It is treated at high temperature, which kills the enzymes, and the result is non-diastatic malt.

Crushing malted grain in water produces malt syrup. This dissolves the maltose and soluble enzymes. The liquid is concentrated, producing the syrup. If the process is continued, a dry crystallized product called dried malt syrup is obtained.

Malt syrup has a peculiar flavor, which many people find desirable. It is used in candy, malted milk, and many other products. The alcoholic beverage industry is the largest consumer of malt by far, but considerable quantities are used in syrup and dried malt syrup, both of which are divided into diastatic and non-diastatic malt.

Both diastatic and non-diastatic malts add sweetness, color, and flavor to baked products. Both are valuable since they contain malt sugar, which is fermented by the yeast in the later stages of fermentation. Other sugars such as glucose and levulose are used up rapidly by fermenting yeast in the early stages of fermentation.

Diastatic malt is made with various levels of active enzymes. Malt with medium diastatic activity is recommended. Normally, bread bakers will find sufficient enzymes in well-balanced flour from a good mill, so it is unnecessary to use diastatic malt.

When using dry diastatic malt, about the same weight should be used as liquid regular diastatic malt. Adjustment is made at the factory insofar as the enzyme level is increased in the dry product to compensate. Since the dry type contains about 20% less moisture than the liquid type, add water to make up the difference if dry diastatic malt is substituted for malt syrup.

The main uses of malt in the bakery are to:

- Add nutritive value, as it is rich in vitamins and essential amino acids

- Lengthen shelf life through its ability to attract moisture

- Help fermentation by strengthening the gluten and feeding the yeast

- Make products more appealing through browning of the crust

- Add unique flavor to products when used in sufficient quantity

Table 2 shows the suggested use levels for malt.

Product	Percentage of Flour Weight
White pan bread	0.5-1.5
Sweet goods	1.5-3.0
French/Italian bread	0.5-2.0
Whole wheat bread	5.0-9.0
Pretzels	1.5-6.0
Hard rolls	3.0-5.5

Maple Syrup

Canada is responsible for 84% of the world's maple syrup production, with the United States being responsible for the remaining 16%. Maple syrup is made by boiling and evaporating the sap of the sugar maple tree. Because sap is only 2% or 3% sugar, it takes almost 40 liters of sap to make 1 liter of syrup.

This makes maple syrup a very expensive sweetener. It is prized for its unique flavor and sweet aroma. Don't confuse maple-flavored pancake or table syrup with real maple syrup. Table syrup is made from inexpensive glucose or corn syrup, with added caramel coloring and maple flavoring.

Maple syrup in Canada has two categories:

Canada Grade A, which has four color/flavor classes

1. golden, delicate taste

2. amber, rich taste

3. dark, robust taste

4. very dark, strong taste

Canada Processing Grade, which has no color descriptors (any maple syrup that possesses minimal food quality defects but still meets all government regulatory standards for food quality and safety for human consumption)

This definition and grading system gives consumers more consistent and relevant information about the varieties, and helps them make informed choices when choosing maple syrup.

Darker maple syrups are better for baking as they have a more robust flavor. Using maple sugar is also a good way to impart flavor. Maple sugar is what remains after the sap of the sugar maple is boiled for longer than is needed to create maple syrup. Once almost all the water has been boiled off, all that is left is a solid sugar. It can be used to flavor some maple products and as an alternative to cane sugar.

Sugar Substitutes

In Canada, food additives such as sugar substitutes, which cover both artificial sweeteners and intense sweeteners obtained from natural sources, are subject to rigorous controls under theFood and Drugs Act
and Regulations. New food additives (or new uses of permitted food additives) are permitted only once a safety assessment has been conducted and regulatory amendments have been enacted.

Several sugar substitutes have been approved for use in Canada. These include acesulfame-potassium, aspartame, polydextrose, saccharin, stevia, sucralose, thaumatin, and sugar alcohols (polyols) like sorbitol, isomalt, lactitol, maltitol, mannitol, and xylitol. Please see the Health Canada website for more information on sugar substitutes.

Bakers must be careful when replacing sugar (sucrose) with these sugar substitutes in recipes. Even though the sweetness comparison levels may be similar (or less), it is generally not possible to do straight 1-for-1 substitution. Sugar (sucrose) plays many roles in a recipe:

- It is a bulking agent.
- It absorbs moisture.
- It is a tenderizer.
- It adds moisture and extends shelf life. It adds colour (caramelization).

Sugar substitutes may not work in a recipe in the same way.

3. VITAMINS AND MINERALS

The importance of vitamins and minerals (micronutrients) in metabolism has been discussed in detail in section 17.4. Micronutrient needs in adults differ slightly according to sex. Young men and women who are very athletic and perspire a great deal also require extra sodium, potassium, and magnesium. Males require more of vitamins C and K, along with thiamine, riboflavin, and niacin. Females require extra iron due to menstruation. Therefore, it can be beneficial for some young adults to follow a daily multivitamin regimen to help meet nutrient needs. But as always, it is important to remember "food first, supplements second." Table shows the micronutrient recommendations for adult men and women.

Table 11.3 Micronutrient Levels during Adulthood.

Nutrient	Adult Males	Adult Females
Vitamin A (mcg)	900.0	700.0
Vitamin B6 (mg)	1.3	1.3
Vitamin B12 (mcg)	2.4	2.4
Vitamin C (mg)	90.0	75.0
Vitamin D (mcg)	5.0	5.0
Vitamin E (mg)	15.0	15.0

Vitamin K (mcg)	120.0	90.0
Calcium (mg)	1,000.0	1,000.0
Folate (mcg)	400.0	400.0
Iron (mg)	8.0	18.0
Magnesium (mg)	400.0	310.0
Niacin (mg)	16.0	14.0
Phosphorus (mg)	700.0	700.0
Riboflavin (mg)	1.3	1.1
Selenium	55.0	55.0
Thiamin (mg)	1.2	1.1
Zinc (mg)	11.0	8.0

Source: Institute of Medicine. 2006. Dietary Reference Intakes: The Essential Guide to Nutrient Requirements. Washington, DC: The National Academies Press. https://doi.org/10.17226/11537. Accessed December 10, 2017.

Body Fluids and Electrolytes

Maintaining the right level of water in your body is crucial to survival, as either too little or too much water in your body will result in less-than-optimal functioning. One mechanism to help ensure the body maintains water balance is thirst. Thirst is the result of your body's physiology telling your brain to initiate the thought to take a drink. Sensory proteins detect when your mouth is dry, your blood volume too low, or blood electrolyte concentrations too high and send signals to the brain stimulating the conscious feeling to drink.

The latest National Health and Nutrition Examination Survey, covering the period from 2005 to 2008, reports that about 50 percent of Americans consume sugary drinks daily.

Excess consumption of sugary soft drinks have been scientifically proven to increase the risk for dental caries, obesity, Type 2 diabetes, and cardiovascular disease. In addition to sugary soft drinks, beverages containing added sugars include fruit drinks, sports drinks, energy drinks and sweetened bottled waters.

Sports drinks are designed to rehydrate the body after excessive fluid depletion. Electrolytes in particular promote normal rehydration to prevent fatigue during physical exertion. Are they a good choice for achieving the recommended fluid intake? Are they performance and endurance enhancers like they claim? Who should drink them?

Typically, eight ounces of a sports drink provides between fifty and eighty calories and 14 to 17 grams of carbohydrate, mostly in the form of simple sugars. Sodium and potassium are the most commonly included electrolytes in sports drinks, with the levels of these in sports drinks being highly variable. The American College of Sports Medicine says a sports drink should contain 125 milligrams of sodium per 8 ounces as it is helpful in replenishing some of the sodium lost in sweat and promotes fluid uptake in the small intestine, improving hydration.

In the summer of 1965, the assistant football coach of the University of Florida Gators requested scientists affiliated with the university study why the withering heat of Florida caused so many heat-related illnesses in football players and provide a solution to increase athletic performance and recovery post-training or game. The discovery was that inadequate replenishment of fluids, carbohydrates, and electrolytes was the reason for the "wilting" of their football players. Based on their research, the scientists concocted a drink for the football players containing water, carbohydrates, and electrolytes and called it "Gatorade." In the next football season the Gators were nine and two and won the Orange Bowl. The Gators' success launched the sports-drink industry, which is now a multibillion-dollar industry that is still dominated by Gatorade.

University of Florida football player Chip Hinton testing Gatorade in 1965, pictured next to the leader of its team of inventors.

Regulation of Daily Water Input

Total water output per day averages 2.5 liters (Figure 4). This must be balanced with water input. Our tissues produce around 300 milliliters of water per day through metabolic processes. The remainder of water output must be balanced by drinking fluids and eating solid foods. The average fluid consumption per day is 1.5 liters, and water gained from solid foods approximates 700 milliliters.
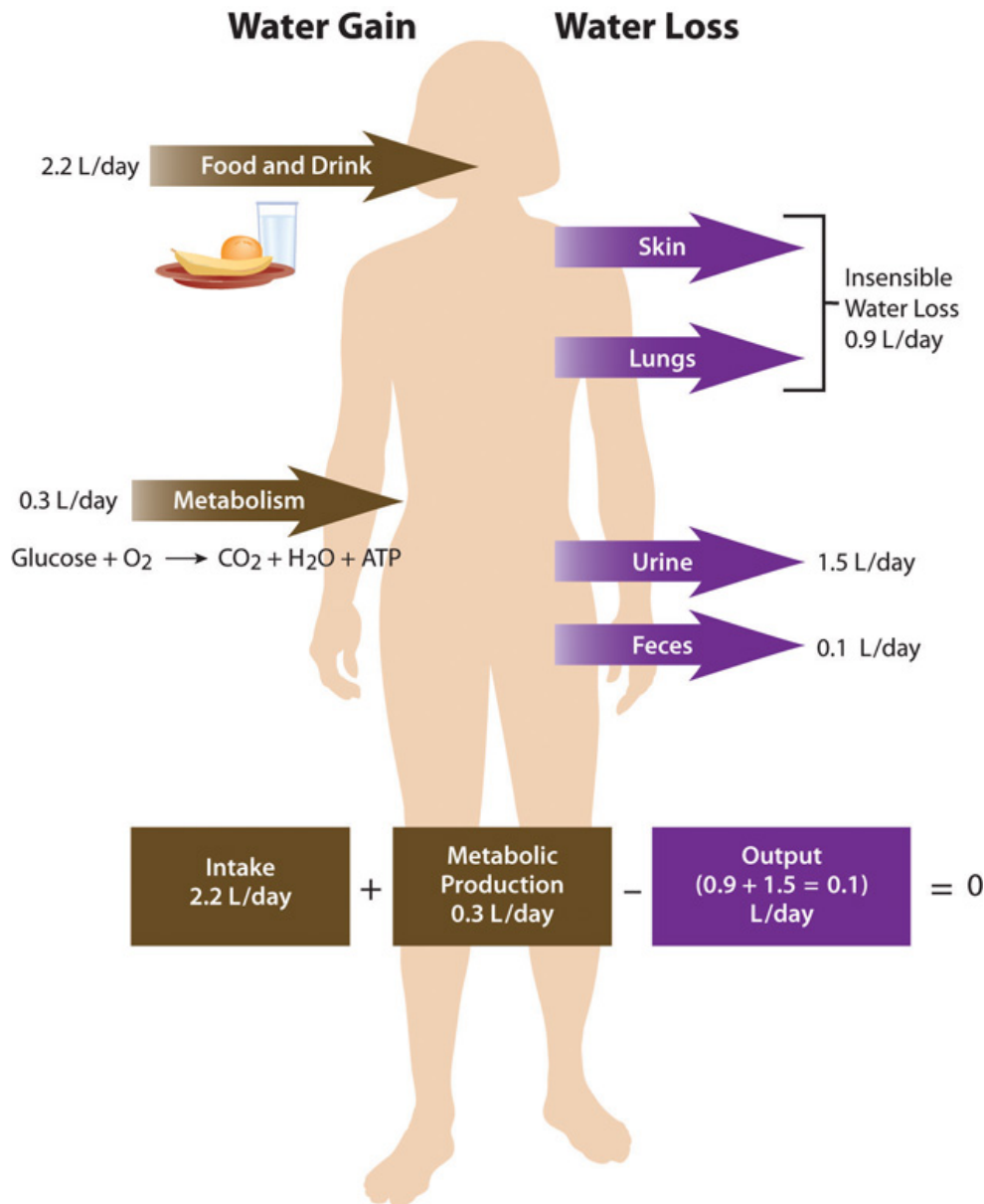
Figure 19.2.1 *Daily fluid loss and gain.*

The Food and Nutrition Board of the Institute of Medicine (IOM) has set the Adequate Intake (AI) for water for adult males at 3.7 liters (15.6 cups) and at 2.7 liters (11 cups) for adult females. These intakes are higher than the average intake of 2.2 liters. It is important to note that the AI for water includes water from all dietary sources; that is, water coming from food as well as beverages. People are not expected to consume 15.6 or 11 cups of pure water per day. In America, approximately 20 percent of dietary water comes from solid foods.

Consequences of Deficiency or Excess

As with all nutrients, having too much or too little water has health consequences. Excessive water intake can dilute the levels of critical electrolytes in the blood. Water intoxication is rare, however when it does happen, it can be deadly. On the other hand, having too little water in the body is common. In fact, diarrhea-induced dehydration is the

number-one cause of early-childhood death worldwide. In this section we will discuss subtle changes in electrolytes that compromise health on a chronic basis.

High-Hydration Status: Water Intoxication/Hyponatremia

Water intoxication mainly affects athletes who overhydrate. Water intoxication is extremely rare, primarily because healthy kidneys are capable of excreting up to one liter of excess water per hour. Overhydration was unfortunately demonstrated in 2007 by Jennifer Strange, who drank six liters of water in three hours while competing in a "Hold Your Wee for a Wii" radio contest. Afterward she complained of a headache, vomited, and died.

Low-Hydration Status: Dehydration

Dehydration refers to water loss from the body without adequate replacement. It can result from either water loss or electrolyte imbalance, or, most commonly, both. Dehydration can be caused by prolonged physical activity without adequate water intake, heat exposure, excessive weight loss, vomiting, diarrhea, blood loss, infectious diseases, malnutrition, electrolyte imbalances, and very high glucose levels. Physiologically, dehydration decreases blood volume. The water in cells moves into the blood to compensate for the low blood-volume, and cells shrink. Signs and symptoms of dehydration include thirst, dizziness, fainting, headaches, low blood-pressure, fatigue, low to no urine output, and, in extreme cases, loss of consciousness and death. Signs and symptoms are usually noticeable after about 2 percent of total body water is lost.

Chronic dehydration is linked to higher incidences of some diseases. There is strong evidence that low-hydration status increases the risk for kidney stones and exercise-induced asthma. There is also some scientific evidence that chronic dehydration increases the risk for kidney disease, heart disease, and the development of hyperglycemia in people with diabetes. Older people often suffer from chronic dehydration as their thirst mechanism is no longer as sensitive as it used to be.

Summary

- Micronutrient needs in adults differ slightly according to sex. Young men and women who are very athletic and perspire a great deal also require extra sodium, potassium, and magnesium. Males require more of vitamins C and K, along with thiamine, riboflavin, and niacin. Females require extra iron due to menstruation.

- The Food and Nutrition Board of the Institute of Medicine (IOM) has set the Adequate Intake (AI) for water for adult males at 3.7 liters (15.6 cups) and at 2.7 liters (11 cups) for adult females. It is important to note that the AI for water includes water from all dietary sources; that is, water coming from food as well as beverages.

- Excessive water intake can dilute the levels of critical electrolytes in the blood. Water intoxication is rare, however when it does happen, it can be deadly. On the other hand, having too little water in the body is common.

4. FOOD AND CALORIES

The U.S. Dietary Guidelines for Americans and the DRI are important scientific reports to educate health professionals about nutrition and to guide government and other health-related organizations to develop evidence-based health policies that improve the health of all Americans. The United States government has also been providing food and nutrition guidance directly to the public for more than a century to help individuals make healthier dietary and lifestyle choices . You may have heard about "the Four Food Groups" or "The Food Guide Pyramid" or most recently, "My

Plate." The government food guidance system has evolved over the years as our understanding of nutrition science and the impact of diet and lifestyle on health has grown.

MyPlate

MyPlate is the most up-to-date nutrition teaching tool. MyPlate was developed by the United States Department of Agriculture (U.S.D.A.) Center for Nutrition Policy and Promotion as an easy to use visual guide to help all American develop healthy eating patterns. It replaces the former MyPyramid teaching tool and correlates with the 2015 - 2020 U.S. Dietary Guidelines.

MyPlate organizes foods with similar nutritional value into specific food groups and provides recommendations about how to build a healthy diet. The ChooseMyPlate.gov website also provides a wide range of support materials including information about each food group, an individualized meal planner, recipes and professional videos and handouts such as the MyPlate, MyWins poster shown below to support learning for people of all ages.
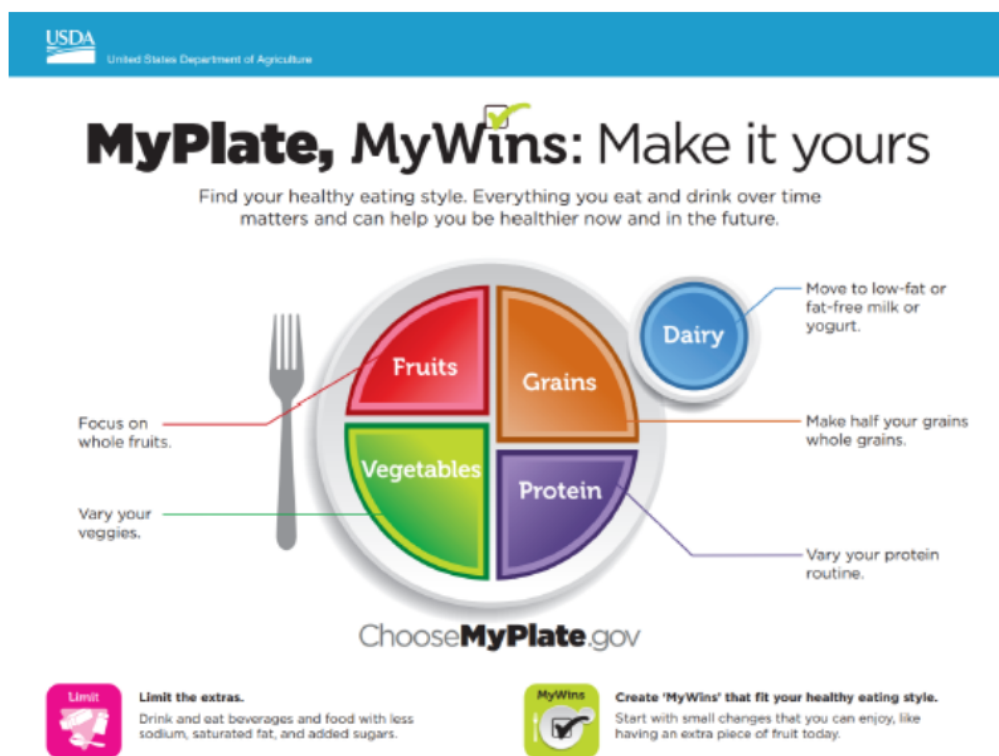
Figure 12.2 *The ideal healthy plate.*

MyPlate Key Messages include:

- Focus on whole fruits

- Vary your veggies

- Vary your protein routine

- Make half your grains whole grains

- Move to low-fat or fat-free milk or yogurt

- Drink and eat beverages and food with less sodium saturated fat and added sugars

- Start with small changes that you can enjoy, like having an extra piece of fruit today

Acceptable Macronutrient Distribution Range

Young men typically have higher nutrient needs than young women. For ages nineteen to thirty, the energy requirements for women are 1,800 to 2,400 calories, and 2,400 to 3,000 calories for men, depending on activity level. These estimates do not include women who are pregnant or breastfeeding, who require a higher energy intake.

AMDR describes the proportions of daily caloric intake that should be carbohydrates, lipids, and proteins. The range in caloric intake in a daily diet should be:

Macronutrient	AMDR	Additional Information
Carbohydrates	45 to 65 % All age groups	All adults, young and old, should eat fewer energy-dense carbohydrates, especially refined, sugar-dense sources, particularly for those who lead a more sedentary lifestyle.
Protein	10-35% (Adults) 10-30% (4-18 years old) 5-20% (1-3 years old)	The diet should include a variety of lean meat and poultry, eggs, beans, peas, nuts, and seeds. The guidelines also recommend that adults eat two 4-ounce servings (or one 8-ounce serving) of seafood per week.
Total Fat	20-35% (Adults) 25-35% (4-18 years old) 30-40% (1-3 years old)	• Keep saturated fatty acids to less than 10 percent of total calories by replacing them with monounsaturated and polyunsaturated fatty acids. • Avoid trans fats by limiting foods that contain synthetic sources, such as partially hydrogenated oils.
Fiber	22 to 28 grams per day for women and 28 to 34 grams per day for men	Soluble fiber may help improve cholesterol and blood sugar levels, while insoluble fiber can help prevent constipation.

Planning a healthy diet using the MyPlate approach is not difficult. Half of your plate should have fruits and vegetables, one-quarter should have whole grains, and one-quarter should have protein. Dairy products should be low-fat or non-fat. The ideal diet gives you the most nutrients within the fewest calories. This means choosing nutrient-rich foods.

Fill half of your plate with red, orange, and dark green vegetables and fruits, such as kale, bok choy, kalo (taro), tomatoes, sweet potatoes, broccoli, apples, mango, papaya , guavas, blueberries, and strawberries in main and side dishes. Vary your choices to get the benefit of as many different vegetables and fruits as you can. You may choose to drink fruit juice as a replacement for eating fruit. (As long as the juice is 100 percent fruit juice and only half your fruit intake is replaced with juice, this is an acceptable exchange.) For snacks, eat fruits, vegetables, or unsalted nuts.

Fill a quarter of your plate with grains such cereals, breads, crackers, rice, and pasta. Half of your daily grain intake should be whole grains. Read the ingredients list on food labels carefully to determine if a food is comprised of whole grains such as 100% whole wheat bread, brown rice and whole grain oats.

Select a variety of protein foods to improve nutrient intake and promote health benefits. Each week, be sure to include a nice array of protein sources in your diet, such as nuts, seeds, beans, legumes, poultry, soy, and seafood. The recommended consumption amount for seafood for adults is two 4-ounce servings per week. When choosing meat, select lean cuts. Be conscious to prepare meats using little or no added saturated fat, such as butter.

If you enjoy drinking milk or eating milk products, such as cheese and yogurt, choose low-fat or nonfat products. Low-fat and nonfat products contain the same amount of calcium and other essential nutrients as whole-milk products, but with much less fat and calories. Calcium, an important mineral for your body, is also available in lactose-free and fortified soy beverage and rice beverage products. You can also get calcium in vegetables and other fortified foods and beverages.

Fats are essential for your diet as they contain valuable essential fatty acids, but the type you choose and the amount you consume is important. Be sure to choose primarily plant-based liquid oils like olive, soybean and canola oil rather than solid animal fats like butter and lard. You can also get oils from many types of fish, as well as avocados, and unsalted nuts and seeds. Although oils are essential for health they do contain about 120 calories per tablespoon. It is vital to balance oil consumption with total caloric intake. The Nutrition Facts label provides the information to help you make healthful decisions.

In short, substituting vegetables and fruits in place of foods high in added sugars, solid/saturated fats, and sodium is a good way to make a nutrient-poor diet healthy again. Vegetables are full of nutrients and antioxidants that help promote good health and reduce the risk for developing chronic diseases such as stroke, heart disease, high blood pressure, Type 2 diabetes, and certain types of cancer. Starting with these small shifts in your diet as mentioned above will boost your overall health profile.

Dietary Reference Intakes (DRIs) are more than numbers in the table, even though that is often how many people view them. DRIs and Dietary Guidelines provide different information for different audiences.

