

**GENERAL
CHEMISTRY-
PRINCIPLES,
PATTERNS, AND
APPLICATIONS**

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Preface

In this new millenium, as the world faces new and extreme challenges, the importance of acquiring a solid foundation in chemical principles has become increasingly important to understand the challenges that lie ahead. Moreover, as the world becomes more integrated and interdependent, so too do the scientific disciplines. The divisions between fields such as chemistry, physics, biology, environmental sciences, geology, and materials science, among others, have become less clearly defined. The goal of this text is to address the increasing close relationship among various disciplines and to show the relevance of chemistry to contemporary issues in a pedagogically approachable manner. Because of the enthusiasm of the majority of first-year chemistry students for biologically and medically relevant topics, this text uses an integrated approach that includes explicit discussions of biological and environmental applications of chemistry. Topics relevant to materials science are also introduced to meet the more specific needs of engineering students. To facilitate integration of such material, simple organic structures, nomenclature, and reactions are introduced very early in the text, and both organic and inorganic examples are used wherever possible. This approach emphasizes the distinctions between ionic and covalent bonding, thus enhancing the students' chance of success in the organic chemistry course that traditionally follows general chemistry.

The overall goal is to produce a text that introduces the students to the relevance and excitement of chemistry.

Although much of first-year chemistry is taught as