- Dietary Guidelines provide **qualitative** advice to the public about diet and chronic disease prevention and maintaining health.
- DRIs provide **quantitative** advice to professionals about amounts of nutrients or food components to be of benefit.
- DRIs are a collective term to refer to these components:
  - Estimated Average Requirement (EAR)
  - Recommended Dietary Allowance (RDA)
  - Adequate Intake (AI)
  - Tolerable Upper Intake Level (UL). A number of people refer to the UL as simply the "upper limit", leaving off "tolerable".

The RDA is the measure that professionals use to assess the quality of people's diets. It is the requirement estimated to meet the needs of 97.5% of the population. But the RDA is calculated using the EAR. Therefore, the EAR needs to be

set before an RDA can be set. There must be applicable research in order to set an EAR. An EAR is the estimated requirement for 50% of the population (hence the average in its name).

Nutrition and the Athlete

The total number of calories a person needs each day varies depending on a number of factors, including the person's age, sex, height, weight, and level of physical activity. In addition, a need to lose, maintain, or gain weight and other factors affect how many calories should be consumed. Estimated amounts of calories needed to maintain calorie balance for various age and sex groups at three different levels of physical activity are provided in the web link below. These estimates are based on the Estimated Energy Requirements (EER) equations, using reference heights (average) and reference weights (healthy) for each age-sex group. For children and adolescents, reference height and weight vary. For adults, the reference man is 5 feet 10 inches tall and weighs 154 pounds. The reference woman is 5 feet 4 inches tall and weighs 126 pounds.

Estimates range from 1,600 to 2,400 calories per day for adult women and 2,000 to 3,000 calories per day for adult men. Within each age and sex category, the low end of the range is for sedentary individuals; the high end of the range is for active individuals. Due to reductions in basal metabolic rate that occur with aging, calorie needs generally decrease for adults as they age. Estimated needs for young children range from 1,000 to 2,000 calories per day, and the range for older children and adolescents varies substantially from 1,400 to 3,200 calories per day, with boys generally having higher calorie needs than girls.

Differing conditions and objectives suggest the need for athletes to ensure that their sports nutritional approach is appropriate for their situation. Factors that may affect an athlete's nutritional needs include type of activity (aerobic vs. anaerobic), gender, weight, height, body mass index, workout or activity stage (pre-workout, intro-workout, recovery), and time of day (e.g. some nutrients are utilized by the body more effectively during sleep than while awake).Most culprits that get in the way of performance are fatigue, injury and soreness. A proper diet will reduce these disturbances in performance. The key to a proper diet is to get a variety of food, and to consume all the macronutrients, vitamins, and minerals needed. According to Eblere's article (2008), it is ideal to choose raw foods, for example unprocessed foods such as oranges instead of orange juice. Eating foods that are natural means the athlete is getting the most nutritional value out of the food. When foods are processed, the nutritional value is normally reduced

Nutrition and a Healthy Diet

There are five key factors that make up a healthful diet:

1. A diet must be adequate, by providing sufficient amounts of each essential nutrient, as well as fiber and adequate calories.

2. A balanced diet results when you do not consume one nutrient at the expense of another, but rather get appropriate amounts of all nutrients.

3. Calorie control is necessary so that the amount of energy you get from the nutrients you consume equals the amount of energy you expend during your day's activities.

4. Moderation means not eating to the extremes, neither too much nor too little.

5. Variety refers to consuming different foods from within each of the food groups on a regular basis.

A healthy diet is one that favors whole foods. As an alternative to modern processed foods, a healthy diet focuses on "real" fresh whole foods that have been sustaining people for generations. Whole foods supply the needed vitamins,

minerals, protein, carbohydrates, fats, and fiber that are essential to good health. Commercially prepared and fast foods are often lacking nutrients and often contain inordinate amounts of sugar, salt, saturated and trans fats, all of which are associated with the development of diseases such as atherosclerosis, heart disease, stroke, cancer, obesity, diabetes, and other illnesses. A balanced diet is a mix of food from the different food groups (vegetables, legumes, fruits, grains, protein foods, and dairy).

Adequacy

An adequate diet is one that favors nutrient-dense foods. Nutrient-dense foods are defined as foods that contain many essential nutrients per calorie. Nutrient-dense foods are the opposite of "empty-calorie" foods, such as sugary carbonated beverages, which are also called "nutrient-poor." Nutrient-dense foods include fruits and vegetables, lean meats, poultry, fish, low-fat dairy products, and whole grains. Choosing more nutrient-dense foods will facilitate weight loss, while simultaneously providing all necessary nutrients.

Balance

Balance the foods in your diet. Achieving balance in your diet entails not consuming one nutrient at the expense of another. For example, calcium is essential for healthy teeth and bones, but too much calcium will interfere with iron absorption. Most foods that are good sources of iron are poor sources of calcium, so in order to get the necessary amounts of calcium and iron from your diet, a proper balance between food choices is critical. Another example is that while sodium is an essential nutrient, excessive intake may contribute to congestive heart failure and chronic kidney disease in some people. Remember, everything must be consumed in the proper amounts.

Moderation

Eat in moderation. Moderation is crucial for optimal health and survival. Eating nutrient-poor foods each night for dinner will lead to health complications. But as part of an otherwise healthful diet and consumed only on a weekly basis, this should not significantly impact overall health. It's important to remember that eating is, in part, about enjoyment and indulging with a spirit of moderation. This fits within a healthy diet.

Monitor food portions. For optimum weight maintenance, it is important to ensure that energy consumed from foods meets the energy expenditures required for body functions and activity. If not, the excess energy contributes to gradual, steady accumulation of stored body fat and weight gain. In order to lose body fat, you need to ensure that more calories are burned than consumed. Likewise, in order to gain weight, calories must be eaten in excess of what is expended daily.

Variety

Variety involves eating different foods from all the food groups. Eating a varied diet helps to ensure that you consume and absorb adequate amounts of all essential nutrients required for health. One of the major drawbacks of a monotonous diet is the risk of consuming too much of some nutrients and not enough of others. Trying new foods can also be a source of pleasure—you never know what foods you might like until you try them.

Developing a healthful diet can be rewarding, but be mindful that all of the principles presented must be followed to derive maximal health benefits. For instance, introducing variety in your diet can still result in the consumption of too many high-calorie, nutrient poor foods and inadequate nutrient intake if you do not also employ moderation and calorie control. Using all of these principles together will promote lasting health benefits.

Summary

- MyPlate is the most up-to-date nutrition teaching tool developed by the United States Department of Agriculture (U.S.D.A.) Center for Nutrition Policy and Promotion as an easy to use visual guide to help all American develop healthy eating patterns.

- Planning a healthy diet using the MyPlate approach is not difficult. According to the icon, half of your plate should have fruits and vegetables, one-quarter should have whole grains, and one-quarter should have protein. Dairy products should be low-fat or non-fat.

- There are five key factors that make up a healthful diet namely: a. adequacy, b. balance, c. calorie control, d. moderation, and e. variety.

- The total number of calories a person needs each day varies depending on a number of factors, including the person's age, sex, height, weight, and level of physical activity.

5. WEIGHT LOSS AND BMI

Learning Objectives

- Learn about various recommendations for weight management

- Be able to calculate body mass index (BMI) given a particular weight and height.

- Know other methods for determining body composition.

Successful weight loss is defined as individuals intentionally losing at least 10 percent of their body weight and keeping it off for at least one year. Results from lifestyle intervention studies suggest fewer than 20 percent of participants are successful at weight loss. An evaluation of successful weight loss, involving more than fourteen thousand participants published in the November 2011 issue of the International Journal of Obesity estimates that more than one in six Americans (17 percent) who were overweight or obese were successful in achieving long-term weight loss. However, these numbers are on the high end because many similar studies report fewer than 10 percent of participants as successful in weight loss.

The National Weight Control Registry (NWCR) tracks over ten thousand people who have been successful in losing at least 30 pounds and maintaining this weight loss for at least one year. Their research findings are that 98 percent of participants in the registry modified their food intake and 94 percent increased their physical activity (mainly walking).

Although there are a great variety of approaches taken by NWCR members to achieve successful weight loss, most report that their approach involved adhering to a low-calorie, low-fat diet and doing high levels of activity (about one hour of exercise per day). Moreover, most members eat breakfast every day, watch fewer than ten hours of television per week, and weigh themselves at least once per week. About half of them lost weight on their own, and the other half used some type of weight-loss program. In most scientific studies successful weight loss is accomplished only by changing the diet and by increasing physical activity. Doing one without the other limits the amount of weight lost and the length of time that weight loss is sustained. On an individual level it is quite possible to achieve successful weight loss, as over ten thousand Americans can attest. Moreover, losing as little as 10 percent of your body weight can significantly improve health and reduce disease risk.

You do not have to be overweight or obese to reap benefits from eating a healthier diet and increasing physical activity as both provide numerous benefits beyond weight loss and maintenance.

Diet: Evidence-Based Dietary Recommendations

The 2015 Dietary Guidelines for Americans offers specific, evidence-based recommendations for dietary changes aimed at keeping calorie intake in balance with physical activity, which is key for weight management. These recommendations include:

Follow a healthy eating pattern that accounts for all foods and beverages within an appropriate calorie level that includes:

- A variety of vegetables from all of the subgroups—dark green, red and orange, legumes (beans and peas), starchy, and other
- Fruits, especially whole fruits
- Grains, at least half of which are whole grains
- Fat-free or low-fat dairy, including milk, yogurt, cheese, and/or fortified soy beverages
- A variety of protein foods, including seafood, lean meats and poultry, eggs, legumes (beans and peas), and nuts, seeds, and soy products
- Oils

A healthy eating pattern limits:

- Saturated fats and trans fats
- Added sugars
- Sodium

Key quantitative recommendations are provided for several components of the diet that should be limited. These components are of particular public health concern in the United States, and the specified limits can help individuals achieve healthy eating patterns within calorie limits[5]:

- Consume less than 10 percent of calories per day from added sugars
- Consume less than 10 percent of calories per day from saturated fats
- Consume less than 2,300 milligrams (mg) per day of sodium

If alcohol is consumed, it should be consumed in moderation—up to one drink per day for women and up to two drinks per day for men—and only by adults of legal drinking age.

In the past, health was regarded merely as the absence of illness. However, a growing understanding of the complexity and potential of the human condition has prompted a new way of thinking about health. Today, we focus on the idea of wellness, which involves a great deal more than just not being sick. Wellness is a state of optimal well-being that enables an individual to maximize their potential. This concept includes a host of dimensions—physical, mental, emotional, social, environmental, and spiritual—which affect one's quality of life. Striving for wellness begins with an examination of dietary choices.

Dietary Food Trends

Hundreds of years ago, when food was less accessible and daily life required much more physical activity, people worried less about obesity and more about simply getting enough to eat. In today's industrialized nations, conveniences have solved some problems and introduced new ones, including the hand-in-hand obesity and diabetes epidemics.

Fad diets gained popularity as more North Americans struggled with excess pounds. However, new evidence-based approaches that emphasize more holistic measures are on the rise. These new dietary trends encourage those seeking to lose weight to eat healthy, whole foods first, while adopting a more active lifestyle. These sound practices put dietary choices in the context of wellness and a healthier approach to life.

Functional Foods

Many people seek out foods that provide the greatest health benefits. This trend is giving rise to the idea of functional foods, which not only help meet basic nutritional needs but also are reported to fight illness and aging. According to the Academy of Nutrition and Dietetics (AND), formerly known as the The American Dietetic Association, functional foods may reduce the risk of disease or promote optimal health. The AND recognizes four types of functional foods. They are: conventional foods, modified foods, medical foods, and special dietary use foods.

The first group, conventional foods, represents the simplest form of functional foods. They are whole foods that have not been modified. Examples include whole fruits and vegetables (which are abundant in phytochemicals and antioxidants), yogurt and kefir (which contain natural probiotic bacteria that can help maintain digestive system health), and moderate amounts of dark chocolate, made with 70% or more cacao (which contains antioxidants).

Modified foods have been fortified, enriched, or enhanced with additional nutrients or bioactive compounds. Foods are modified using biotechnology to improve their nutritional value and health attributes. Examples of modified foods include calcium-fortified orange juice, breads enriched with B vitamins, iodized salt, cereals fortified with vitamins and minerals, margarine enhanced with plant sterols, and energy drinks that have been enriched with herbs (ginseng or guarana) or amino acids (taurine). It is important to consider that the health claims of some modified foods may be debatable, or entirely fraudulent. Check with a health professional regarding the effects of modified foods on your health.

Medical foods are designed for enteric administration under the guidance of a medical professional. (During enteric administration, food is treated so that it goes through the stomach undigested. Instead, the food is broken down in the intestines only.) Medical foods are created to meet very specific nutritional requirements. Examples of medical foods include liquid formulas for people with kidney disease, liver disease, diabetes, or other health issues. Medical food is also given to comatose patients through a gastronomy tube because they cannot eat by mouth.

Special dietary use foods do not have to be administered under a doctor's care and can be found in a variety of stores. Similar to medical foods, they address special dietary needs and meet the nutritional requirements of certain health conditions. For example, a bottled oral supplement administered under medical supervision is a medical food, but it becomes a special dietary use food when it is sold to retail customers. Examples of special dietary use foods include gluten-free foods, lactose-free dairy products, and formulas and shakes that promote weight loss.

Popular Diets

The concept of functional foods represents initiatives aimed at addressing health problems. Certain diet plans take this concept one step further, by striving to prevent or treat specific conditions. For example, it is widely understood that people with diabetes need to follow a particular diet. Although some of these diet plans may be nutritionally sound, use caution because some diets may be fads or be so extreme that they actually cause health problems.

Before experimenting with a diet, discuss your plans with your doctor or a registered dietitian. Table 3 lists the pros and cons of the more popular diets. Some fall under the category of fad diets, while others are backed by scientific evidence. Those that fall into the latter category provide a good foundation to build a solid regimen for optimal health.

Table 19.3.1 The Pros and Cons of Seven Popular Diets.

Diet	Pros	Cons
DASH Diet	Recommended by the National Heart, Lung, and Blood Institute, the American Heart Association, and many physicians Helps to lower blood pressure and cholesterol Reduces risk of heart disease and stroke Reduces risk of certain cancers Reduces diabetes risk	There are very few negative factors associated with the DASH diet Risk for hyponatremia
Gluten-Free Diet	Reduces the symptoms of gluten intolerance, such as chronic diarrhea, cramping, constipation, and bloating Promotes healing of the small intestines for people with celiac disease, preventing malnutrition May be beneficial for other autoimmune diseases, such as Parkinson's disease, rheumatoid arthritis, and multiple sclerosis	Risk of folate, iron, thiamin, riboflavin, niacin, and vitamin B6 deficiencies Special gluten-free products can be hard to find and expensive Requires constant vigilance and careful food label reading, since gluten is found in many products
Low-Carb Diet	Restricts refined carbohydrates, such as white flour and white sugar May temporarily improve blood sugar or blood cholesterol levels	Not entirely evidence-based Results in higher fat and protein consumption Does not meet the RDA for carbohydrates to provide glucose to the brain
Macrobiotic Diet	Low in saturated fats and high in fiber Emphasizes whole foods and de-emphasizes processed foods Rich in phytoestrogens, which may reduce the risk of estrogen-related cancers	Not entirely evidence-based Lacks certain vitamins and minerals; supplements are often required Can result in a very low caloric intake Lack of energy may result from inadequate protein

Mediterranean Diet	A reduced risk of cardiovascular disease and mortality A lower risk of cancer De-emphasizes processed foods and emphasizes whole foods and healthy fats Lower sodium intake, due to fewer processed foods Emphasis on monosaturated fats leads to lower cholesterol Highlighting fruits and vegetables raises consumption of antioxidants	Does not specify daily serving amounts Potential for high fat and high calorie intake as nuts and oils are calorie-dense foods Drinking one to two glasses of wine per day may not be healthy for those with certain conditions
Raw Food Diet	Emphasizes whole foods Focuses on nutritionally-rich foods	Not entirely evidence-based Very restrictive and limits protein and healthy fat intake Could encourage the development of foodborne illness Extremely difficult to follow High in fiber which can cause essential nutrient deficiencies
Vegetarianism and Veganism	May reduce some chronic diseases such as cancer, heart disease, and Type 2 diabetes May help with weight reduction and weight maintenance	Guidelines regarding fat and nutrient consumption must be followed Higher risk for nutrient deficiencies such as protein, iron, zinc, omega-3, vitamin B12 Consumption of a high fiber diet interferes with mineral and nutrient bioavailability Vegetarian and vegan protein sources are lower quality with majority missing at least one essential amino acids

Exercise for Weight Loss: Evidence-Based Physical Activity Recommendations

The other part of the energy balance equation is physical activity. The Dietary Guidelines are complemented by the 2008 Physical Activity Guidelines for Americans issued by the Department of Health and Human Services (HHS) in an effort to provide evidence-based guidelines for appropriate physical activity levels. The 2008 Physical Activity Guidelines provide guidance to Americans aged six and older about how to improve health and reduce chronic disease risk through physical activity. Increased physical activity has been found in scientific studies to lower the risk of heart disease, stroke, high blood pressure, Type 2 diabetes, colon, breast, and lung cancer, falls and fractures, depression, and early death. Increased physical activity not only reduces disease risk, but also improves overall health by increasing cardiovascular and muscular fitness, increasing bone density and strength, improving cognitive function, and assisting in weight loss and weight maintenance.[6]

The key guidelines for adults are the following :

- Even small amounts of activity are beneficial to your health.

- More substantial health benefits are obtained by doing at least two hours and thirty minutes per week of moderate-intensity, or one hour and fifteen minutes per week of vigorous-intensity aerobic physical activity, or an equivalent combination thereof. Aerobic activity has better benefits if performed for at least ten minutes at a time, spread throughout the week.

- More extensive health benefits occur when moderate-intensity physical activity is increased to five hours per week, or to two hours and thirty minutes of vigorous-intensity aerobic physical activity, or a combination thereof. Additional health benefits are gained by going beyond these recommended amounts of physical activity.

- Muscle-strengthening activities at moderate or high intensity involving all major muscle groups two or more days per week provides additional health benefits to aerobic exercise.

The 2008 Physical Activity Guidelines broadly classify moderate physical activities as those when "you can talk while you do them, but can't sing" and vigorous activities as those when "you can only say a few words without stopping to catch your breath." Examples of moderate and vigorous physical activities are given below.

Table 19.3.2: Moderate and Vigorous Physical Activities

Moderate Activities	Vigorous Activities
Ballroom/line dancing	Aerobic dance
Biking on level ground	Biking (more than 10 miles per hour)
Canoeing	Heavy gardening (digging, hoeing)
Gardening	Hiking uphill
Baseball, softball, volleyball	Fast dancing

Summary

- The 2015 Dietary Guidelines for Americans offers specific, evidence-based recommendations for dietary changes aimed at keeping calorie intake in balance with physical activity, which is key for weight management.

- A healthy eating pattern limits saturated fats and trans fats, added sugars, and sodium

What should you weigh? This has been a difficult question to answer because humans come in so many different sizes and shapes. We do know that carrying too much fat is not good for one's health. Thus fat is a huge factor in determining fitness. Ideal body weight (IBW) has been used to determine one's desirable weight. To standardize the "ideal" body weight and relate it to health, scientists have devised mathematical formulas to better define a healthy weight. These mathematically derived measurements are used by health professionals to correlate disease risk with populations of people and at the individual level. A clinician will take two measurements, one of weight and one of fat mass, in order to diagnose obesity. Some measurements of weight and body fat that do not require using technical equipment can easily be calculated and help provide an individual with information on weight, fat mass, and distribution, and their relative risk of some chronic diseases.

Ideal Body Weight

The "ideal" healthy body weight for a particular person is dependent on many things, such as frame size, sex, muscle mass, bone density, age, and height. The perception of the "ideal" body weight is additionally dependent on cultural factors and the mainstream societal advertisement of beauty.

Body Mass Index: How to Measure It and Its Limitations

Body mass index (BMI) is calculated using height and weight measurements and is more predictive of body fatness than weight alone. BMI measurements are used to indicate whether an individual may be underweight (with a BMI less than 18.5), overweight (with a BMI over 25), or obese (with a BMI over 30). High BMI measurements can be warning signs of health hazards ahead, such as cardiovascular disease, Type 2 diabetes, and other chronic diseases. BMI-associated health risks vary by race. Asians face greater health risks for the same BMI than Caucasians, and Caucasians face greater health risks for the same BMI than African Americans.

Very high AND very low BMI's appear to increase a person's risk of dying. If you look at a graph of BMI (Figure 5 as it relates to your risk of dying, it has a "J-shaped Curve" or a "U-shaped Curve" because being too low and/or too high both raise your risk of mortality. Instead, you'd like to be in the middle range of the BMI which is what they use for "Normal weight".

Figure 19.4: *Relationship between body mass index and mortality.*
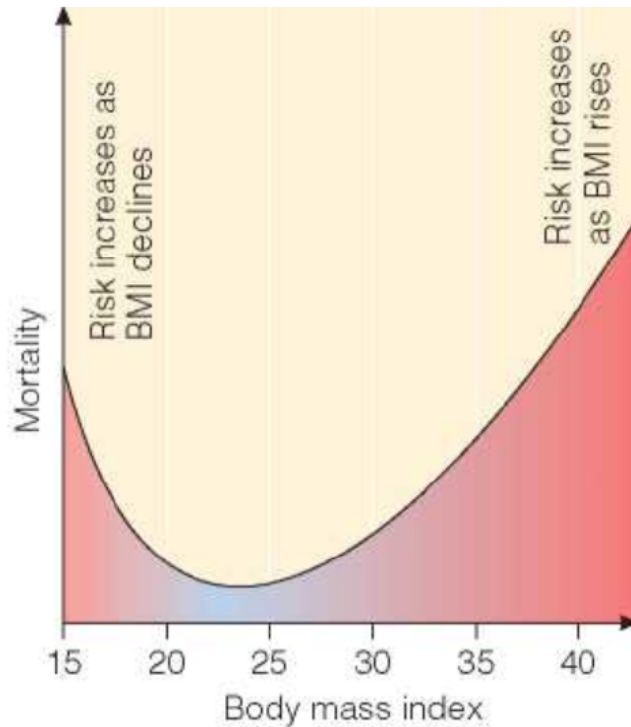
Calculating BMI

BMI is calculated the same way for both adults and children. The calculation is based on the following formulas:

Measurement Units	Formula and Calculation
Kilograms and meters/centimeters	Formula: weight (kg) / [height (m)]² With the metric system, the formula for BMI is weight in kilograms divided by height in meters squared. Since height is commonly measured in centimeters, divide height in centimeters by 100 to obtain height in meters. Example: Weight = 68 kg, Height = 165 cm (1.65 m) Calculation: 68 ÷ (1.65)² = 24.98
Pounds and Inches	Formula: weight (lb) / [height (in)]² x 703 Calculate BMI by dividing weight in pounds (lbs) by height in inches (in) squared and multiplying by a conversion factor of 703. Example: Weight = 150 lbs, Height = 5'5" (65") Calculation: [150 ÷ (65)²] x 703 = 24.96

BMI Categories

Categories	BMI
Underweight	< 18.5
Normal weight	18.5–24.9
Overweight	25–29.9
Obese	30.0-34.9
Severe	35-40
Source: National Heart, Lung, and Blood Institute. Accessed November 4, 2012. http://www.nhlbi.nih.gov.	

6. CAFFEINE AND OTHER DRUGS

Thermogenic products

A thermogenic is a broad term for any supplement that the manufacturer claims will cause thermogenesis, resulting in increased body temperature, increased metabolic rate, and consequently an increased rate in the burning of body fat and weight loss. Until 2004 almost every product found in this supplement category comprised the "ECA stack": ephedrine, caffeine, and aspirin. However, on February 6, 2004, the Food and Drug Administration (FDA) banned the sale of ephedra and its alkaloid, ephedrine, for use in weight loss formulas. Several manufacturers replaced the ephedra component of the "ECA" stack with bitter orange or citrus aurantium (containing synephrine) instead of the ephedrine.

Caffeine

Caffeine is a chemical called xanthine found in the seeds, leaves, and fruit of many plants, where it acts as a natural pesticide. It is the most widely consumed psychoactive substance and is such an important part of many people's lives that they might not even think of it as a drug. Up to 90 percent of adults around the world use it on a daily basis. According to both the FDA and the American Medical Association, the moderate use of caffeine is "generally recognized as safe." It is considered a legal psychoactive drug and, for the most part, is completely unregulated.

Typical Doses and Dietary Sources

What is a "moderate intake" of caffeine? Caffeine intakes are described in the following manner:

- **Low–moderate intake.** 130–300 milligrams per day
- **Moderate intake.** 200–300 milligrams per day

- **High intake.** 400 or more milligrams per day

The average caffeine consumption for American adults is considered moderate at 280 milligrams per day, although it is not uncommon for people to consume up to 600 milligrams per day. This works out to almost 4 ½ cups of coffee per day. The bitter taste of caffeine is palatable for many and coffee is the most readily available source of it, accounting for 70 percent of daily caffeine consumption. The second readily available source of caffeine is soft drinks, delivering 16 percent of daily caffeine. (In this case, the bitter caffeine taste is usually masked by a large amount of added sugar.) Tea is the third common source of caffeine, at 12 percent.

Just how much caffeine is there in a cup of coffee? It varies. The caffeine content of an average cup of coffee can range from 102 to 200 milligrams, and the range of tea is 40 to 120 milligrams. Table 15.6.2 provides useful information on the levels of caffeine found in common beverages. When estimating your total caffeine consumption remember its not only in beverages but also some foods and medicine.

Table 15.6.1: Caffeine Content in Various Beverages and Foods

Beverage/Food	Milligrams
Starbuck's Grande Coffee (16 oz.)	380
Plain brewed coffee (8 oz.)	102–200
Espresso (1 oz.)	30–90
Plain, decaffeinated coffee (8 oz.)	3–12
Tea, brewed (8 oz.)	40–120
Green tea (8 oz.)	25–40
Coca-Cola Classic (12 oz.)	35
Dr. Pepper (12 oz.)	44
Jolt Cola (12 oz.)	72

Mountain Dew (12 oz.)	54
Mountain Dew, MDX (12 oz.)	71
Pepsi-Cola (12 oz.)	38
Red Bull (8.5 oz.)	80
Full Throttle (16 oz.)	144
Monster Energy (16 oz.)	160
Spike Shooter (8.4 oz.)	300

Source: MedicineNet.com. "Caffeine." Accessed October 2, 2011. http://www.medicinenet.com/caffeine/article.htm.

Health Benefits of Caffeine

The most renowned effects of caffeine on the body are increased alertness and delay of fatigue and sleep. How does caffeine stimulate the brain? Watch "Video 15.6.1" to see a graphic account of a brain on caffeine. Caffeine is chemically similar to a chemical in our brains (adenosine). Caffeine interacts with adenosine's specific protein receptor. It blocks the actions of the adenosine, and affects the levels of signaling molecules in the brain, leading to an increase in energy metabolism. At the molecular level, caffeine stimulates the brain, increasing alertness and causing a delay of fatigue and sleep. At high doses caffeine stimulates the motor cortex of the brain and interferes with the sleep-wake cycle, causing side effects such as shakiness, anxiety, and insomnia. People's sensitivity to the adverse effects of caffeine varies and some people develop side effects at much lower doses. The many effects caffeine has on the brain do not diminish with habitual drinking of caffeinated beverages.

Scientific studies suggest caffeine can improve endurance capacity by increasing energy available during exercise. The effect may only work in non-caffeine drinkers and it only takes 1-3 days for the body to become "caffeine-naive."

Bicarbonate

The term bicarbonate refers to sodium bicarbonate a salt that disassociates in water to form sodium and bicarbonate ions. Remember, the small intestine produces and uses bicarbonate to neutralize the acid in your stomach. Baking soda is sodium bicarbonate. There is limited scientific evidence that bicarbonate can improve athletic performance. The mechanism of action is through increased buffering of the blood which may be beneficial for high-intensity exercise.

Growth Hormone

Growth hormone (GH) is a hormone our body produces. In sports, athletes use this the abbreviations GH or HGH (human growth hormone) to refer to growth hormone. GH is a prescription medication so possession and use of it without a prescription is illegal. There is limited scientific evidence that it will increase muscle mass and improve athletic performance. Adverse effects of inappropriately using GH include weakened heart wall and premature death.

Thermogenic products

A thermogenic is a broad term for any supplement that the manufacturer claims will cause thermogenesis, resulting in increased body temperature, increased metabolic rate, and consequently an increased rate in the burning of body fat and weight loss. Until 2004 almost every product found in this supplement category comprised the "ECA stack": ephedrine, caffeine and aspirin. However, on February 6, 2004 the Food and Drug Administration (FDA) banned the sale of ephedra and its alkaloid, ephedrine, for use in weight loss formulas. Several manufacturers replaced the ephedra component of the "ECA" stack with bitter orange or citrus aurantium (containing synephrine) instead of the ephedrine.

Controversies of Fitness Supplements

Mislabeling: According to University of Helsinki food safety professor Marina Heinonen, more than 90% of dietary supplement health claims are incorrect. While many of the claims are based on scientifically based physiological or biochemical processes, their use in bodybuilding parlance is often heavily colored by bodybuilding lore and industry marketing and as such may deviate considerably from traditional scientific usages of the terms. In addition, ingredients listed have been found at times to be different from the contents. In 2015, Consumer Reports reported unsafe levels of arsenic, cadmium, lead and mercury in several of the protein powders that were tested. Other studies in 2013 showed that one-third of the supplements tested contained unlisted steroids. In 2015 a CBC investigative report found that protein spiking (the addition of amino acid filler to manipulate analysis) was not uncommon, however many of the companies involved challenged these claims.

Health problems: The US FDA reports 50,000 health problems a year due to dietary supplements and these often involve bodybuilding supplements. For example, the "natural" best-seller Craze, 2012's "New Supplement of the Year" by bodybuilding.com, sold in Walmart, Amazon etc., was found to contain undisclosed amphetamine-like compounds. Also other products by Matt Cahill have contained dangerous substances causing blindness or liver damages, and experts say that Cahill is emblematic for the whole industry.

Liver damage: The incidence of liver damage from dietary supplements has tripled in a decade, the majority of these involved bodybuilding supplements. This resulted in liver transplants and, in some cases, death to the patient. Some have argued that the liver damage is more often caused by prescription drugs rather than supplements.

Lack of effectiveness: In addition to being potentially harmful, some have argued that there is little evidence to indicate any benefit to using bodybuilding supplements. For example, according to the IOC, no consensus had been reached in determining whether an individual in exercise training benefits from protein and amino acid supplements. "In view of the lack of compelling evidence to the contrary, no additional dietary protein is suggested for healthy adults undertaking resistance or endurance exercise".

Anabolic Steroids

Anabolic steroids are synthetic, or human-made, variations of the male sex hormone testosterone. The proper term for these compounds is anabolic-androgenic steroids. "Anabolic" refers to muscle building, and "androgenic" refers to increased male sex characteristics. Some common names for anabolic steroids are Gear, Juice, Roids, and Stackers.

348

Health care providers can prescribe steroids to treat hormonal issues, such as delayed puberty. Steroids can also treat diseases that cause muscle loss, such as cancer and AIDS. But some athletes and bodybuilders misuse these drugs in an attempt to boost performance or improve their physical appearance.

The majority of people who misuse steroids are male weightlifters in their 20s or 30s. Anabolic steroid misuse is much less common in women. It is difficult to measure steroid misuse in the United States because many national surveys do not measure it. However, use among teens is generally minimal. The 2016 NIDA-funded Monitoring the Future study has shown that past-year misuse of steroids has declined among 8th and 10th graders in recent years, while holding steady for 12th graders.

People who misuse anabolic steroids usually take them orally, inject them into muscles, or apply them to the skin as a gel or cream. These doses may be 10 to 100 times higher than doses prescribed to treat medical conditions.

Commons patterns for misusing steroids include:

- cycling—taking multiple doses for a period of time, stopping for a time, and then restarting
- stacking—combining two or more different steroids and mixing oral and/or injectable types
- pyramiding—slowly increasing the dose or frequency of steroid misuse, reaching a peak amount, and then gradually tapering off to zero
- plateauing—alternating, overlapping, or substituting with another steroid to avoid developing a tolerance

There is no scientific evidence that any of these practices reduce the harmful medical consequences of these drugs.

How Anabolic Steroids Work

Anabolic steroids work differently from other drugs of abuse; they do not have the same short-term effects on the brain. The most important difference is that steroids do not directly activate the reward system to cause a "high"; they also do not trigger rapid increases in the brain chemical dopamine, which reinforces most other types of drug taking behavior. Misuse of anabolic steroids might lead to negative mental effects, such as: paranoid (extreme, unreasonable) jealousy, extreme irritability and aggression ("roid rage"), delusions—false beliefs or ideas, impaired judgment, and mania. Aside from mental effects, steroid use commonly causes severe acne. It also causes the body to swell, especially in the hands and feet.

Anabolic steroid misuse might lead to serious, even permanent, health problems such as kidney problems or failure, liver damage and tumors, enlarged heart, high blood pressure, and changes in blood cholesterol, all of which increase the risk of stroke and heart attack, even in young people, and increased risk of blood clots. Several other effects are gender- and age-specific:

- **In men**: shrinking testicles, decreased sperm count, baldness, development of breasts, increased risk for prostate cancer
- **In women**: growth of facial hair or excess body hair, decreased breast size, male-pattern baldness, changes in or stop in the menstrual cycle, enlarged clitoris, deepened voice
- **In teens**: stunted growth (when high hormone levels from steroids signal to the body to stop bone growth too early) and stunted height (if teens use steroids before their growth spurt)

Some of these physical changes, such as shrinking sex organs in men, can add to mental side effects such as mood disorders.

Anabolic Steroids Addiction

Even though anabolic steroids do not cause the same high as other drugs, they can lead to a substance use disorder. A substance use disorder occurs when a person continues to misuse steroids, even though there are serious consequences for doing so. The most severe form of a substance use disorder is addiction. People might continue to misuse steroids despite physical problems, high costs to buy the drugs, and negative effects on their relationships. These behaviors reflect steroids' addictive potential.

Research has further found that some steroid users turn to other drugs, such as opioids, to reduce sleep problems and irritability caused by steroids. People who misuse steroids might experience withdrawal symptoms when they stop use, including:fatigue, restlessness, loss of appetite, sleep problems, decreased sex drive and steroid cravings.

One of the more serious withdrawal symptoms is depression, which can sometimes lead to suicide attempts. Some people seeking treatment for anabolic steroid addiction have found a combination of behavioral therapy and medications to be helpful. In certain cases of addiction, patients have taken medicines to help treat symptoms of withdrawal. For example, health care providers have prescribed antidepressants to treat depression and pain medicines for headaches and muscle and joint pain. Other medicines have been used to help restore the patient's hormonal system.

Summary

- Anabolic steroids are synthetic variations of the male sex hormone testosterone. Health care providers can prescribe steroids to treat various medical conditions. But some athletes and bodybuilders misuse these drugs to boost performance or improve their physical appearance.

- People who abuse anabolic steroids usually take them orally, inject them into the muscles, or apply them to the skin with a cream or gel.

- People misuse steroids in a variety of doses and schedules. Misuse of anabolic steroids might lead to short-term effects, including paranoid jealousy, extreme irritability and aggression, delusions, impaired judgment, and mania. Continued steroid misuse can act on some of the same brain pathways and chemicals that are affected by other drugs, including dopamine, serotonin, and opioid systems.

- Anabolic steroid misuse might lead to serious long-term, even permanent, health problems. Several other effects are gender- and age-specific.

- Even though anabolic steroids do not cause the same high as other drugs, they can lead to addiction. Some people seeking treatment for anabolic steroid addiction have found behavioral therapy and medications to be helpful. Medicines can help treat symptoms of withdrawal in some cases.

Prohormone

Prohormones are precursors to hormones and are most typically sold to bodybuilders as a precursor to the natural hormone testosterone. This conversion requires naturally occurring enzymes in the body. Side effects are not uncommon, as prohormones can also convert further into DHT and estrogen. To deal with this, many supplements also have aromatase inhibitors and DHT blockers such as chrysin and 4-androstene-3,6,17-trione. To date, most prohormone products have not been thoroughly studied, and the health effects of prolonged use are unknown. Although initially available over the counter, their purchase was made illegal without a prescription in the US in 2004, and they hold similar status in many other countries. They remain legal, however, in the United Kingdom and the wider European Union. Their use is prohibited by most sporting bodies.

Drugs, Athletic Performance, and Drug Screening

The use of performance-enhancing tactics or more formally known as PEDs, and more broadly, the use of any external device to nefariously influence the outcome of a sporting event has been a part of the Olympics since its inception in Ancient Greece. One speculation as to why men were required to compete naked was to prevent the use of extra accoutrements and to keep women from competing in events specifically designed for men.[1] Athletes were also known to drink "magic" potions and eat exotic meats in the hopes of giving them an athletic edge on their competition.[2] If they were caught cheating, their likenesses were often engraved into stone and placed in a pathway that led to the Olympic stadium.[1] In the modern Olympic era, chemically enhancing one's performance has evolved into a sophisticated science, but in the early years of the Modern Olympic movement the use of performance-enhancing drugs was almost as crude as its ancient predecessors. For example, the winner of the marathon at the 1904 Games, Thomas Hicks, was given strychnine and brandy by his coach, even during the race.[3]

During the early 20th century, many Olympic athletes discovered ways to improve their athletic abilities by boosting testosterone. As their methods became more extreme, it became increasingly evident that the use of performance-enhancing drugs was not only a threat to the integrity of sport but could also have potentially fatal side effects on the athlete. The only Olympic death linked to athletic drug use occurred at the Rome Games of 1960. During the cycling road race, Danish cyclist Knud Enemark Jensen fell from his bicycle and later died. A coroner's inquiry found that he was under the influence of amphetamine, which had caused him to lose consciousness during the race.[4] Jensen's death exposed to the world how endemic drug use was among elite athletes.[5] By the mid–1960s, sports federations were starting to ban the use of performance-enhancing drugs, and the IOC followed suit in 1967. In 1967 the IOC banned the use of performance-enhancing drugs, instituted a Medical Commission, and created a list of banned substances. Mandatory testing began at the 1968 Summer Olympic Games. In a few cases the IOC has reversed earlier rulings that stripped athletes of medals.

The first Olympic athlete to test positive for the use of performance-enhancing drugs was Hans-Gunnar Liljenwall, a Swedish pentathlete at the 1968 Summer Olympics, who lost his bronze medal for alcohol use, 'two beers to steady his nerves'. Liljenwall was the only athlete to test positive for a banned substance at the 1968 Olympics, as the technology and testing techniques improved, the number of athletes discovered to be chemically enhancing their performance increased as well.

Exercise and the Brain

The **neurobiological effects of physical exercise** are numerous and involve a wide range of interrelated effects on brain structure, brain function, and cognition.[1][2][3][4]A large body of research in humans has demonstrated that consistent aerobic exercise (e.g., 30 minutes every day) induces persistent improvements in certain cognitive functions, healthy alterations in gene expression in the brain, and beneficial forms of neuroplasticity and behavioral plasticity; some of these long-term effects include: increased neuron growth, increased neurological activity (e.g., c-Fos and BDNF signaling), improved stress coping, enhanced cognitive control of behavior, improved declarative, spatial, and working memory, and structural and functional improvements in brain structures and pathways associated with cognitive control and memory.[1][2][3][4][5][6][7][8][9][10] The effects of exercise on cognition have important implications for improving academic performance in children and college students, improving adult productivity, preserving cognitive function in old age, preventing or treating certain neurological disorders, and improving overall quality of life.[1][11][12]

In healthy adults, aerobic exercise has been shown to induce transient effects on cognition after a single exercise session and persistent effects on cognition following regular exercise over the course of several months.[1][10][13] People who regularly perform aerobic exercise (e.g., running, jogging, brisk walking, swimming, and cycling) have greater scores on neuropsychological function and performance tests that measure certain cognitive functions, such as attentional control, inhibitory control, cognitive flexibility, working memory updating and capacity, declarative memory, spatial memory, and information processing speed.[1][5][7][9][10][13] The transient effects of exercise on cognition include improvements in most executive functions (e.g., attention, working memory, cognitive flexibility, inhibitory control, problem solving, and decision making) and information processing speed for a period of up to 2 hours after exercising.[13]

Aerobic exercise induces short- and long-term effects on mood and emotional states by promoting positive affect, inhibiting negative affect, and decreasing the biological response to acute psychological stress.[13] Over the short-term, aerobic exercise functions as both an antidepressant and euphoriant,[14][15][16][17] whereas consistent exercise produces general improvements in mood and self-esteem.

Regular aerobic exercise improves symptoms associated with a variety of central nervous system disorders and may be used as an adjunct therapy for these disorders. There is clear evidence of exercise treatment efficacy for major depressive disorder and attention deficit hyperactivity disorder.[11][16][20][21][22][23] The American Academy of Neurology's clinical practice guideline for mild cognitive impairment indicates that clinicians should recommend regular exercise (two times per week) to individuals who have been diagnosed with this condition.[24] Reviews of clinical evidence also support the use of exercise as an adjunct therapy for certain neurodegenerative disorders, particularly Alzheimer's disease and Parkinson's disease. Regular exercise is also associated with a lower risk of developing neurodegenerative disorders.[28][31] A large body of preclinical evidence and emerging clinical evidence supports the use of exercise as an adjunct therapy for the treatment and prevention of drug addictions. Regular exercise has also been proposed as an adjunct therapy for brain cancers.[37]

CHAPTER 12: PHARMACEUTICALS

1. CHEMOTHERAPY

A very broad definition of a drug would include "all chemicals other than food that affects living processes." If the effect helps the body, the drug is a medicine. However, if a drug causes a harmful effect on the body, the drug is a poison. The same chemical can be a medicine and a poison depending on conditions of use and the person using it. Another definition would be "medicinal agents used for diagnosis, prevention, treatment of symptoms, and cure of diseases." Contraceptives would be outside of this definition unless the pregnancy was considered a disease.

Image taken from: https://torange.biz/fx/drugs-colored...ct-very-124521

Disease Classification

A disease is a condition of impaired health resulting from a disturbance in the structure or function of the body. Diseases may be classified into the following major categories:

1. Infections caused by viruses, rickettsia, bacteria, fungi, protozoa, and worms

2. Allergic diseases caused by antigens and foreign substances

3. Metabolic disorders caused by defects in the body's ability to carry out normal reactions - these may be hereditary, deficiency, and congenital defects

4. Cancer

5. Toxic diseases caused by poisons

6. Psychosomatic and mental diseases

Chemotherapy, broadly defined, means the treatment of any disease by chemicals including infectious and non-infectious diseases. The original definition applied only to drugs which were used in the treatment of infectious diseases. The proper term for the treatment of non-infectious diseases is pharmacodynamics.

Drug Classification

Drugs can be classified according to various criteria including chemical structure or pharmacological action. The preferred classification is the latter one which may be divided into main groups as follows:

1. Chemotherapeutic agents - used to cure infectious diseases and cancer. (Sulfa drugs, Antibiotics)

2. Pharmacodynamic agents - used in non-infectious diseases (Cholinergic, Adrenergic, Hallucinogenic, Sedatives)

3. Miscellaneous agents (Narcotic Analgesics, Local Anesthetics)

Drug Names

Drugs have three or more names including a: chemical name, brand or trade name, and generic or common name. The chemical name is assigned according to rules of nomenclature of chemical compounds. The brand name is always capitalized and is selected by the manufacturer. The generic name refers to a common established name irrespective of its manufacturer.

In most cases, a drug bearing a generic name is equivalent to the same drug with a brand name. However, this equivalency is not always true. Although drugs are chemically equivalent, different manufacturing processes may cause differences in pharmacological action. Several differences may be crystal size or form, isomers, crystal hydration, purity-(type and number of impurities), vehicles, binders, coatings, dissolution rate, and storage stability.

Mode of Drug Action

It is important to distinguish between actions of drugs and their effects. Actions of drugs are the biochemical physiological mechanisms by which the chemical produces a response in living organisms. The effect is the observable consequence of a drug action. For example, the action of penicillin is to interfere with cell wall synthesis in bacteria and the effect is the death of the bacteria.

One major problem of pharmacology is that no drug produces a single effect. The primary effect is the desired therapeutic effect. Secondary effects are all other effects beside the desired effect which may be either beneficial or harmful. **Drugs are chosen to exploit differences between normal metabolic processes and any abnormalities which may be present.** Since the differences may not be very great, drugs may be nonspecific in action and alter normal functions as well as the undesirable ones. This leads to undesirable side effects.

The biological effects observed after a drug has been administered are the result of an interaction between that chemical and some part of the organism. Mechanisms of drug action can be viewed from different perspectives, namely, the site of action and the general nature of the drug-cell interaction.

Killing Foreign Organisms

Chemotherapeutic agents act by killing or weakening foreign organisms such as bacteria, worms, viruses. The main principle of action is selective toxicity, i.e. the drug must be more toxic to the parasite than to the host.

Stimulation and Depression

Drugs act by stimulating or depressing normal physiological functions. Stimulation increases the rate of activity while depression reduces the rate of activity.

Sites of Drug Action

Enzyme Inhibition

Drugs act within the cell by modifying normal biochemical reactions. Enzyme inhibition may be reversible or non-reversible; competitive or non-competitive. Antimetabolites may be used which mimic natural metabolites. Gene functions may be suppressed.

Drug-Receptor Interaction

Drugs act on the cell membrane by physical and/or chemical interactions. This is usually through specific drug receptor sites known to be located on the membrane. A receptor is the specific chemical constituents of the cell with which a drug interacts to produce its pharmacological effects. Some receptor sites have been identified with specific parts of proteins and nucleic acids. In most cases, the chemical nature of the receptor site remains obscure.

Non-specific Interactions

Drugs act exclusively by physical means outside of cells. These sites include external surfaces of skin and gastrointestinal tract. Drugs also act outside of cell membranes by chemical interactions. Neutralization of excess stomach acid by antacids is a good example.
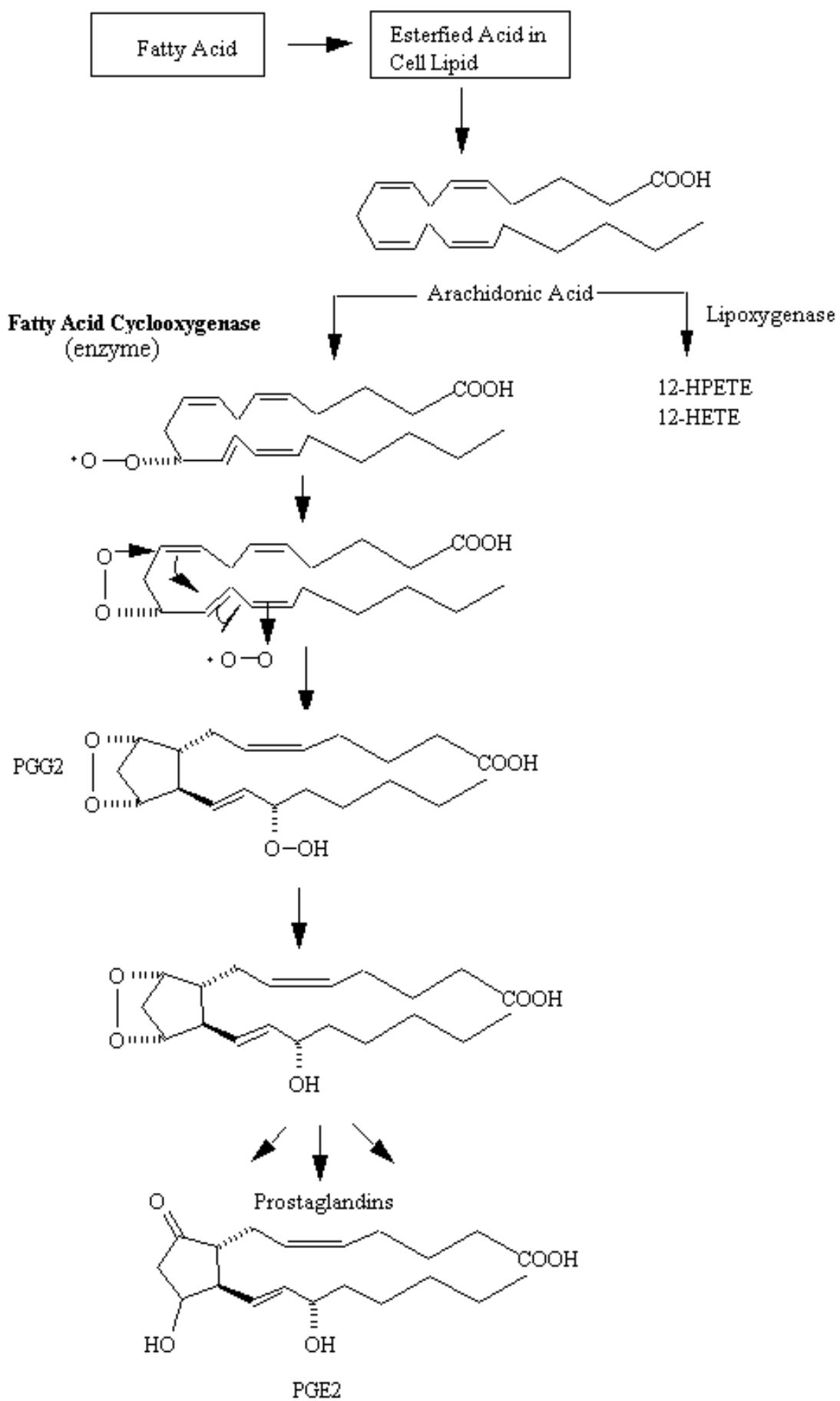
2. ANALGESICS

Aspirin-like Drugs

The anti-inflammatory, analgesic, and antipyretic drugs are a heterogeneous group of compounds, often chemically unrelated (although most of them are organic acids), which nevertheless share certain therapeutic actions and side effects. The prototype is aspirin; hence these compounds are often referred to as aspirin-like drugs. All aspirin-like drugs are antipyretic, analgesic, and anti-inflammatory, but there are important differences in their activities. For example, acetaminophen is antipyretic and analgesic but is only weakly anti-inflammatory. The reason for the differences are not clear; variations in the sensitivity of enzymes in the target tissues may be important.

When employed as analgesics, these drugs are usually effective only against pain of low-to-moderate intensity, particularly that associated with inflammation. Aspirin drugs do not change the perception of sensory modalities other than pain. The type of pain is important; chronic postoperative pain or pain arising from inflammation is particularly well controlled by aspirin-like drugs, whereas pain arising from the hollow viscera is usually not relieved.

As antipyretics, aspirin-like drugs reduce the body temperature in feverish states. Although all such drugs are antipyretics and analgesics, some are not suitable for either routine or prolonged use because of toxicity; phenylbutaxone is an example. This class of drugs finds its chief clinical application as anti inflammatory agents in the treatment of musculoskelatal disorders, such as rheumatoid arthritis, osteoarthritis, and ankylosing spondylitis. In general, aspirin-like drugs provide only symptomatic relief from the pain and inflammation associated with the disease and do not arrest the progression of pathological injury.

Chemistry of Action

There has been substantial progress in elucidating the mechanism of action of aspirin-like drugs, and it is now possible to understand why such heterogeneous agents have the same basic therapeutic activities and often the same side effects. Indeed, their therapeutic activity appears to depend to a large extent upon the inhibition of a defined biochemical pathways responsible for the biosynthesis of prostaglandins (see figure below) and related autacoids.

Fatty Acid → Esterfied Acid in Cell Lipid

Arachidonic Acid

Fatty Acid Cyclooxygenase (enzyme)

Lipoxygenase

COOH

12-HPETE
12-HETE

PGG2

O—OH

OH

Prostaglandins

O

HO   OH

PGE2

356

Aspirin-like drugs inhibit the conversion of arachidonic acid to the unstable endoperoxide intermediate, PGG2, which is catalyzed by the cyclooxygenase. Individual agents have differing modes of inhibitory activity on the cyclooxygenase. Aspirin itself acetylates a serine at the active site of the enzyme. Platelets are especially susceptible to this action because (unlike most other cells) they are incapable of regenerating the enzyme, presumably because they have little or no capacity for protein biosynthesis. In practical terms this means that a single dose of aspirin will inhibit the platelet cyclooxygenase for the life of the platelet (8 to 10 days); in man a dose as small as 40 mg per day is sufficient to produce this effect. In contrast to aspirin, salicylic acid has no acetylating capacity and is almost inactive against cyclooxygenase in vitro. Nevertheless, it is as active as aspirin in reducing the synthesis of prostaglandins in vivo. The basis of this action and, thus, of the anti-inflammatory effect of salicylic acid is not clearly understood. Since aspirin is rapidly hydrolyzed to salicylic acid in vivo (half-life in human plasma, approximately 15 minutes), the acetylated and nonacetylated species probably act as pharmacologically distinct entities.

Most of the other common aspirin-like drugs are irreversible inhibitors of the cyclooxygenase, although there are some exceptions. For indomethacin, the mode of inhibition is particularly complex and probably involves a site on the enzyme different from that which is acetylated by aspirin.

Pain

Prostaglandins are associated particularly with the development of pain that accompanies injury or inflammation. Large doses of PGE2 or PGF2a , given to women by injection to induce abortion, cause intense local pain. Prostaglandins can also cause headache and vascular pain when infused intravenously in man. While the doses of prostaglandins required to elicit pain are high in comparison with the concentrations expected in vivo, induction of hyperalgesia occurs when minute amounts of PGE1 are given intradermally to man. Furthermore, in experiments in man where separate infusions of PGE1, bradykinin, or histamine caused no pain, marked pain was experienced when PGE1 was added to bradykinin or histamine. When PGE1 was infused with histamine, itching was also noted.

Fever

The hypothalamus regulates the set point at which body temperature is maintained. In fever, this set point is elevated, and aspirin-like drugs promote its return to normal. These drugs do not influence body temperature when it is elevated by such factors as exercise or increases in the surrounding temperature.

Fever may be a result of infection, tissue damage, inflammation, graft rejection, malignancy, or other disease states. A multitude of microorganisms can cause fever. There is evidence that bacterial endotoxins act by stimulating the biosynthesis and release by neutrophils and other cells of an endogenous pyrogen, a protein with a molecular weight of 10,000 to 20,000. The current view is that the endogenous pyrogen passes from the general circulation into the central nervous system, where it acts upon discrete sites within the brain, especially the preoptic hypothalamic area. There is evidence that the resultant elevation of body temperature is mediated by the release of prostaglandins and that aspirin-like drugs suppress the effects of endogenous pyrogen by inhibiting the synthesis of these substances. The evidence includes the ability of prostaglandins, especially PGE2, to produce fever when infused into the cerebral ventricles or when infected into the hypothalamus. Fever is a frequent side effect of prostaglandins when they are administered to a women as abortifacients. Moreover some studies have demonstrated an increase in prostaglandin-like substances in the cerebrospinal fluid when endogenous pyrogen is injected intravenously. The fever produced by the administration of pyrogen, but not that by prostaglandins, is reduced by aspirin-like drugs.

Side Effects

Aspirin is very useful, but it has many side effects and therefore must be used carefully. Like most powerful drugs, an overdose of aspirin or salicylates can be fatal. If a child or adult takes an overdose of aspirin, induce vomiting to empty the unabsorbed medication from the stomach (if the person is still awake and conscious). Obtain emergency medical care right away.

The most common side effects of aspirin are heartburn and other symptoms of stomach irritation such as indigestion, pain, nausea, and vomiting. The stomach irritation may lead to bleeding from the stomach, which may cause black stools. These symptoms may be reduced by taking aspirin with meals, with an antacid, with a glass of milk, or by taking enteric-coated or timed-release aspirin. Also, it is best not to take aspirin with alcohol or coffee (or other beverages containing caffeine, such as tea or cocoa and many soft drinks). Alcohol and caffeine make the stomach more sensitive to irritation. The non aspirin salicylate preparations sometimes are less irritating to the stomach and may be substituted for aspirin by your doctor.

A few people develop asthma, hay fever, nasal congestion, or hives from aspirin or non-steroid anti-inflammatory drugs (NSAIDs). These people should never take aspirin, nor should people who have active stomach or duodenal ulcers. Anyone who has ever had a peptic ulcer should be very careful about taking aspirin because it can lead to a recurrence.

Aspirin is known to interfere with the action of the platelets. As a result, some people who take a lot of aspirin experience easy bruising of the skin. Therefore, people who have major bleeding problems should not take aspirin. Also, keep in mind that aspirin should not be taken for 10-14 days before surgery (including surgery in the mouth) to avoid excessive bleeding during or after the operation. These side effects probably depend on aspirin-like drugs' ability to block endogenous prostaglandin biosynthesis. Platelet function appears to be disturbed because aspirin-like drugs prevent the formation by the platelets of thrombozane A2 (TXA2), a potent aggregating agent. This accounts for the tendency of these drugs to increase the bleeding time.

Aspirin increases oxygen consumption by the body, increasing carbon dioxide production-an effect that stimulates respiration. Therefore, overdose with aspirin is often characterized by marked increases in respiratory rate, which cause the overdosed individual to appear to pant. This occurrence results in other, severe, metabolic consequences.

Prolongation of gestation by aspirin-like drugs has been demonstrated in both experimental animals and the human female. Furthermore, prostaglandins of the E and F series are potent uterotropic agents , and their biosynthesis by the uterus increases dramatically in the hours before parturition. It is thus hypothesized that prostaglandins play a major role in the initiation and progression of labor and delivery.

High doses of salicylate may cause ringing in the ears and slight deafness. Sometimes, however, these symptoms indicate mild overdose, which could become more serious.

Aspirin and NSAIDs sometimes affect the normal function of the kidneys and aspirin-like drugs promote the retention of salt and water by reducing the prostaglandin-induced inhibition of both the reabsorption of chloride and the action of antidiuretic hormone. This may cause edema in some patients with arthritis who are treated with an aspirin-like drug.

Recent reports have said there could be a link between the use of aspirin and the development of Reye's syndrome. Reye's syndrome is a rare but possibly fatal disease seen most often in children and teenagers. It usually affects those recovering from chicken pox or a viral illness such as the flu. These reports have raised concern in pediatricians (doc-

tors who specialize in treating children) and parents of children with arthritis who need to take large doses of aspirin to control their disease.
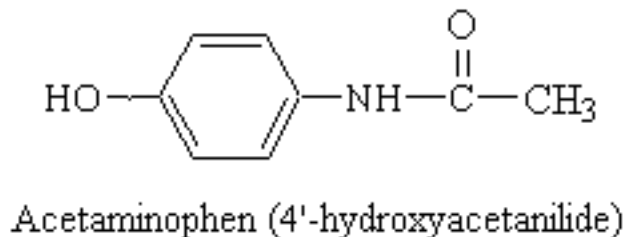
Aspirin

In the U.S., about 10 to 20 thousand tons of aspirin are consumed each year; it is our most popular analgesic. Aspirin is one of the most effective analgesic, antipyretic, and anti-inflammatory agents.

CO₂H

Acetylsalicylic acid
"Aspirin"
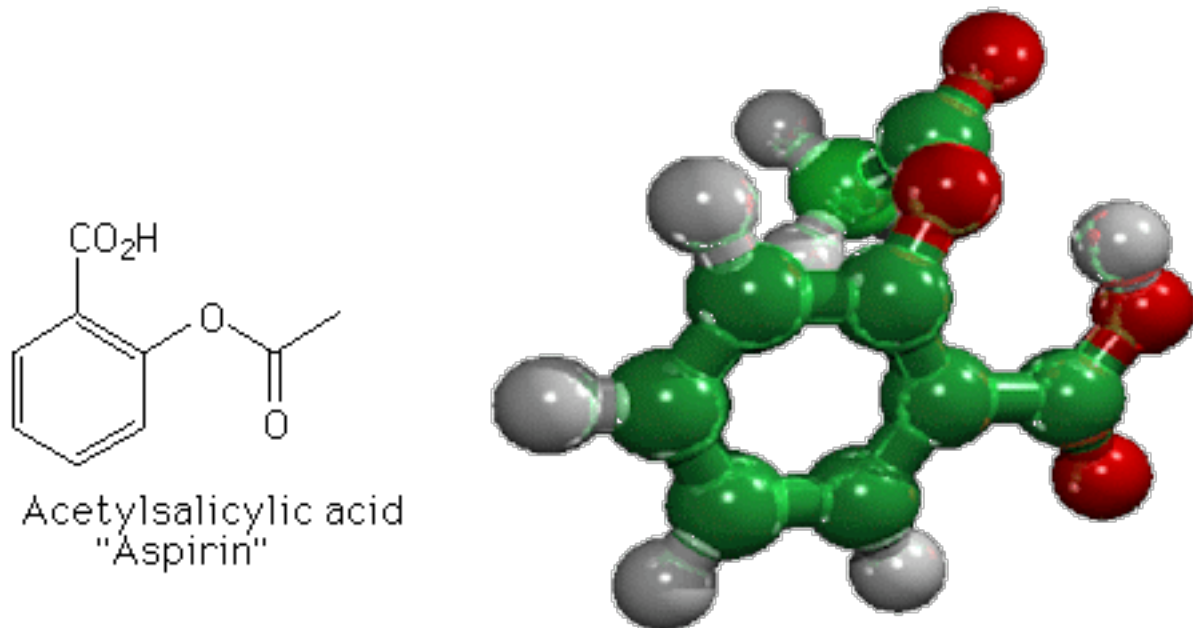
Chemical structure

Acetaminophen (Tylenol)

Acetaminophen is an effective alternative to aspirin as an analgesic and antipyretic agent. However, its anti-inflammatory effect is minor and not clinically useful. It is commonly felt that acetaminophen may have fewer side effects than aspirin, but it should be noted that an acute overdose may produce severe or even fatal liver damage. Acetaminophen does not inhibit platelet aggregation and therefore is not useful for preventing vascular clotting.

Acetaminophen (4'-hydroxyacetanilide)

Side effects are usually fewer than those of aspirin; the drug produces less gastric distress and less ringing in the ears. However, as stated previously, overdose can lead to severe damage of the liver.

Acetaminophen has been proved to be a reasonable substitute for aspirin when analgesic or antipyretic effectiveness is desired, especially in patients who cannot tolerate aspirin. This might include patients with peptic ulcer disease of gastric distress or those in whom the anticoagulant action of aspirin might be undesirable.

Aspirin is often combined with acetaminophen in a single tablet for relief of arthritis and other painful conditions. Sometimes other drugs such as caffeine, an antihistamine, nasal drying agents, and sedatives are also added. Although some of these preparations may have special uses for certain acute conditions such as a cold or a headache, they should not be taken for a chronic (long-term) form of arthritis. If a combination is required, each drug should be prescribed separately. The dose of each should be adjusted individually to achieve the greatest benefit with the fewest side effects.

Researchers attribute the pain-relieving activity of acetaminophen to the drug's ability to elevate the pain threshold, although the precise mechanisms involved in this process have not been clearly identified. The antipyretic, or fever-reducing, effect of acetaminophen is far better understood. Research shows that the drug inhibits the action of fever-producing agents on the heat-regulating centers of the brain by blocking the formation and release of prostaglandins in the central nervous system. However, unlike aspirin and other NSAIDs, acetaminophen has no significant effect on the prostaglandins involved in other body processes.

Despite claims to the contrary, stomach upset and hepatic toxicity are statistically as much a problem with acetaminophen as with aspirin-like drugs. Acetaminophen is normally metabolized in the liver and kidney by P450 enzymes. No toxicity is observed with therapeutic doses, however, after ingestion of large quantities (>2,000 mg/kg), a highly reactive metabolite, N-acetyl-p-benzoquinoneimine, is generated (see figure below). This species is electrophilic intermediate which is conjugated with glutathion to a non-toxic compound. Overdosing depletes glutithione and N-acetyl-p-benzoquinone reacts with nucleophilic portions (sulfhdryl groups) of critical liver cell protein. This results in cellular dysfunction and hepatic and renal toxicity. Antidote treatment consists of amino acid supplements to replenish glutathione. The P450 metabolizing enzymes differ somewhat in character between the liver and kidney. Factors that enhance renal toxicity include chronic liver disease, possibly gender, concurrent renal insults, and conditions that alter the activity of P450-metabolizing enzyme systems.
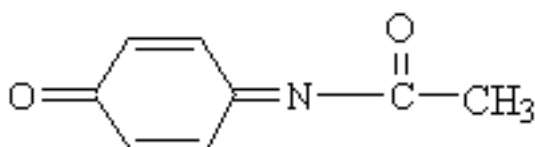
N-acetyl-p-benzoquinoneimine

Other Aspirin-Like Drugs

Other aspirin-like drugs include diflunisal, phenylbutazone, apazone, indomethacine, sulindac, fenamates, tolmetin, ibuprofen (see figure below), and piroxicam.
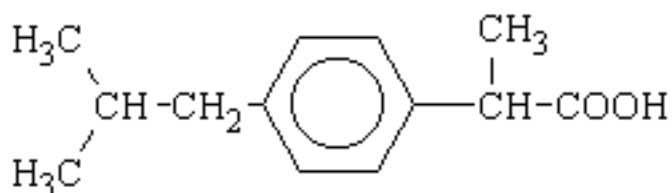
Ibuprofen

Gold

Gold is not of course an aspirin-like drug. However, its end effect is similar to aspirin, so it will be briefly considered here. Gold in elemental form has been employed for centuries as an antipruritic (anti itch medication) to relieve the itching palm. At present, gold treatment includes different forms of gold salts used to treat rheumatoid arthritis and related diseases. In some people, it helps relieve joint pain and stiffness, reduce swelling and bone damage, and reduce the chance of joint deformity and disability.

The significant preparations of gold are all compounds in which the gold is attached to sulfur. The three prominent drugs are aurothioglucose, auranofin, and gold sodium thiomalate.
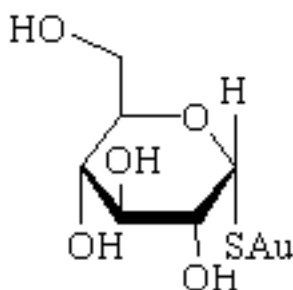
Aurothioglucose

It takes months for gold compounds to leave the body. This means that side effects to gold therapy may take some time to resolve. Sometimes side effects even appear after the last gold injection. Rash and a metallic taste in the mouth are side effects of gold injections that may not seem serious at first. However, they are early warning signs for more serious reactions. If either of these side effects develop, the health care provider should be contacted promptly.

Some side effects may cause multiple symptoms, not all of which may occur. Side effects with multiple symptoms are:

1. Low platelet count (thrombocytopenia). Most often this appears to be an immunological disturbance that results in an accelerated degradation of platelets. Symptoms may include: black, tarry stools, blood in urine, stool, or vomit, small red dots on the skin, nose bleeds, unusual bruising or bleeding.

2. Anaphylaxis. Symptoms include sudden onset of the following soon after a gold injection: trouble swallowing, tightness in the throat, fainting, trouble breathing, wheezing, hives, swelling of the face, usually the lips or around the eyes, liver damage, abdominal pain for more than a few days, light colored stools, albuminuria, yellow eyes or skin, ulcerative colitis, severe abdominal pain or cramps, diarrhea that lasts more than a few days, blood in stool.

## Opiates, Opiate Antagonists, and Opiate Receptors

The term opiate refers to any natural or synthetic drug that exerts actions upon the body similar to those induced by morphine, the major pain-relieving agent obtained from the opium poppy (Papaver somniferum). They were so highly regarded in the nineteenth century as remedies for pain, anxiety, cough, and diarrhea that some physicians referred to them as G.O.M.- `God's Own Medicine'. Opiates interact with what appear to be several closely related receptors, and they share some of the properties of certain naturally occurring peptides, the enkephalins, endorphins, and dynorphins.

Opiates

The term opium refers to the crude resinous extract obtained from the opium poppy. Crude opium contains a wide variety of ingredients, including morphine and codeine, both of which are widely used in medicine. The bulk of the ingredients of opium, however, consists of such organic substances as resins, oils, sugars, and proteins that account for more than 75 % of the weight of the opium but exert little pharmacological activity. Morphine is the major pain relieving drug found in opium, being approximately 10% of the crude exudate. Codeine is structurally close to morphine (see figs below), although it is much less potent and amounts to only 0.5% of the opium extract. Heroin does not occur naturally but is a semisynthetic derivative produced by a chemical modification of morphine that increases the potency (see figs. below). It takes only 3 mg. of heroin to produce the same analgesic effect as 10 mg of morphine. However, at these equally effective doses, it may be difficult to distinguish between the effects of the two compounds.
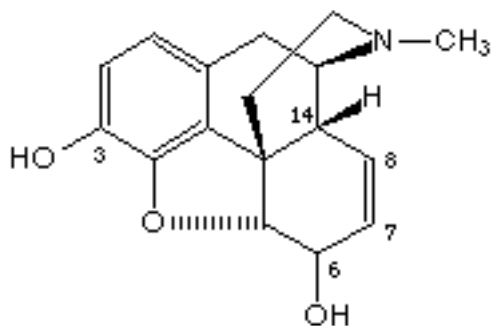
Morphine
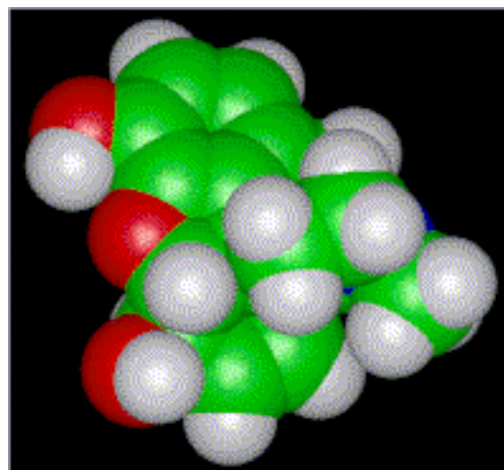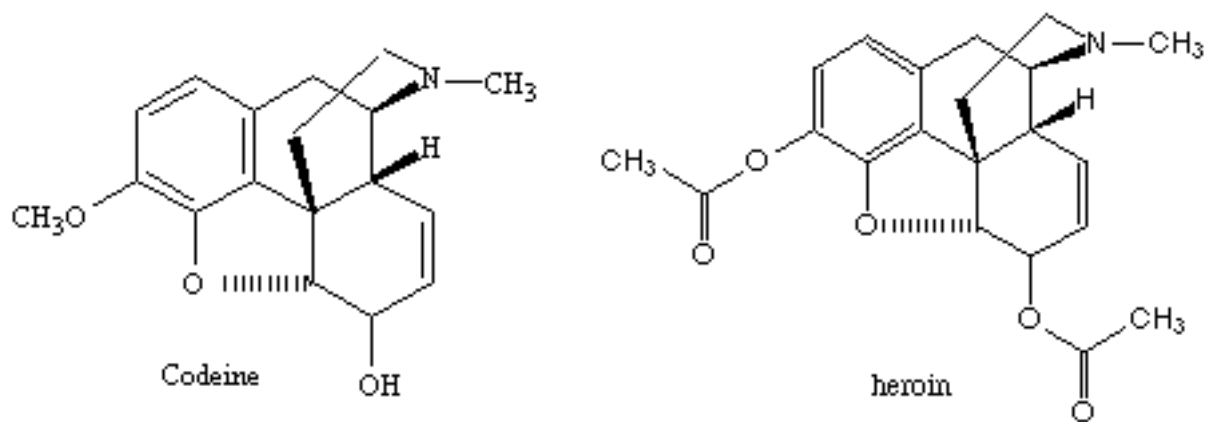
Filled structure of morphine

Mechanism of Action

Studies of the binding of opioid drugs and peptides to specific sites in brain and other organs have suggested the existence of perhaps as many as eight types of receptors. In the CNS, there is reasonably firm evidence for four major categories of receptors, designated m, k, d , and s . To add confusion, there may well be subtypes of each of these receptors. Although there is considerable variation in binding characteristics and anatomical distribution among different species, inferences have been drawn from data that attempt to relate pharmacological effects to interactions with a particular constellation of receptors. For example, analgesia has been associated with both m and k receptors, while dysphoria or psychotomimetic (alteration of behavior or personality) effects have been ascribed to s receptors; based primarily on their localization in limbic regions of the brain, d receptors are thought to be involved in alterations of affective behavior. The actions of opioid drugs that are currently available have usually been interpreted with respect to the participation of only three types of receptors - m, k, and s ; at each, a given agent may act as an agonist, a partial agonist, or an antagonist (see table). The m receptor is thought to meduate supraspinal analgesia, respiratory depression, euphoria, and physical dependance; the k receptor, spinal analgesia, miosis, and sedation; the s receptor, dysphoria, hallucinations, and respiratory and vasomotor stimulation.

It has been observed that opioids can selectively inhibit certain excitatory inputs to identified neurons. For example, the iontophoretic administration (the induction of an ionized substance through intact skin by the application of a direct current) of morphine into the substantia gelatinosa suppresses the discharge of spinal neurons in lamina IV of the dorsal horn that is evoked by noxious stimuli (e.g. heat) without changing responses to other inputs. While a postsynaptic action at discrete dedritic sites cannot be excluded, these findings suggest that opioids selectively inhibit the release of excitatory transmitters from terminals of nerves carrying pain related stimuli. In other situations, postsynaptic actions of opioids appear to be important. For example, application of opioids to neurons in the locus ceruleus reduces both spontaneous discharge and responses evoked by noxious stimuli. However, excitation of the neurons by antidromic stimulation (i.e. causing the neurons to fire backwards) is also suppressed, and the cells are hyperpolarized by the drugs.

Opioids have been observed to inhibit prostaglandin-induced increases in the accumulation of cyclic AMP in in brain tissue. Of potential relevance to mechanisms that underlie the phenomena of tolerance and withdrawal, the responses to prostaglandins recover in the continued presence of opioids.

Opioid-induced analgesia is due to actions of several sites within the CNS and involves several systems of neurotransmitters. Although opioids do not alter the threshold or responsivity of afferent nerve endings to noxious stimulation or impair the conduction of the nerve impulses along peripheral nerves, they may decrease conduction of impulses of primary afferent fibers when they enter the spinal cord and decrease activity in other sensory endings. There are opioid binding sites (m receptors) on the terminal axons of primary afferents within laminae I and II (substantia gelatinosa) of the spinal cord and in the spinal nucleus of the trigeminal nerve. Morphine-like drugs acting at this site are thought to decrease the release of neurotransmitters, such as substance P, that mediate transmission of pain impulses.

High doses of opioids can produce muscular rigidity in man, and both opioids and endogenous peptides cause catalepsy, circling, and stereotypical behavior in rats and other animals. These effects are probably related to actions at opioid receptors in the substania nigra and striatum, and involve interactions with both dopaminergic and GABA-ergic neurons.

The mechanism by which opioids produce euphoria, tranquility, and other alterations of mood remains unsettled. Microinjections of opioids into the ventral tegmentum activate dopaminergic neurons that project to the nucleus accumbens. Animals will work to receive such injections, and activation (or disinhibition) of these neurons has been postulated to be a critical element in the reinforcing effects of opioids and opioid-induced euphoria. However, the administration of dopaminergic antagonists does not consistently prevent these reinforcing effects. The neural systems that mediate opioid reinforcement in the ventral tegmentum appear to be distinct from those involved in the classical manifestations of physical dependence and analgesia.

Basic Effects of Morphine

CNS. Morphine exerts a narcotic action manifested by analgesia, drowsiness, changes in mood, and mental clouding. The major medical action of morphine sought in the CNS is analgesia, which may usually be induced by doses below those that cause other effects on the CNS, such as sedation or respiratory depression. The relief of pain by morphine-like opioids is relatively selective, in that other sensory modalities (touch, vibration, vision, hearing, etc.) are not inhibited. Patients frequently report that the pain is still present but that they feel more comfortable. Continuous dull pain is relieved more effectively than sharp intermittent pain, but with sufficient amounts of morphine it is possible to relieve even the severe pain associated with renal or biliary colic. In fact, its analgesic action appears to result not from a decrease of pain impulses into the CNS but from an altered perception of the painful stimuli.

Respiration. A second major action of morphine-like drugs is to depress respiration through interaction with m receptors located in the brainstem. At high doses, respiration may become so slow and irregular that life is threatened. In man, death from morphine poisoning is nearly always due to respiratory arrest. The primary mechanism of respiratory depression by morphine involves a reduction in the responsiveness of the brain stem respiratory centers to increases in carbon dioxide tension (PCO_2). High concentrations of opioid receptors, as well, as endogenous peptides, are found in the medullary areas believed to be important in ventilatory control. Respiratory depression is mediated by a subpopulation of m receptors (m 1), distinct from those that are involved in the production of analgesia (m 2). Thus, a 'pure' m 1-opioid agonist could theoretically produce analgesia with little respiratory depression.

Cough. Opiates suppress the "cough center" which is also located in the brainstem, the medulla. Such an action is thought to underlie the use of opiate narcotics as cough suppressants. Codeine appears to be particularly effective in this action and is widely used for this purpose.

Gastrointestinal Tract. The opiates have been used for centuries for the relief of diarrhea and for the treatment of dysentery, and these uses were developed long before these agents were used as analgesics or euphoiants. Opiates appear to exert their effect on the gastrointestinal tract primarily in the intestine, where peristaltic movements, which normally propel food down the intestine, are markedly diminished. Also, the tone of the intestine is greatly increased to the point where almost complete spastic paralysis of movement occurs. This combination of decreased propulsion and increased tone leads to a marked decrease in the movement of food through the intestine. This stasis is followed by a dehydration of the feces, which hardens the stool and further retards the advance of material. All these effects contribute to the constipating properties of opiates. Indeed, nothing more effective has yet been developed for treating sever diarrhea.

Opiate Antagonists

Naloxone, when administered to normal individuals, produces no analgesia, euphoria, or respiratory depression. However, it rapidly precipitates withdrawal in narcotic-dependent individuals. Naloxone antagonizes the actions of morphine at all its receptors; however its affinity for m receptors is generally more than ten fold higher than for k or d receptors.

The uses of naloxone include the reversal of the respiratory depression that follows acute narcotic intoxication and the reversal of narcotic-induced respiratory depression in newborns of mothers who have received narcotics. The use of naloxone is limited by a short duration of action and the necessity of parenteral route of administration.
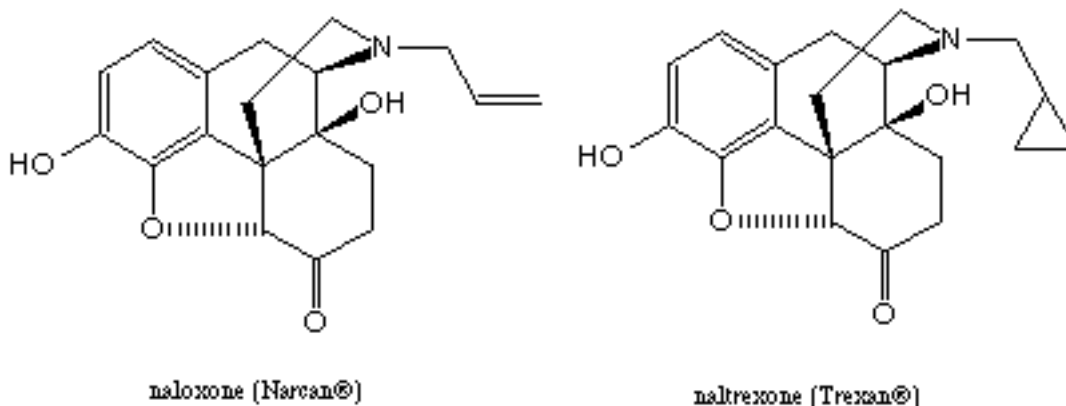
naloxone (Narcan®)   naltrexone (Trexan®)

Naltrexone became clinically available in 1985 as a new narcotic antagonist. Its actions resemble those of naloxone, but naltrexone is well is well absorbed orally and is long acting, necessitating only a dose of 50 to 100 mg. Therefore, it is useful in narcotic treatment programs where it is desired to maintain an individual on chronic therapy with a narcotic antagonist. In individuals taking naltrexone, subsequent injection of an opiate will produce little or no effect. naltrexone appears to be particularly effective for the treatment of narcotic dependence in addicts who have more to gain by being drug-free rather than drug dependant.

Contributors

- Edward B. Walker (Weber State University)

Prostaglandins were first discovered and isolated from human semen in the 1930s by Ulf von Euler of Sweden. Thinking they had come from the prostate gland, he named them prostaglandins. It has since been determined that they exist and are synthesized in virtually every cell of the body. Prostaglandins, are like hormones in that they act as chemical messengers, but do not move to other sites, but work right within the cells where they are synthesized.

Introduction

Prostaglandins are unsaturated carboxylic acids, consisting of of a 20 carbon skeleton that also contains a five member ring. They are biochemically synthesized from the fatty acid, arachidonic acid. See the graphic on the left. The unique shape of the arachidonic acid caused by a series of cis double bonds helps to put it into position to make the five member ring. See the prostaglandin in the next panel
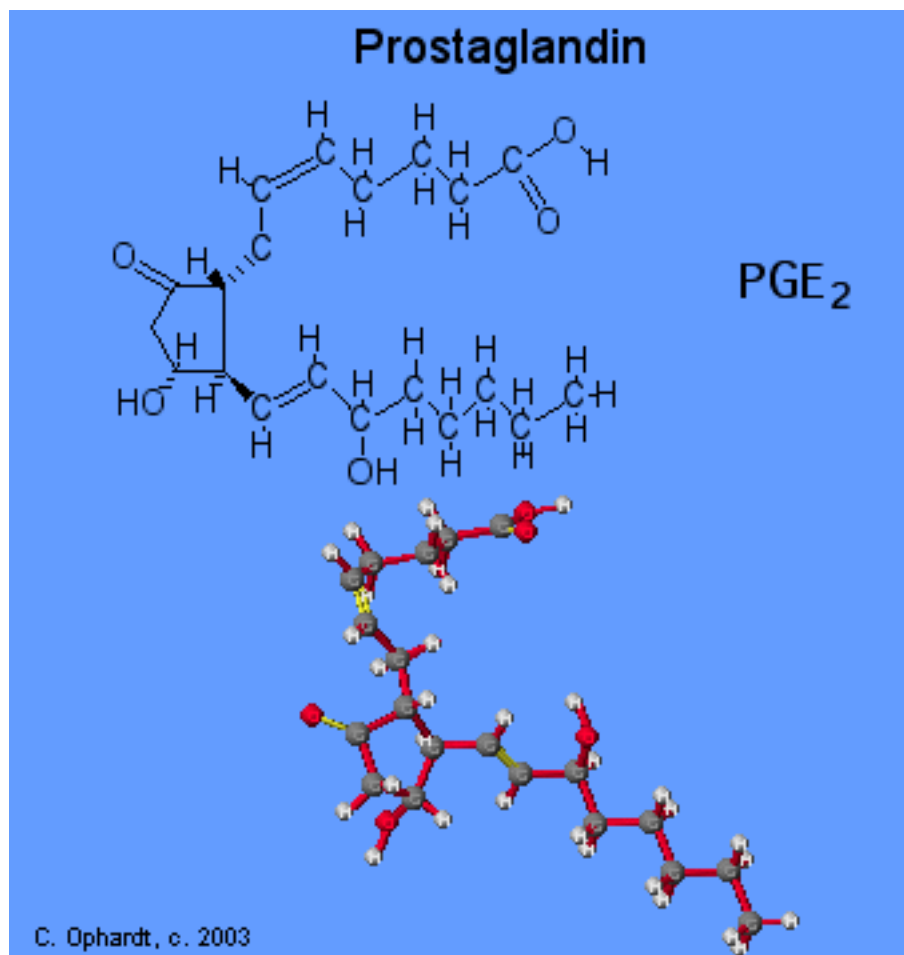

Prostaglandin Structure

Prostaglandins are unsaturated carboxylic acids, consisting of of a 20 carbon skeleton that also contains a five member ring and are based upon the fatty acid, arachidonic acid. There are a variety of structures one, two, or three double bonds. On the five member ring there may also be double bonds, a ketone, or alcohol groups. A typical structure is on the left graphic.

Functions of Prostaglandins

There are a variety of physiological effects including:

1.   Activation of the inflammatory response, production of pain, and fever. When tissues are damaged, white blood cells flood to the site to try to minimize tissue destruction. Prostaglandins are produced as a result.

2. Blood clots form when a blood vessel is damaged. A type of prostaglandin called thromboxane stimulates constriction and clotting of platelets. Conversely, PGI2, is produced to have the opposite effect on the walls of blood vessels where clots should not be forming.

3. Certain prostaglandins are involved with the induction of labor and other reproductive processes. PGE2 causes uterine contractions and has been used to induce labor.

4. Prostaglandins are involved in several other organs such as the gastrointestinal tract (inhibit acid synthesis and increase secretion of protective mucus), increase blood flow in kidneys, and leukotriens promote constriction of bronchi associated with asthma.

Aspirin

Acetyl group

Acetyl group bonds to serine in COX enzyme

COX

C. Ophardt, c. 2003
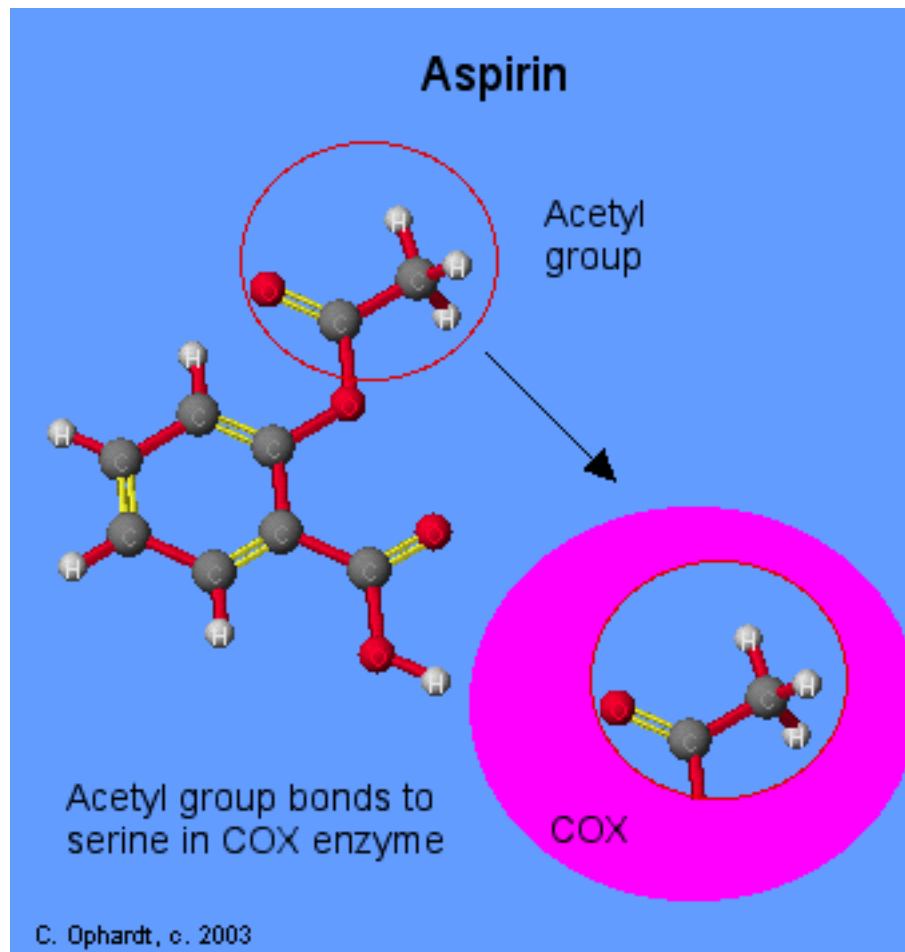
Effects of Aspirin and other Pain Killers

When you see that prostaglandins induce inflammation, pain, and fever, what comes to mind but aspirin. Aspirin blocks an enzyme called cyclooxygenase, COX-1 and COX-2, which is involved with the ring closure and addition of oxygen to arachidonic acid converting to prostaglandins. The acetyl group on aspirin is hydrolzed and then bonded to the alcohol group of serine as an ester. This has the effect of blocking the channel in the enzyme and arachidonic can not enter the active site of the enzyme. By inhibiting or blocking this enzyme, the synthesis of prostaglandins is blocked, which in turn relives some of the effects of pain and fever. Aspirin is also thought to inhibit the prostaglandin synthesis involved with unwanted blood clotting in coronary heart disease. At the same time an injury while taking aspirin may cause more extensive bleeding.

3. STOMACH MEDICINE

Heartburn is caused by a buildup of excessive amounts of stomach acid, particularly HCl. This acid is used to digest the food we eat, but it can often back up into the esophagus causing that burning sensation many of us are familiar with. The symptoms of heartburn can be treated with a mild base, which acts to neutralize the excess HCl. For example, Tums is a very commonly used antacid that can be bought over the counter. Other antacids, such as Alka Seltzer, work in similar ways. Below, show the mechanism and products for reaction in which calcium carbonate (the active ingredient in Tums) neutralizes HCl in a simple proton transfer reaction. Following this acid-base reaction, carbonic acid quickly degrades into CO_2 and H_2O.
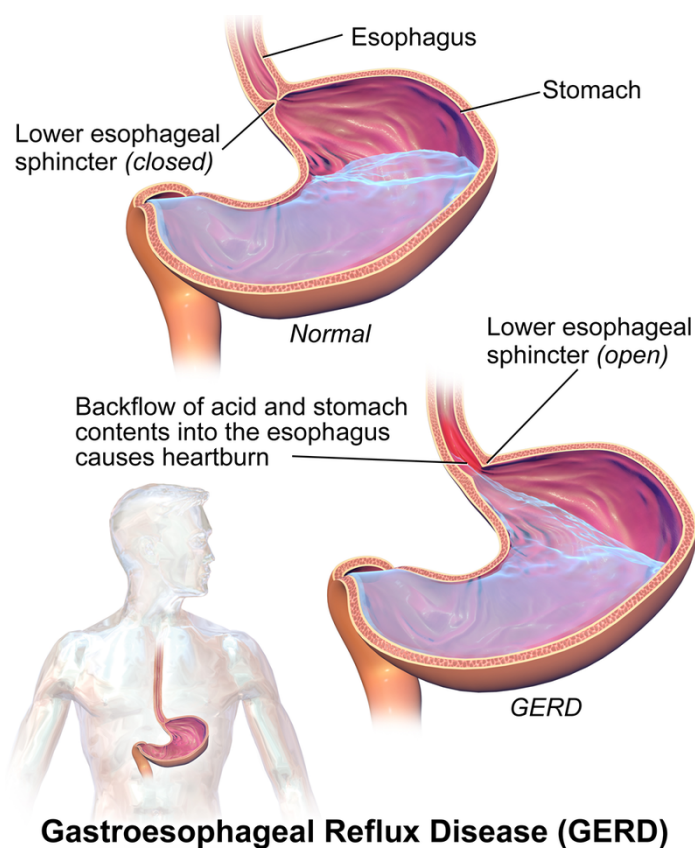
A comparison of a healthy condition to GERD. Image used with permission (Cc BY-SA 4.0; BruceBlaus .

4. NARCOTICS

Narcotic agents are potent analgesics which are effective for the relief of severe pain. Analgesics are selective central nervous system depressants used to relieve pain. The term analgesic means "without pain". Even in therapeutic doses, narcotic analgesics can cause respiratory depression, nausea, and drowsiness. Long term administration produces tolerance, psychic, and physical dependence called addiction.

Introduction

Narcotic agents may be classified into four categories:

1. Morphine and codeine - natural alkaloids of opium.

2. Synthetic derivatives of morphine such as heroin.

3. Synthetic agents which resemble the morphine structure.

4. Narcotic antagonists which are used as antidotes for overdoses of narcotic analgesics.

The main pharmacological action of analgesics is on the cerebrum and medulla of the central nervous system. Another effect is on the smooth muscle and glandular secretions of the respiratory and gastro-intestinal tract. The precise mechanism of action is unknown although the narcotics appear to interact with specific receptor sites to interfere with pain impulses.

Receptor Site

A schematic for an analgesic receptor site may look as shown in the graphic below with morphine. Three areas are needed: a flat areas to accommodate a flat nonpolar aromatic ring, a cavity to accept another series of rings perpendicular, and an anionic site for polar interaction of the amine group.

Analgesic Receptor Site

Morphine

flat area for
aromatic ring

anioinc
site

cavity for rings
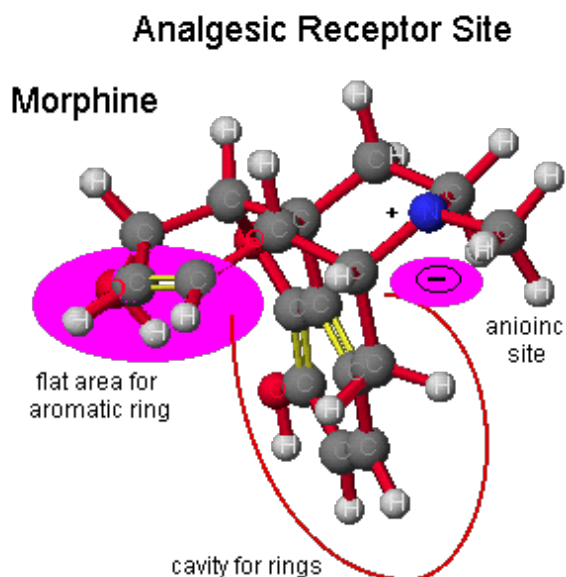
C. Ophardt, c. 2003

Enkephalins

Recently investigators have discovered two compounds in the brain called enkephalins which resemble morphine in structure. Each one is a peptide composed of 5 amino acids and differ only in the last amino acid. The peptide sequences are: tyr-gly-gly-phe-leu and tyr-gly-gly-phe-met. Molecular models show that the structures of the enkephalins has some similarities with morphine. The main feature in common appears to be the aromatic ring with the -OH group attached (tyr). Methadone and other similar analgesics have 2 aromatic rings which would be similar to the enkephalins (tyr and phe).

Analgesics may relieve pain by preventing the release of acetylcholine. Enkephalin molecules are released from a nerve cell and bind to analgesic receptor sites on the nerve cell sending the impulse. The binding of enkephalin or morphine-like drugs changes the shape of the nerve sending the impulse in such a fashion as to prevent the cell from releasing acetylcholine. As a result, the pain impulse cannot be transmitted and the brain does not preceive pain.

Morphine and Codeine

Morphine exerts a narcotic action manifested by analgesia, drowsiness, changes in mood, and mental clouding. The major medical action of morphine sought in the CNS is analgesia. Opiates suppress the "cough center" which is also located in the brain stem, the medulla. Such an action is thought to underlie the use of opiate narcotics as cough suppressants. Codeine appears to be particularly effective in this action and is widely used for this purpose.

Narcotic analgesics cause an addictive physical dependence. If the drug is discontinued, withdrawal symptoms are experienced. Although the reasons for addiction and withdrawal symptoms are not completely known, recent experiments have provided some information. A nucleotide known as cyclicadenosine monophosphate (cAMP) is synthesized with the aid of the enzyme adenylate cyclase. Enkephalin and morphine-like drugs inhibit this enzyme and thus decrease the amount of cAMP in the cells. In order to compensate for the decreased cAMP, the cells synthesize more enzyme in an attempt to produce more cAMP. Since more enzyme has been produced, more morphine is required as an inhibitor to keep the cAMP at a low level. This cycle repeats itself causing an increase in the tolerance level and increasing the amounts of morphine required. If morphine is suddenly withheld, withdrawal symptoms are probably caused by a high concentration of cAMP since the synthesizing enzyme, adenylate cyclase, is no longer being inhibited.

Narcotic Analgesics

Morphine

Codeine

C. Ophardt, c. 2003
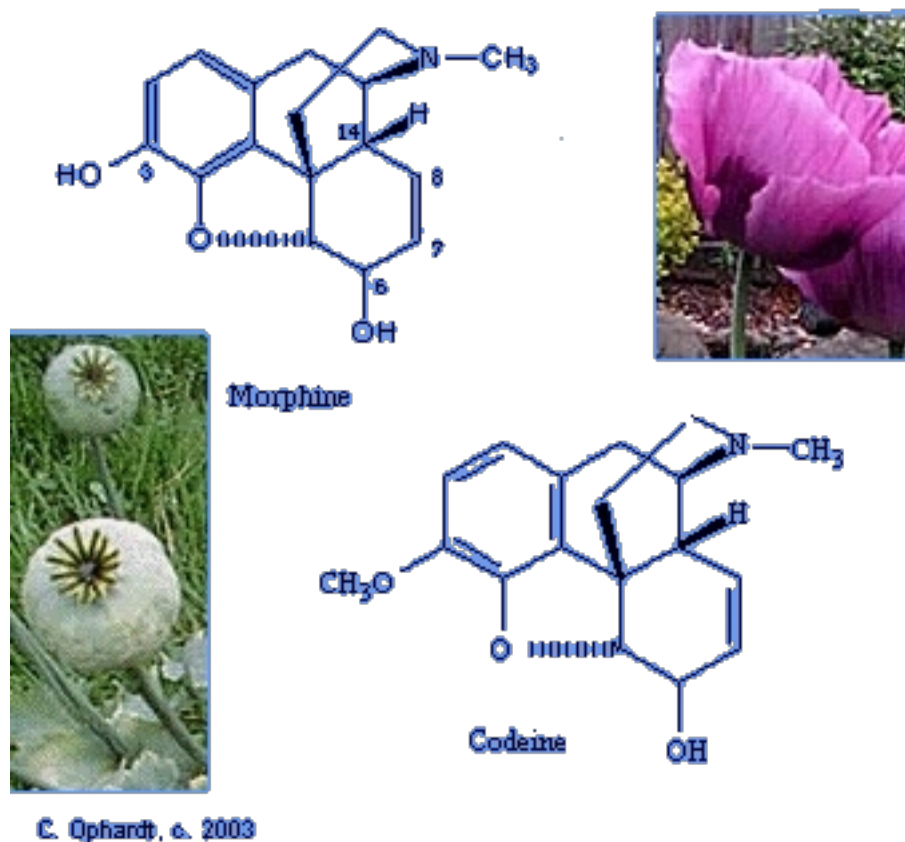
Morphine and codeine are contained in opium from the poppy (Papaver Somniterum) plant found in Turkey, Mexico, Southeast Asia, China, and India. This plant is 3-4 feet tall with 5-8 egg shaped capsules on top. Ten days after the poppy blooms in June, incisions are made in the capsules permitting a milky fluid to ooze out. The following day the gummy mass (now brown) is carefully scraped off and pressed into cakes of raw opium to dry.

Opium contains over 20 compounds but only morphine (10%) and codeine (0.5%) are of any importance. Morphine is extracted from the opium and isolated in a relatively pure form. Since codeine is in such low concentration, it is synthesized from morphine by an ether-type methylation of an alcohol group. Codeine has only a fraction of the potency compared to morphine. It is used with aspirin and as a cough suppressant.

Heroin

Heroin is synthesized from morphine by a relatively simple esterification reaction of two alcohol (phenol) groups with acetic anhydride (equivalent to acetic acid). Heroin is much more potent than morphine but without the respiratory depression effect. A possible reason may be that heroin passes the blood-brain barrier much more rapidly than morphine. Once in the brain, the heroin is hydrolyzed to morphine which is responsible for its activity.

Synthetic narcotic analgesics include meperidine and methadone. Meperidine is the most common subsitute for morphine. It exerts several pharmacological effects: analgesic, local anesthetic, and mild antihistamine. This multiple activity may be explained by its structural resemblance to morphine, atropine, and histamine.

Methadone is more active and more toxic than morphine. It can be used for the relief of may types of pain. In addition it is used as a narcotic substitute in addiction treatment because it prevents morphine abstinence syndrome.

Methadone was synthesized by German chemists during Wold War II when the United States and our allies cut off their opium supply. And it is difficult to fight a war without analgesics so the Germans went to work and synthesized a number of medications in use today, including demerol and darvon which is structurally simular to methadone. And before we go further lets clear up another myth. Methadone, or dolophine was not named after Adolf Hitler. The "dol" in dolophine comes from the latin root "dolor." The female name Dolores is derived from it and the term dol is used in pain research to measure pain e.g., one dol is 1 unit of pain.

Methadone

C. Ophardt, c. 2003
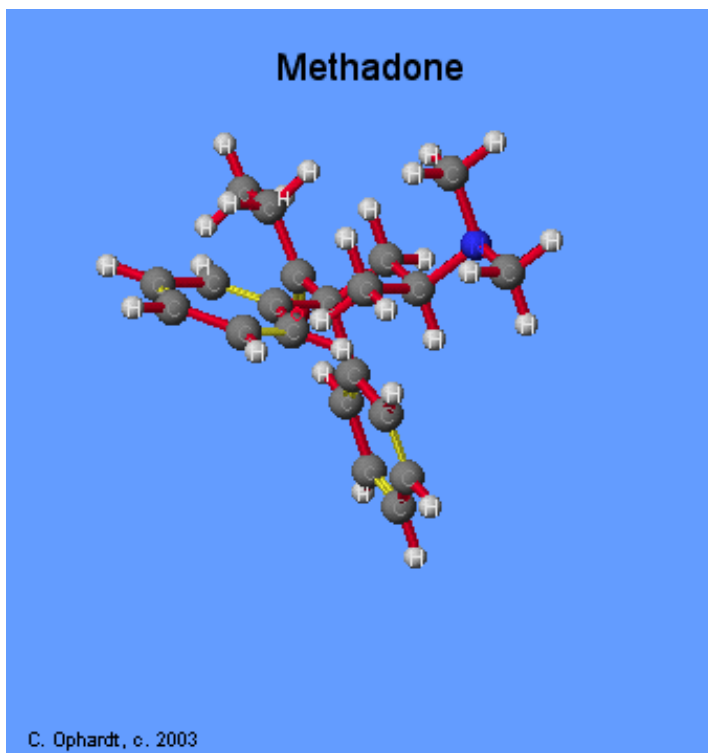
Even methadone, which looks strikingly different from other opioid agonists, has steric forces which produce a configuration that closely resembles that of other opiates. See the graphic on the left and the top graphic on this page. In other words, steric forces bend the molecule of methadone into the correct configuration to fit into the opiate receptor. When you take methadone it first must be metabolized in the liver to a product that your body can use. Excess methadone is also stored in the liver and blood stream and this is how methadone works its 'time release trick' and last for 24 hours or more. Once in the blood stream metabolized methadone is slowly passed to the brain when it is needed to fill opiate receptors. Methadone is the only effective treatment for heroin addiction. It works to smooth the ups and down of heroin craving and allows the person to function normally.

Narcotic Antagonists

Narcotic Antagonists prevent or abolish excessive respiratory depression caused by the administration of morphine or related compounds. They act by competing for the same analgesic receptor sites. They are structurally related to morphine with the exception of the group attached to nitrogen.

Narcotic Antagonists

Naloxone (Narcan)

Naltrexone (Trexan)
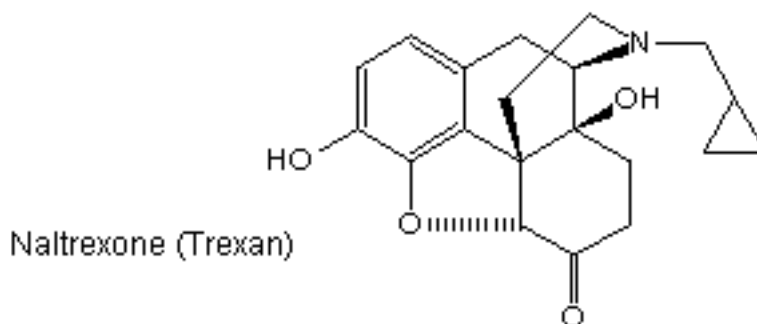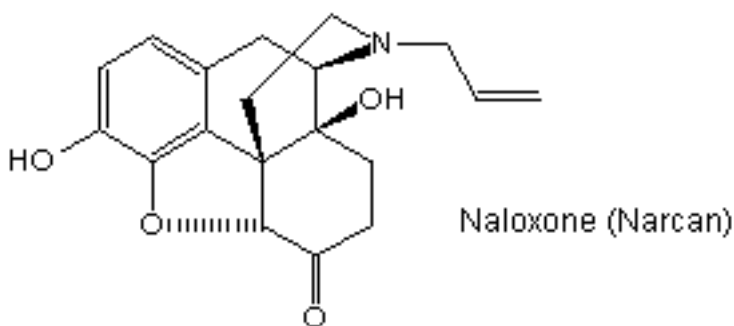
C. Ophardt, c. 2003

Nalorphine precipitates withdrawal symptoms and produces behavioral disturbances in addition to the antogonism action. Naloxane is a pure antagonist with no morphine like effects. It blocks the euphoric effect of heroin when given before heroin. Naltrexone became clinically available in 1985 as a new narcotic antagonist. Its actions resemble those of naloxone, but naltrexone is well is well absorbed orally and is long acting, necessitating only a dose of 50 to 100 mg. Therefore, it is useful in narcotic treatment programs where it is desired to maintain an individual on chronic therapy with a narcotic antagonist. In individuals taking naltrexone, subsequent injection of an opiate will produce little or no effect. Naltrexone appears to be particularly effective for the treatment of narcotic dependence in addicts who have more to gain by being drug-free rather than drug dependant

5. BASICS OF NEUROTRANSMITTERS

Dopamine (DA), 4,5-dihydroxyphenethylamine or 4-(2-aminoethyl)1,2-benzenediol, is a known neurotransmitter that is involved in the chemical transmission of nerve impulses in the mammalian brain. It is a member of the catecholamine family and a precursor to epinephrine (adrenaline) and norepinephrine (noradrenaline) in the biosynthetic pathways.

Dopamine

Norepinephrine
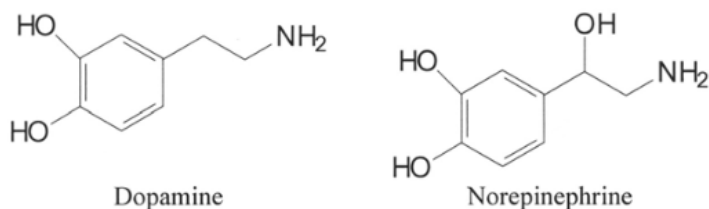
DA has a molecular formula of $C_8H_{11}NO_2$ and a formula weight of 153.18 [ref. 1]. It is a water-soluble hormone released by the hypothalamus. Imbalance in dopamine activity can cause brain dysfunction related to two major disorders, Parkinson's disease and schizophrenia [ref. 2,3]. Researchers are also looking at dopamine neurotransmission in drug abuse ranging from stimulants, such as amphetamines and cocaine, to depressants, such as morphine and other opioids, and alcohol [ref. 3].

Several amine neurotransmitters such as DA, noradrenaline (norepinephrine), adrenaline and serotonin are electroactive so that they can be monitored electrochemically. Most undergo a chemical reaction following the initial electron transfer step, an ec mechanism, as evaluated by cyclic voltammetry (CV) in this experiment. In biological fluids, prior separation with HPLC is recommended in conjunction with an electrochemical detector (HPLC-ECD).

Great strides in learning about the role and fate of DA and other neurotransmitters in brains have come about in recent years due to the ability to monitor these compounds in-vivo. The major breakthrough making this possible came when Adams and co-workers [ref. 4] implanted small carbon electrodes (fibers) in rat brain to detect in-vivo catecholamine neurotransmitters. The development and application of the methodology are discussed in "Probing Brain Chemistry: Voltammetry Comes of Age" [ref. 5]. This article is available online and is a recommended reading as background to this experiment. Venton and Wightman [ref. 6] in a more recent article propose calling this new subject area "psychoanalytical chemistry" in which sensors, like microelectrodes, can detect neurotransmitter dopamine and determine how its neurochemistry affects and correlates with animal behavior.

6. ANTI-DEPRESSANTS

Antidepressant drugs are used to restore mentally depressed patients to an improved mental status. Depression results from a deficiency of norepinephrine at receptors in the brain. Mechanisms that increase their effective concentration at the receptor sites should alleviate depression.

Introduction

Antidepressant drugs act by one or more of the following stimulation type mechanisms:

1. Increase release of norepinephrine:Amphetamines and electroconvulsive therapy act by this mechanism. Amphetamines mimic norepinephrine.

2. Prevent inactivation of norepinephrine:Monoamine oxidase (MAO) inhibitors are thought to act as antidepressant agents in part by preventing the breakdown and inactivation of norepinephrine.

3. Prevent the re-uptake of norepinephrine:The action of norepinephrine at the receptor site is terminated by the re-uptake of norepinephrine by the neuron from which it was originally released.

Tricyclic Antidepressants

The tricyclic antidepressants are the most effective drugs presently available for the treatment of depression. These act by increasing the release of norepinephrine. Amphetamine and cocaine can also act in this manner. Imipramine, amitriptylin, and other closely related drugs are among the drugs currently most widely used for the treatment of major depression.

- imipramine (Tofranil)

- desipramine (Norpramin)

Tricyclic Antidepressants

Imipramine
(Tofranil)

Desipramine
(Norpramin)
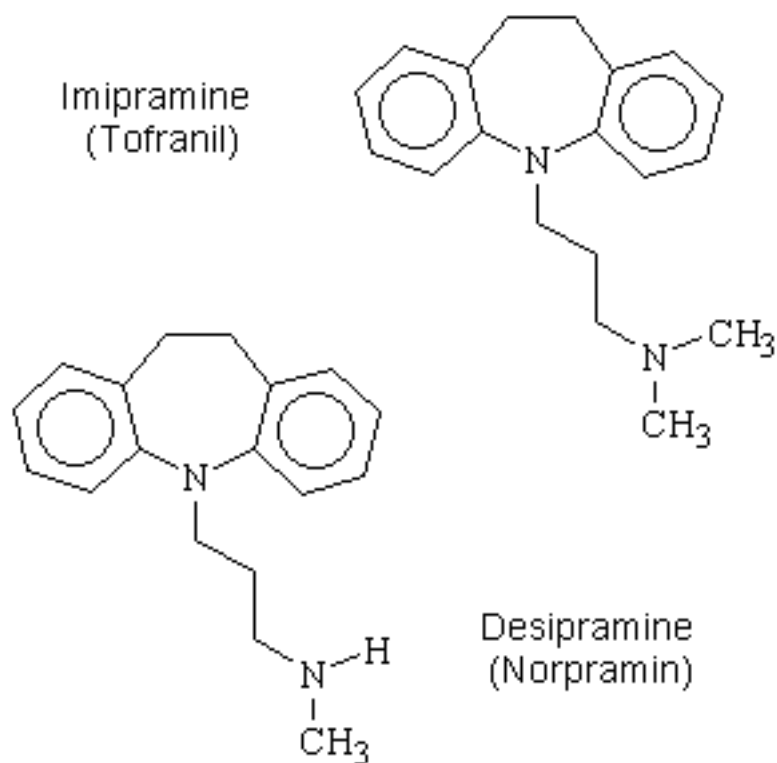
C. Ophardt, c. 2003

The activity of the tricyclic drugs depends on the central ring of seven or eight atoms which confers an angled or twisted conformation. The side chain must have at least 2 carbons although 3 appear to be better. The amine group may be either tertiary or secondary. All tricyclic antidepressants block the re-uptake of norepinephrine at nerve terminals. However, the potency and selectivity for the inhibition of the uptake of norepinephrine, serotonin, and dopamine vary greatly among the agents. The tertiary amine tricyclics seem to inhibit the serotonin uptake pump, whereas the secondary amine ones seem better in switching off the NE pump. For instance, imipramine is a potent and selective blocker of serotonin transport, while desipramine inhibits the uptake of norepinephrine.

Serotonin

Serotonin (5-hydroxytryptamine or 5-HT) is a monoamine neurotransmitter found in cardiovascular tissue, in endothelial cells, in blood cells, and in the central nervous system. The role of serotonin in neurological function is diverse, and there is little doubt that serotonin is an important CNS neurotransmitter. Although some of the serotonin is metabolized by monoamine oxidase, most of the serotonin released into the post-synaptic space is removed by the neuron through a re-uptake mechanism inhibited by the tricyclic antidepressants and the newer, more selective antidepressant re-uptake inhibitors such as fluoxetine and sertraline.
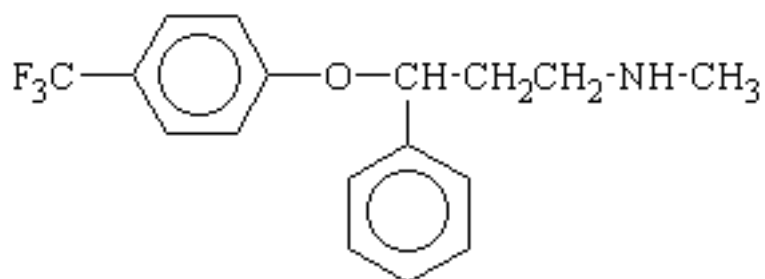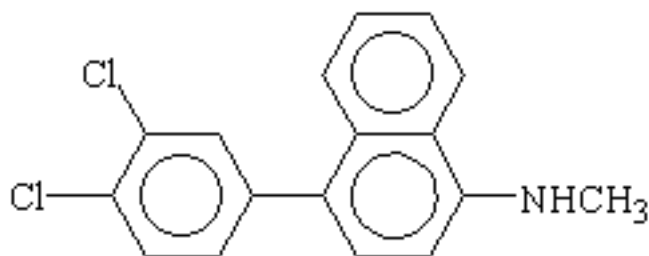
Serotonin
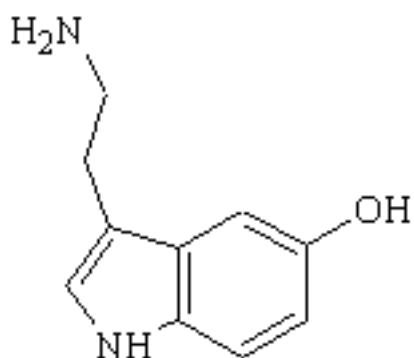
Selective Serotonin Reuptake Inhibitors

In recent years, selective serotonin reuptake inhibitors have been introduced for the treatment of depression. Prozac is the most famous drug in this class. Clomiprimine, fluoxetine (Prozac), sertraline and paroxetine selectively block the re-uptake of serotonin, thereby increasing the levels of serotonin in the central nervous system. Note the similarities and differences between the tricyclic antidepressants and the selective serotonin re-uptake inhibitors. Clomipramine has been useful in the treatment of obsessive-compulsive disorders.

Serotonin Reuptake Inhibitors

Fluoxetine (Prozac)

Sertraline (Zoloft)
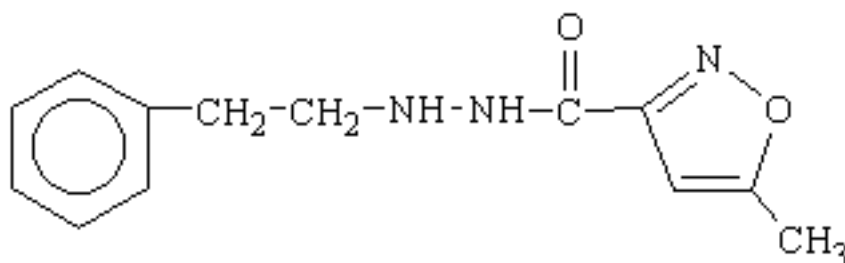
C. Ophardt, c. 2003

376

Monoamine Oxidase Inhibitors

Monoamine oxidase (MAO) causes the oxidative deamination of norephinephrine, serotonin, and other amines. This oxidation is the method of reducing the concentration of the neurotransmitter after it has sent the signal at the receptor site. A drug which inhibits this enzyme has the effect of **increasing the concentration of the norepinephrine which in turn causes a stimulation effect.** Most MAO inhibitors are hydrazine derivatives. Hydrazine is highly reactive and may form a strong covalent bond with MAO with consequent inhibition for up to 5 days.

These drugs are less effective and produce more side effects than the tricyclic antidepressants. For example, they lower blood pressure and were at one time used to treat hypertension. Their use in psychiatry has also become very limited as the tricyclic antidepressants have come to dominate the treatment of depression and allied conditions. Thus, MAOIs are used most often when tricyclic antidepressants give unsatisfactory results.

Monoamine Oxidase (MAO) Inhibitors
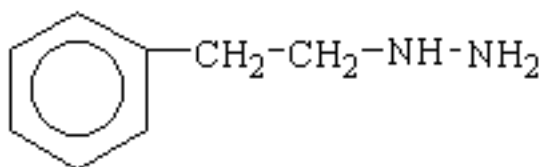
Phenelzine (Nardil)

Isocarboxazide (Marplan)

C. Ophardt, c. 2003

Phenelzine is the hydrazine analog of phenylethylamine, a substrate of MAO. This and several other MAOIs, such as isocarboxazide, are structurally related to amphetamine and were synthesized in an attempt to enhance central stimulant properties.

- phenelzine (Nardil)
- isocarboxazid (Marplan)

7. END OF CHAPTER MATERIAL

Jim Redwood had been summoned by the Quinault Indian Nation Tribal Planning Committee to return to the long house for an important vote. The Tribal Council elected in 1995 had been approached by the Forest Service to "lease" its remaining land to Bristol-Myers for the bio-prospecting of the Pacific yew (Taxus brevifolia), needed for the development of the new drug, taxol. Taxol was one of a few drugs that showed incredible promise in the treatment of rapidly growing cancers.

"Great," he thought, "I've got a backlog of sick patients in the clinic already and now I've got to rush over there to vote on the land issue. Why can't they ever plan these things better?" But Jim knew his last thought was just a way to blame someone else for his lack of help at the clinic. The Tribal Elders had planned this meeting, and it had been well in advance, so the expert advisors would have time to converge on their small reservation of a little over 200,000 acres in the Southwest corner of the Olympic Peninsula on the Pacific coastal area of Washington. "They're probably all there, waiting for me," he thought. It was going to be one of those days.

Jim hadn't realized when he was elected to the Tribal Planning Committee how important the position would become. Who could have anticipated that one of the smaller understory trees, the red cedar, would become the primary source of a "miracle drug" for cancer patients? He only hoped that the drug would be developed in time to help his mother, recently diagnosed with metastatic breast cancer.

Jim took a deep breath. The other 10 members of the Planning Committee were already seated. The only seat remaining was his, front and center as the moderator. He swiftly took his place, gave a quick nod to the other committee members, raised his arms, closed his eyes, and began with the traditional opening prayer. "Oh, Great Spirit, we ask for Your guidance today as we consider the important issues before us. Grant us wisdom in deciding the fate of the land You have given Your children." He lowered his arms and sat down.

"We will begin by introducing our expert advisors. On my left is Dick Shaffer, Assistant Director of Timber Management for the U.S. Forest Service Regional Office in Portland, Oregon. Next to him is Dr. Gordon Cragg, Chief of the Natural Products Branch of the National Cancer Institute. On my far right is Dr. Mark Plotkin, Executive Director, Ethnobiology and Conservation Team, Smithsonian Institution. Next to him is Hal Hartzell, Jr., Vice President of the Native Yew Conservation Society. Mr. Shaffer will begin with his statement."

"Thank you, Dr. Redwood. Let's just get to the bottom line. Women are dying every day of ovarian and breast cancer. The Forest Service places a high priority on helping Bristol-Myers in every way we can, legally and environmentally. This taxol stuff that comes from the Pacific yew is the best thing to come along for treating these women. Let's get in there and harvest those trees. Who knows how many lives are being lost while we waste time debating this."

Dr. Gordon Cragg chimed in. "I agree, Mr. Shaffer. We need to get started since the process takes some time to extract the taxol. The current yield of taxol is 1 gram per 30 pounds of bark, assuming a 73% recovery rate. Since these trees are not that large, that means we need 1.5 trees for every gram of taxol. A patient typically requires 500 milligrams per course of treatment, with four courses necessary, for a total of 2 grams per patient. That's three trees per patient and there are about 40,000 women needing this treatment now."

"Do you use the whole tree to get this medicine or only certain parts? Must the tree be killed to get it?" asked Billie Rainfeather, a tribal member.

Dr. Plotkin responded. "You know, that's a legitimate concern. It's primarily in the bark and only 10% of the yew population in your forested areas are the size preferred by bark collectors, trees 10 inches or larger in diameter. I think that if Bristol-Meyers plans on meeting that level of demand in the form of bark from the tree, the species would be in great jeopardy. As I'm sure you know, removing the bark automatically kills the tree. So, we risk eradicating trees of this yew species with any significant dimension, and endanger the future of the species by removing the seed source for future generations."

Hal Hartzell jumped in. "Yes, Mark, and that's not all. The Fish and Wildlife Service estimates that three to four million large yew trees remain on federal lands. To treat a year's worth of ovarian and breast cancer patients combined, that's 150,000 treatments and would require the bark from 1.5 million trees. How often can you justify harvesting that much?"

"Can't the Forest Service figure out some way to grow this tree on a tree farm?" asked Billie. "I really hate to see our land ruined. Do we know what this removal will do to the rest of the plants and animals? Our people use this tree to make traditional ceremonial crafts like bows, arrows, masks, and other items. We also depend on the forest for deer and elk and other game animals to feed our families. How will we be able to live off the land if it is ruined to harvest one kind of tree?"

Hal added, "Yew habitat is old growth forest. Remove that and yew species will decline. The yew is difficult to start from seed, and it produces few seeds, which only germinate after passing through the gut of some animal. It's a shade tolerant species, slow growing, and is a favored browse food for elk and deer. Harvesting these trees would definitely impact the populations of some animals in this area."

Billie turned to Dick Shaffer. She decided to get to the heart of the matter. "The cancer cure is good but is that the real reason you want our land? You know, there is always some doubt in our minds when the government wants Indian lands. I'll bet the drug company stands to make a big profit from this drug. How much compensation are you offering the tribe? We have done a better job in the last 80 years managing our Tribal lands than you folks did for the 150 years before that. Will our land be able to recover from the loss of this tree?"

The crowd in the Council House was getting unruly. Jim decided it was time to call for a vote. "It's time for the Planning Committee to consider the advice of the experts. We will reconvene in two hours and let you know our decision."

Jim had heard so many contradictory statements his head was spinning. How should he vote?

Questions

1. What tree does the drug company Bristol-Myers want to harvest?

2. What important substance is contained within the tree?

3. What part of the tree contains the substance?

4. Why is the drug Taxol valuable to humans?

5. Where does the tree grow?

6. What "function" does the tree have in its natural environment?

7. How many trees must be harvested to treat one person?

8. How do the Quinault Indians traditionally use the tree?

9. What percent of the yew trees have a diameter smaller than the optimum size for collection?

10. Why can't the drug company just collect the bark?

11. Why can't the drug company grow the yew tree in a tree farm?

Originally published at http://www.sciencecases.org/taxol/taxol.asp

CHAPTER 13: ATOMIC SPECTROSCOPY

1. CONTINUOUS SPECTRUM

A rainbow is an example of a continuous spectrum. Here, the colors displayed are within the visible spectrum (between 380-760 nm). Light in this wavelength range is visible to the naked eye. Unlike the visible spectrum, light that is of different wavelengths (see the electromagnetic spectrum below) is not visible. Looking at Figure x.x, note the different areas of the light (or electromagnetic spectrum). Areas of light that possess short wavelengths are located on the left of the spectrum. All wavelengths from UV (ultraviolet) to γ (gamma) range have the potential to ionize tissues and/or DNA. As a result, individuals who have been exposed to large amounts of these types of radiation in acute time periods could develop cancer. In contrast, visible light (see the rainbow area in Figure x.x) and radiation on the right side of the spectrum has longer wavelengths and does not have the potential to ionize tissues and/or DNA. Visible, infrared (labeled IR), microwave, and radio waves are classified as being non-ionizing radiation and have not been linked to cancer.
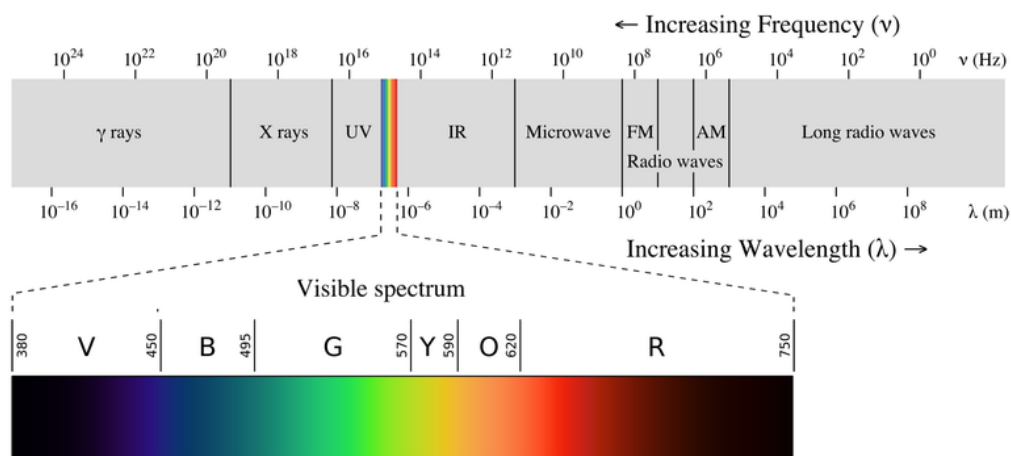

Figure 13.1: *The electromagnetic spectrum is an example of a continuous spectrum. It contains various frequencies (cycle/time) and wavelengths. Image used with permission (CC BY-SA 3.0; Philip Ronan, Gringer).*

Please be aware of what types of light are ionizing and nonionizing. Do not memorize the wavelengths or frequencies of the electromagnetic spectrum. It is important that you know that the electromagnetic spectrum is an example of a continuous spectrum.
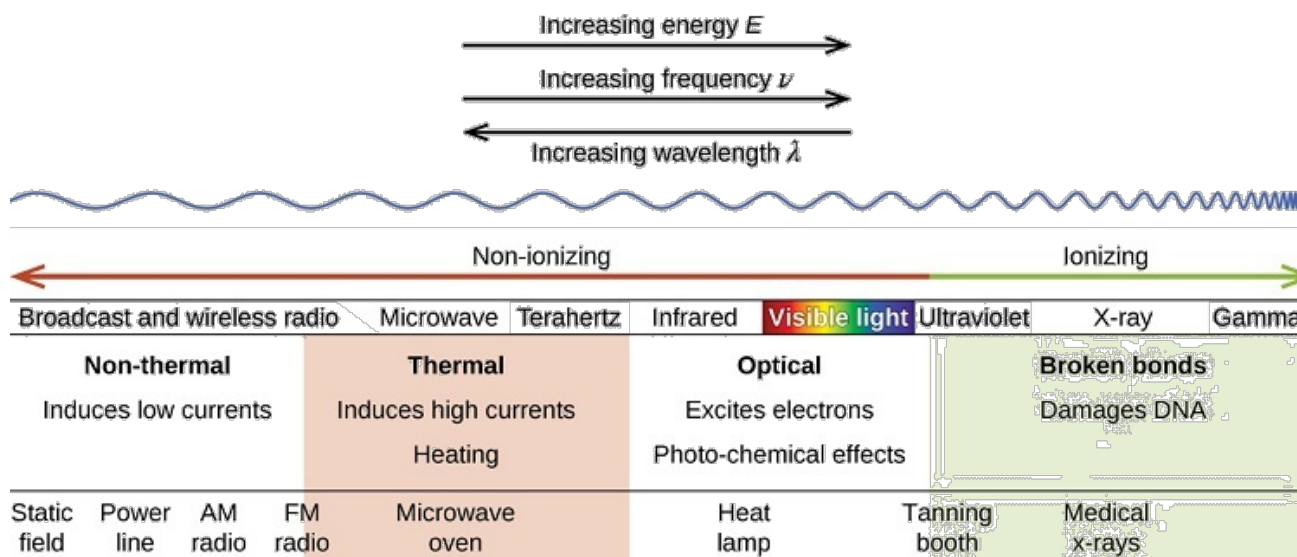

Figure 13.2: *Lower frequency, lower-energy electromagnetic radiation is nonionizing, and higher frequency, higher-energy electromagnetic radiation is ionizing. Image used with permission. (CC BY-SA, OpenStax)*

Atomic Emission Spectra

The electrons in an atom tend to be arranged in such a way that the energy of the atom is as low as possible. The **ground state** of an atom is the lowest energy state of the atom. When those atoms are given energy, the electrons absorb the energy and move to a higher energy level. These energy levels of the electrons in atoms are quantized, meaning again that the electron must move from one energy level to another in discrete steps rather than continuously. An **excited state** of an atom is a state where its potential energy is higher than the ground state. An atom in the excited state is not stable. When it returns back to the ground state (Figure X.3), it releases the energy that it had previously gained often in the form of electromagnetic radiation (although it can be released via heat).

Figure 13.3: *Gas discharge tubes are enclosed glass tubes filled with a gas at low pressure through which an electric current is passed. Electrons in the gaseous atoms first become excited, and then fall back to lower energy levels, emitting light of a distinctive color in the process. Shown are gas discharge tubes of helium, neon, argon, krypton, and xenon.*
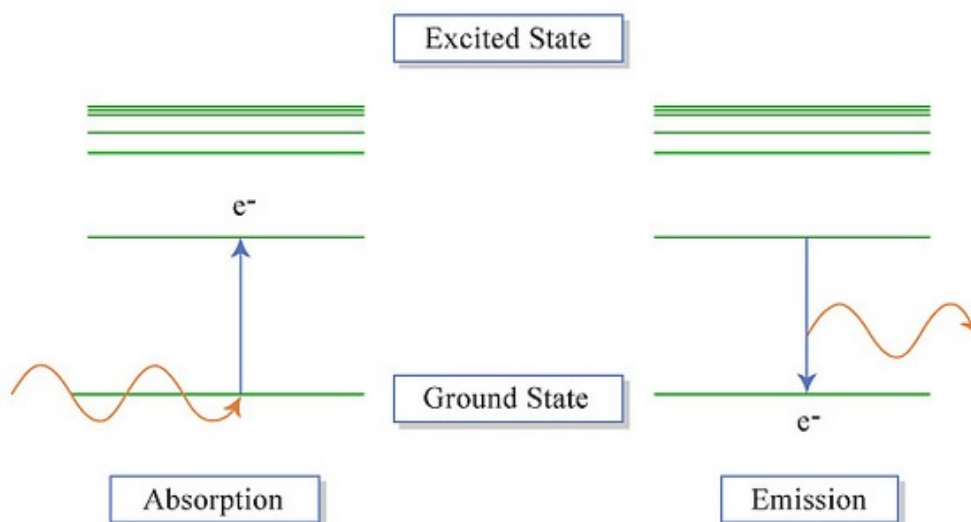
Figure 13.4: *Atomic absorption and emission in excited and ground states. Image used with permission (CC BY-SA-NC 4.0; MIT OpenCourseWare).*

Atoms can gain energy to induce these transitions from various sources. The gases in the image below have been excited with the use of electrical current. The atoms in each of these noble gases produce distinctive colors that can be used to identify the elements (Figure 13.4). Each of these species contains a different number of electrons that can undergo different types of excitations. In turn, each gas produces a signature color.

Figure 13.5: *Flame Test demonstration.*

Metal Ion	Flame Color
Li	Red
Na	Orange
Ca	Orange-red
Sr	Red
K	Light Purple
Ba	Light green
Cu	Blue

2. DISCONTINUOUS SPECTRA

If the light emitted from the excited atoms is viewed through a prism, then individual patterns of lines will be produced. These lines are called spectra and correspond to fingerprint wavelengths (symbol for wavelength is $\lambda\lambda$) for a specific element. Figure 13.6 illustrates how the light from excited electrons can be diffracted to produce line spectra for the elements of hydrogen, helium, and iron. The specific elements produce wavelengths within the visible spectrum (between 400-700 nm) and can be seen by the naked eye. In order to obtain the numerical wavelengths (in nanometers), one would need to employ some type of detector.
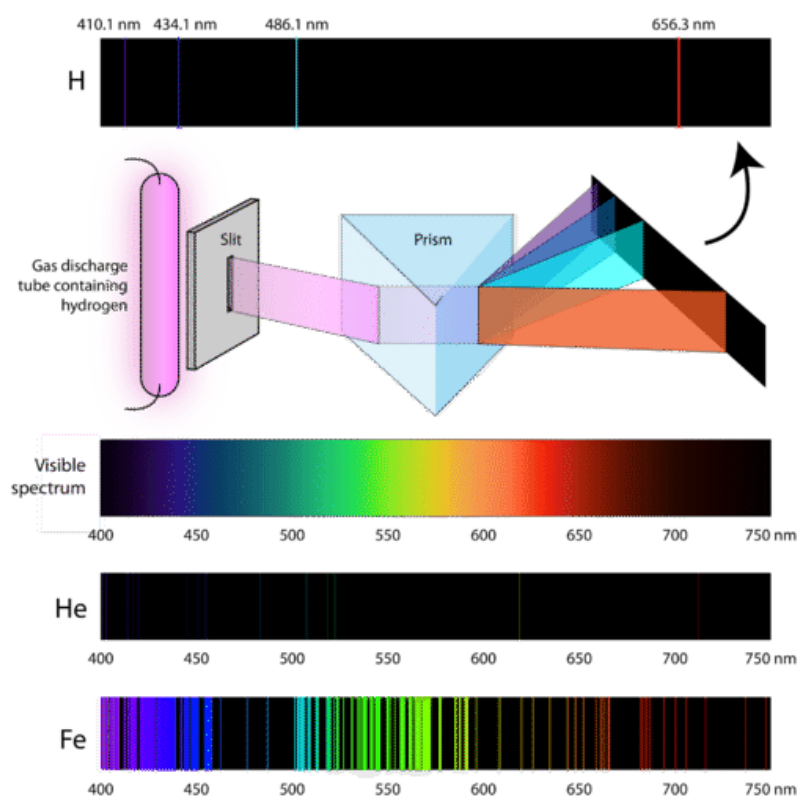
Figure 13.6: *When light from a hydrogen gas discharge tube is passed through a prism, the light is split into four visible lines. Each of these spectral lines corresponds to a different electron transition from a higher energy state to a lower energy state. Every element has a unique atomic emission spectrum, as shown by the examples of helium (He) and iron (Fe).*

EXAMPLE 1

Which statements is/are true?

a. Microwaves can give you cancer.

b. When exploding fireworks, you will see the color when the metal atoms absorb energy from the detonater.

c. When using an AA or an AE spectrometer, a scientist will obtain a line spectra, not continuous spectra.

d. The flame test gives specific colors for metal atoms.

e. Gamma rays are ionizing and can cause cancer.

f. In the light spectrum, you can see IR and visible with only your eyes.

g. Continuous spectra can be used to identify an atom.

Figure 13.7: *Spectral lines. Image used with permission (Public Domain; Jhausauer).*

KEY TAKEAWAYS

❖   Atomic emission spectra are produced when excited electrons return to the ground state.

❖   When electrons return to a lower energy level, they emit energy in the form of light.

❖   Bohr's model suggests each atom has a set of unchangeable energy levels and electrons in the electron cloud of that atom must be in one of those energy levels.

❖   Bohr's model suggests that the atomic spectra of atoms are produced by electrons gaining energy from some source, jumping up to a higher energy level, then immediately dropping back to a lower energy level and emitting the energy difference between the two energy levels.

❖   The existence of the atomic spectra is support for Bohr's model of the atom.

❖   Bohr's model was only successful in calculating energy levels for the hydrogen atom.

❖   The emitted light corresponds to energies of the specific electrons.

Vocabulary

- Emission spectrum (or atomic spectrum): The unique pattern of light given off by an element when it is given energy

- Ground state: to be in the lowest energy level possible.

- Excited state: to be in a higher energy level.

3. ATOMIC SPECTROSCOPY APPLICATIONS

Sample Preparation for Atomic Absorption or Atomic Emission

LEARNING OBJECTIVES
1. Understand why samples need to be digested.
2. Know what type of elements are detected by using AA or AE
3. Recall practical applications of AA or AE (what businesses use these methods)

Chemists employ atomic spectrophotometers to determine the identity and/or concentration of a metallic species. Samples must be in liquid form before being placed in the analyzer. In order to do this, a chemist will use certain acids (nitric or hydrochloric) to extract the metallic component of a sample. This process is called digestion and will not affect the analysis of the sample.

Once the sample has transformed into liquid form, it enters the spectrophotometer by a capillary tube. Then, it is atomized, or transformed into fine mist, by a flame. A light source (cathode lamp) bombards the misted sample. The metallic atoms inside the sample gain energy from the light source and jump to excited states. At different intervals of time, the excited atoms release energy and fall back to their ground states. This quantized energy that is involved in the absorption (AA) or emission (AE) process corresponds to a fingerprint wavelength pattern that can be used to identify a specific metal atom.

Applications

AA or AE spectrometers have been used in many different industrial and academic settings. For example, a medical laboratory could detect the type and amount of toxic metals that could be present in patient's urine or blood. Environmental scientists could monitor metal pollutants in soil and water. The pharmaceutical industry uses these machines to determine if a metal catalyst after a drug has been purified. Lastly, the mining industry would utilize these devices to detect the quantity and presence of precious metals like gold and silver.

Academic and industrial laboratories consider several factors before selecting spectrometer. For example, some labs require a large number of samples to be analyzed in one day while other labs might use the instrument occasionally. Specific analyzers might require a smaller amount of sample. In addition, a toxicology lab might need an instrument to report values in micro or nanograms. Lastly, academic (more often than industrial) facilities must consider the cost of the analyzer before purchasing.

Other options besides flame based AA/AE are graphite furnace (GFAA) and inductively coupled plasma (ICP-AE or ICP-OES). With the GFAA method, a furnace is used to excite the metallic sample. This technique can detect lower concentrations of metal than a flame AA/AE. Also, smaller volumes of sample are needed for a GFAA. ICP machines utilize a plasma (gas with charged ions) for the excitation process. Some of these instruments can directly analyze solid samples. Unfortunately, ICP-AE instruments are slower in producing data. Peruse Table 4.3.14.3.1 and note the general differences between the instruments.

Instrument	Levels of detection	Volume of sample required	Elements analyzed per unit of time	Range of cost
Flame AA/AE	High ppb	>5.0 mL	1 element per 3-10 seconds	$15,000-$25,000
Graphite Furnace AA	Mid ppb	<5.0 mL	1 element per 2-3 minutes	$40,000-$70,000
ICP-AES (OES)	Mid ppb	>5.0 mL	73 different elements per minute	$70,000-$100,000
ICP-MS	Low ppb	>5.0 mL	80 elements (isotopes) per 3 minutes	$150,000-$250,000

Units of Low Concentration: Parts per billion (ppb)

The letters ppb represent a concentration parts per billion. This translates to the metal atom being one part while the sample contains a billion parts. Imagine measuring one inch in 16,000 miles or counting one cent in $10 million dollars. These two values are comparable to one ppb. In water chemistry, ppb is often referred to as µg of contaminant per liter of a sample. Table 4.3.14.3.1 above shows that a flame AA/AE detects only large amounts of ppb. This would be the least sensitive technique of the three listed.

Exercise: Analysis of Materials Using AA and AE

Forensic science and bushfires: part 1 – discrimination of matches

As recent issues of the Bulletin have suggested, investigating the causes of bushfires is a challenging exercise. It is often difficult to make definitive assessments when so many volatile variables, such as climatic conditions, come into play.

Police services also face a difficult task when investigating arson fires. It can be an uphill battle to identify suspects and gather enough physical and circumstantial evidence to mount a case. This Bulletin looks at the first of two recently published studies that show how developments in forensic science are providing tools to assist arson investigators meet these challenges.

Matches are one of the most common means of igniting fires. First-responding fire crews or investigators may locate burned or unburned matches near a point of ignition, but it may not always be clear whether the matches found were the source of ignition. In cases where serial arson is occurring, burned or unburned matches may be found at multiple fire scenes. Suspects are sometimes found with matches in their possession. Being able to link matches from a fire scene with matches from other fire scenes, or matches found on a suspect, can provide police with valuable corroborative evidence.

Researchers from the National Research Institute of Police Science in Chiba, Japan have shown that it is possible to forensically discriminate matches by combining observations such as the shape of the matchstick and the colour of the match head with analysis of the chemical elements of the matches (Kazamatsu, Suzuki, Sugita and Suzuki 2005). Kazamatsu et al. used a technique called inductively coupled plasma-atomic emission spectrometry (ICP-AES) to conduct simultaneous multi-elemental analysis on burned and unburned wood and paper matches. This allowed them to compare the levels of magnesium, aluminium, calcium, iron, zinc and barium in a sample of matches. Using all of these elements, all 28 pairs could be clearly discriminated from one another in both burned and unburned samples.

Kazamatsu et al. also used X-ray diffraction analysis (XRD) to investigate differences in the crystal structures of burned and unburned matches. They burned matches for one second, two seconds and until they burned out, finding

that all crystals were destroyed in the first second and longer burning times did not affect the crystal structure. They concluded these results show that "match heads from a single source should show similar elemental compositions even after combustion" (Kazamatsu et al.: 3).

Kazamatsu et al. note that matches found at fire scenes are usually combusted, while those found with suspects are usually unused. They advise that a sample of the unburned matches should be combusted to allow comparison. Their work demonstrates the scientific validity of this comparison, without a need to control the burning conditions of the matches.

The work of Kazamatsu et al. has shown that it is possible to scientifically link matches found at one fire scene with those found at another fire scene or in the possession of a suspect. By showing that burned matches from a given matchbox or matchbook retain chemical elements that discriminate them from matches in other samples, they have provided arson investigators with a potentially vital evidentiary tool. The question then becomes whether arson investigators have access to the scientific techniques necessary to make use of it.

a. In this article, what material are scientists analyzing? Why are they doing this?

b. What method-AA or AE are they using the determine the metals of the interest?

c. What metals does this article mention?

d. Why are they using XRD in this article?

This module provides an introduction to Atomic Emission Spectroscopy (AES). AES is a broad area that includes several analytical chemistry techniques focused on elemental analysis, the identification, quantification, and (sometimes) speciation of the elemental makeup of a sample. AES can be an extremely useful tool and is utilized in academic and industrial settings within biological and chemical sciences. It is mainly used in quantitative analysis, but can be used in qualitative work as well.

Atomic spectroscopy began with the realization in the mid-19th century that salts in a flame could emit light of wavelength specific to metallic elements introduced to the flame as powders or solutions, and that light of the same wavelength might be missing from emission from stars (including the sun) because the elements absorbed light. The figure illustrates that sodium emits light at 588.9 nm and 589.5 nm (if the atoms are hot enough), or absorbs light if the atoms are cold. "Hot" and "cold" are vague, and the way to know what wavelengths correspond to which elements aren't obvious. We discuss this later.

Prior to 1922, atomic emission was used to qualitatively identify elements, but was too imprecise for quantitative analysis. Lester Strock developed the use of internal standards (see our page on internal standards as well) to compensate for the sample-to-sample and time-dependent variations in signal generation from a fixed quantity of analyte. Up to the end of the Second World War, the common atomic emission sources were flames, arcs, and sparks (the latter the result of applying a sufficiently high electrical potential between two conducting electrodes to cause ionization of the gas between the electrodes). In the next three decades, there was a burst of creativity, leading to the use of low pressure sources (hollow cathode lamps, glow discharges, electrodeless discharge lamps), atmospheric pressure plasmas (inductively coupled plasma, DC plasma), and laser-initiated plasmas (laser microprobe, laser-induced breakdown) for sampling and excitation of materials. While the details and experimental parameters vary among these sources, the essentials of turning bulk materials into individual atoms, putting energy into the atoms to excite them, and then observing light emitted by those atoms as they drop to lower energies is universal.

Atoms can only exist in certain discrete energy levels. Typically, at low energies, the levels are far apart. At higher energies, they are closer together. At sufficiently high energy, an electron is removed and the atom ionized. The ion has widely spaced energy levels, that in turn get closer and closer together until another electron can be removed. This process can continue until all the electrons are ionized and the nucleus is bare. The only common fully-ionized species is H ion, a bare proton.

A visual way to understand that light emission and absorption occur at the same wavelengths is to sketch a Grotrian diagram (named for Walter Grotrian, a German astronomer from the first half of the 20th century). An atom (or molecule) can go from a lower to a higher energy state by absorbing light or by colliding with another atom or ion with sufficient energy. By convention, emission occurs from an atom that was excited to its upper state by collision or absorption of ambient light. Fluorescence occurs from an atom that was excited to its upper state by light specfically supplied for that purpose.

The inductively coupled plasma (ICP) was developed by Velmer Fassel & Stan Greenfield in the 1960s. The following is a picture showing the highlights of an ICP. There are MANY people that have worked with an ICP in research. Click here to see more information.

The torch itself has a diameter of 0.5 to 1 inch (1.27-2.54 cm). The magnetic field oscillates at 27.2 MHz on the RF coil. Typically argon gas is the plasma gas and nebulizer gas (with the sample). The plasma formed contains a high proportion of cations and electrons. The electron density in a plasma is on the order of 10^{13}-10^{15} electrons/cm^3.

It is relatively simple chemistry! Some of the background that exists is from Ar, OH from H_2O, Black Body, and N_2 (from air). This is much hotter than a flame (10,000 K), which causes a high level of ionization for elements with low ionization energy (which are?). There is more complete atomization/excitation. Based on the flow rates, the sample is in the observation region for ~2.5 msec. This system has good selectivity despite the many emission lines excited. Usually for a particular matrix, one can find an emission line that either has few interferences or for which interferences can be subtracted. The ICP is relatively stable, with relative standard deviation of the signal at ~1-2%. The linearity of response is 5-7 orders of magnitude since there is essentially no self absorption. General limits of detection are on the order of 1-10 ppb for most analytes, but the LODs do vary based on the method of analyte introduction! Multi-detector systems can be used as well.

CHAPTER 14: STANDARDS AND CALIBRATION

1. ANALYTICAL TANDARDS

To standardize an analytical method we use standards containing known amounts of analyte. The accuracy of a standardization, therefore, depends on the quality of the reagents and glassware used to prepare these standards. For example, in an acid–base titration the stoichiometry of the acid–base reaction defines the relationship between the moles of analyte and the moles of titrant. In turn, the moles of titrant is the product of the titrant's concentration and the volume of titrant needed to reach the equivalence point. The accuracy of a titrimetric analysis, therefore, can be no better than the accuracy to which we know the titrant's concentration.

Primary and Secondary Standards. We divide analytical standards into two categories: primary standards and secondary standards. A primary standard is a reagent for which we can dispense an accurately known amount of analyte. For example, a 0.1250-g sample of $K_2Cr_2O_7$ contains 4.249×10^{-4} moles of $K_2Cr_2O_7$. If we place this sample in a 250-mL volumetric flask and dilute to volume, the concentration of the resulting solution is 1.700×10^{-3} M. A primary standard must have a known stoichiometry, a known purity (or assay), and it must be stable during long-term storage. Because of the difficulty in establishing the degree of hydration, even after drying, a hydrated reagent usually is not a primary standard.

Reagents that do not meet these criteria are **secondary standards**. The concentration of a secondary standard must be determined relative to a primary standard. The base NaOH is an example of a secondary standard. Commercially available NaOH contains impurities of NaCl, Na_2CO_3, and Na_2SO_4, and readily absorbs H_2O from the atmosphere. To determine the concentration of NaOH in a solution, it is titrated against a primary standard weak acid, such as potassium hydrogen phthalate, $KHC_8H_4O_4$.

Other Reagents. Preparing a standard often requires additional reagents that are not primary standards or secondary standards. Preparing a standard solution, for example, requires a suitable solvent, and additional reagents may be need to adjust the standard's matrix. These solvents and reagents are potential sources of additional analyte, which, if not accounted for, produce a determinate error in the standardization. If available, reagent grade chemicals conforming to standards set by the American Chemical Society should be used.[3] The label on the bottle of a reagent grade chemical (Figure 5.1) lists either the limits for specific impurities, or provides an assay for the impurities. We can improve the quality of a reagent grade chemical by purifying it, or by conducting a more accurate assay. As discussed later in the chapter, we can correct for contributions to Stotal from reagents used in an analysis by including an appropriate blank determination in the analytical procedure.

Preparing Standard Solutions. It is often necessary to prepare a series of standards, each with a different concentration of analyte. We can prepare these standards in two ways. If the range of concentrations is limited to one or two orders of magnitude, then each solution is best prepared by transferring a known mass or volume of the pure standard to a volumetric flask and diluting to volume.

When working with larger ranges of concentration, particularly those extending over more than three orders of magnitude, standards are best prepared by a serial dilution from a single stock solution. In a serial dilution we prepare the most concentrated standard and then dilute a portion of it to prepare the next most concentrated standard. Next, we dilute a portion of the second standard to prepare a third standard, continuing this process until all we have prepared

all of our standards. Serial dilutions must be prepared with extra care because an error in preparing one standard is passed on to all succeeding standards.
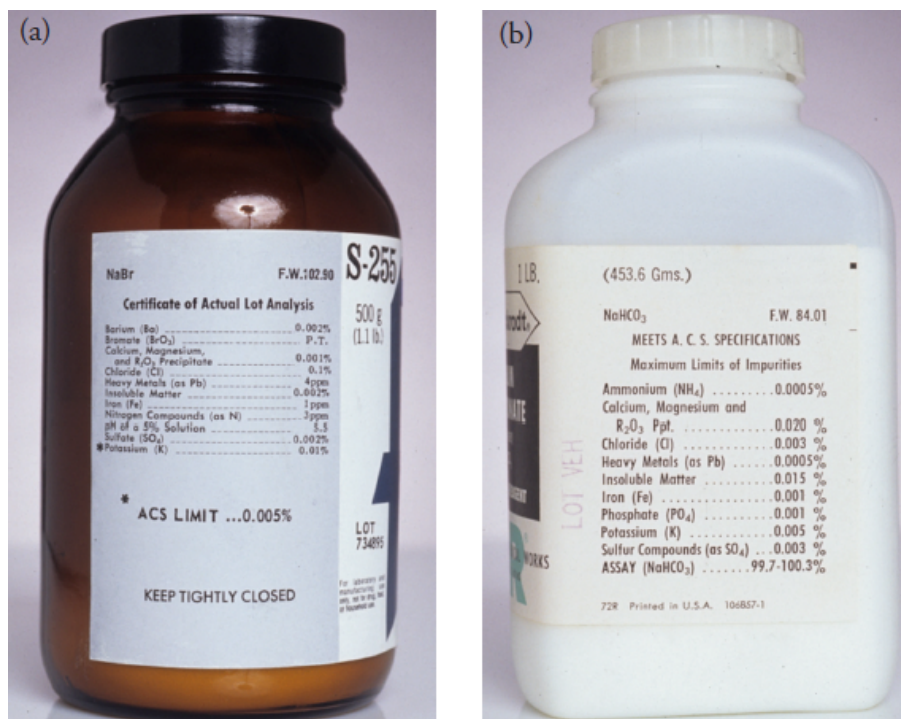

Figure 14.1: *Examples of typical packaging labels for reagent grade chemicals. Label (a) provides the manufacturer's assay for the reagent, NaBr. Note that potassium is flagged with an asterisk (*) because its assay exceeds the limits established by the American Chemical Society (ACS). Label (b) does not provide an assay for impurities, but indicates that the reagent meets ACS specifications. An assay for the reagent, NaHCO3 is provided.*

2: CALIBRATING THE SIGNAL

The accuracy of our determination of the amount or other property of the analyte depends on how accurately we can measure the signal. We measure signals using equipment, such as glassware and balances, and instrumentation, such as spectrophotometers and pH meters. To minimize determinate errors affecting the signal, we first calibrate our equipment and instrumentation.

Here are two examples of how we calibrate signals. When the signal is a measurement of mass, we determine S_{total} using an analytical balance. To calibrate the balance's signal we use a reference weight that meets standards established by a governing agency, such as the National Institute for Standards and Technology or the American Society for Testing and Materials. An electronic balance often includes an internal calibration weight for routine calibrations, as well as programs for calibrating with external weights. In either case, the balance automatically adjusts S_{total} to match S_{std}.

We also must calibrate our instruments. For example, we can evaluate a spectrophotometer's accuracy by measuring the absorbance of a carefully prepared solution of 60.06 mg/L $K_2Cr_2O_7$ in 0.0050 M H_2SO_4, using 0.0050 M H_2SO_4 as a reagent blank. An absorbance of 0.640 ± 0.010 absorbance units at a wavelength of 350.0 nm indicates that the spectrometer's signal is properly calibrated.
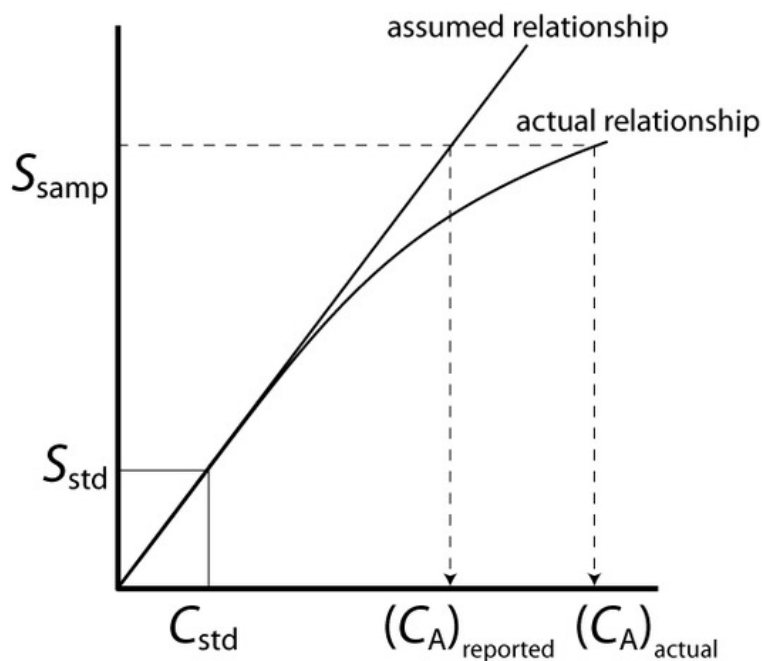
391

Figure 14.2: *Example showing how a single-point standardization leads to a determinate error in an analyte's reported concentration if we incorrectly assume that the value of kA is constant.*

3: DETERMINING THE SENSITIVITY

The simplest way to determine the sensitivity is by a **single-point standardization** in which we measure the signal for a standard containing a known concentration of analyte. Having determined the value for k_A, we can calculate the concentration of analyte in any sample by measuring its signal and calculating its value. A single-point standardization is the least desirable method for standardizing a method. There are at least two reasons for this. First, any error in our determination of this value carries over into our calculation of our analyte's value. Second, our experimental value is for a single concentration of analyte. Extending this value to other concentrations of analyte requires us to assume a linear relationship between the signal and the analyte's concentration, an assumption that often is not true. Figure Y.3.1 shows how assuming a constant value of k_Ak_A may lead to a determinate error in the analyte's concentration. Despite these limitations, single-point standardizations find routine use when the expected range for the analyte's concentrations is small. Under these conditions it is often safe to assume that k_Ak_A is constant (although you should verify this assumption experimentally). This is the case, for example, in clinical labs where many automated analyzers use only a single standard.

The preferred approach to standardizing a method is to prepare a series of standards, each containing the analyte at a different concentration. Standards are chosen such that they bracket the expected range for the analyte's concentration. A **multiple-point standardization** should include at least three standards, although more are preferable. A plot of S_{std} vs. C_{std} is known as a **calibration curve**. The exact standardization, or calibration relationship is determined by an appropriate curve-fitting algorithm.

There are at least two advantages to a multiple-point standardization. First, although a determinate error in one standard introduces a determinate error into the analysis, its effect is minimized by the remaining standards. Second, by

measuring the signal for several concentrations of analyte we no longer must assume that the value of k_Ak_A is independent of the analyte's concentration. Constructing a calibration curve similar to the "actual relationship" in Figure Y.3.1 is possible.

External Standards. The most common method of standardization uses one or more **external standards**, each containing a known concentration of analyte. We call them "external" because we prepare and analyze the standards separate from the samples.

Appending the adjective "external" to the noun "standard" might strike you as odd at this point, as it seems reasonable to assume that standards and samples must be analyzed separately. As you will soon learn, however, we can add standards to our samples and analyze them simultaneously.

Example 14.1

A spectrophotometric method for the quantitative analysis of Pb^{2+} in blood yields an Sstd of 0.474 for a single standard whose concentration of lead is 1.75 ppb What is the concentration of Pb^{2+} in a sample of blood for which S_{samp} is 0.361?
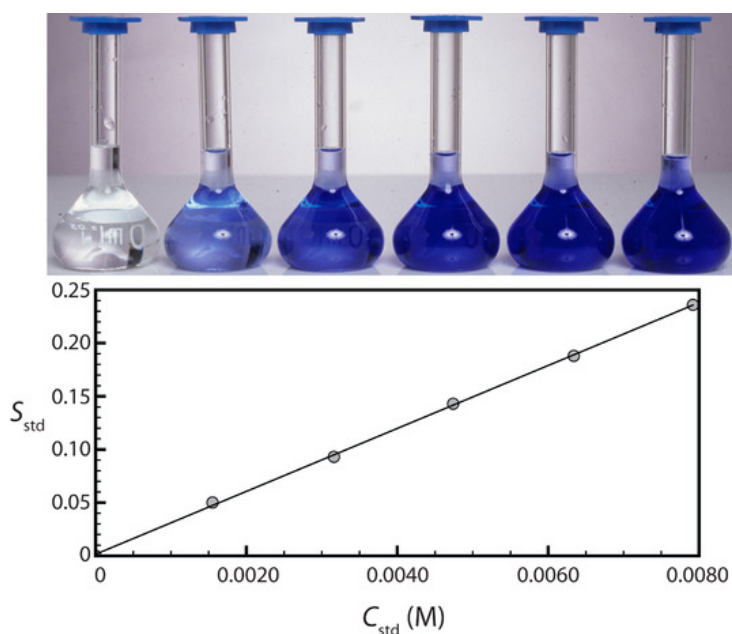
Figure 14.3: *Shown at the top is a reagent blank (far left) and a set of five external standards for Cu^{2+} with concentrations increasing from left to right. Shown below the external standards is the resulting normal calibration curve. The absorbance of each standard, Sstd, is shown by the filled circles.*

Figure 14.2 shows a typical multiple-point external standardization. The volumetric flask on the left is a reagent blank and the remaining volumetric flasks contain increasing concentrations of Cu^{2+}. Shown below the volumetric flasks is the resulting calibration curve. Because this is the most common method of standardization the resulting relationship is called a **normal calibration curve**.

When a calibration curve is a straight-line, as it is in Figure Y.3.2, the slope of the line gives the value of kA. This is the most desirable situation since the method's sensitivity remains constant throughout the analyte's concentration range. When the calibration curve is not a straight-line, the method's sensitivity is a function of the analyte's concentration. In Figure Y.3.2, for example, the value of kA is greatest when the analyte's concentration is small and decreases continu-

ously for higher concentrations of analyte. The value of k_A at any point along the calibration curve in Figure 14.2 is given by the slope at that point. In either case, the calibration curve provides a means for relating S_{samp} to the analyte's concentration.

Example 14.2

A second spectrophotometric method for the quantitative analysis of Pb^{2+} in blood has a normal calibration curve for which

$$S_{std} = (0.296\ ppb^{-1}) \times C_{std} + 0.003$$

What is the concentration of Pb^{2+} in a sample of blood if S_{samp} is 0.397?

Solution

To determine the concentration of Pb^{2+} in the sample of blood we replace S_{std} in the calibration equation with S_{samp} and solve for C_A.

$$C_A = \frac{S_{samp} - 0.003}{0.296\ ppb^{-1}} = \frac{0.397 - 0.003}{0.296\ ppb^{-1}} = 1.33\ ppb$$

It is worth noting that the calibration equation in this problem includes an extra term that does not appear in the equation. Ideally, we expect the calibration curve to have a signal of zero when C_A is zero. This is the purpose of using a reagent blank to correct the measured signal. The extra term of +0.003 in our calibration equation results from the uncertainty in measuring the signal for the reagent blank and the standards.

Exercise 14.3

Figure 14.3 shows a normal calibration curve for the quantitative analysis of Cu^{2+}. The equation for the calibration curve is

$$S_{std} = 29.59\ M^{-1} \times C_{std} + 0.0015$$

What is the concentration of Cu^{2+} in a sample whose absorbance, S_{samp}, is 0.114? Compare your answer to a one-point standardization where a standard of 3.16×10^{-3} M Cu^{2+} gives a signal of 0.0931.

(The one-point standardization in this exercise uses data from the third volumetric flask in Figure 5.3.2)

An external standardization allows us to analyze a series of samples using a single calibration curve. This is an important advantage when we have many samples to analyze. Not surprisingly, many of the most common quantitative analytical methods use an external standardization.

There is a serious limitation, however, to an external standardization. When we determine the value of k_A using Equation 5.3.5, the analyte is present in the external standard's matrix, which usually is a much simpler matrix than that of our samples. When using an external standardization, we assume that the matrix does not affect the value of k_A. If this is not true, then we introduce a proportional determinate error into our analysis. This is not the case in Figure Y.3.3, for instance, where we show calibration curves for the analyte in the sample's matrix and in the standard's matrix. In this example, a calibration curve using external standards results in a negative determinate error. If we expect that matrix effects are important, then we try to match the standard's matrix to that of the sample. This is known as **matrix matching**. If we are unsure of the sample's matrix, then we must show that matrix effects are negligible, or use an alternative method of standardization.
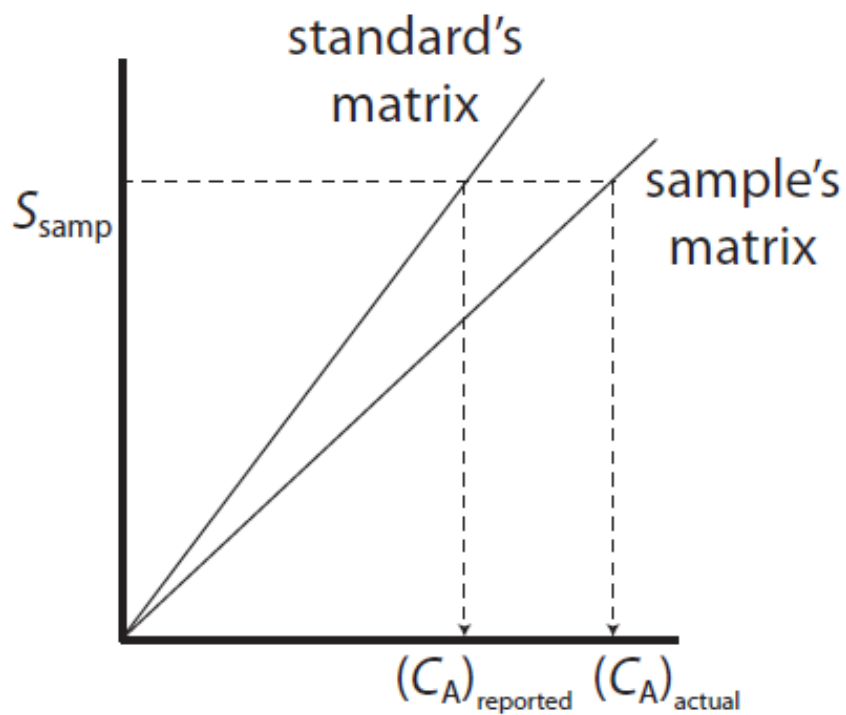
Figure 14.4: Calibration curves for an analyte in the standard's matrix and in the sample's matrix. If the matrix affects the value of k_A, as is the case here, then we introduce a determinate error into our analysis if we use a normal calibration curve.

The matrix for the external standards in Figure Y.3.3, for example, is dilute ammonia, which is added because the $Cu(NH_3)_4^{2+}$ complex absorbs more strongly than Cu^{2+}. If we fail to add the same amount of ammonia to our samples, then we will introduce a proportional determinate error into our analysis.

APPENDIX: PERIODIC TABLE OF THE ELEMENTS

In this chapter, we present some data on the chemical elements. The periodic table, introduced in Chapter 3 "Atoms, Molecules, and Ions", lists all the known chemical elements, arranged by atomic number (that is, the number of protons in the nucleus). The periodic table is arguably the best tool in all of science; no other branch of science can summarize its fundamental constituents in such a concise and useful way.

Many of the physical and chemical properties of the elements are either known or understood based on their positions on the periodic table. Periodic tables are available with a variety of chemical and physical properties listed in each element's box. What follows here is a more complex version of the periodic table than what was presented in Chapter 3 "Atoms, Molecules, and Ions". The Internet is a great place to find periodic tables that contain additional information.

One item on most periodic tables is the atomic mass of each element. For many applications, only one or two decimal places are necessary for the atomic mass. However, some applications (especially nuclear chemistry; see Chapter 15 "Nuclear Chemistry") require more decimal places. The atomic masses in Table 17.1 "The Basics of the Elements of the Periodic Table" represent the number of decimal places recognized by the International Union of Pure and Applied Chemistry, the worldwide body that develops standards for chemistry. The atomic masses of some elements are known very precisely, to a large number of decimal places. The atomic masses of other elements, especially radioactive elements, are not known as precisely. Some elements, such as lithium, can have varying atomic masses depending on how their isotopes are isolated. The web offers many interactive periodic table resources. For example, see http://www.pt-able.com.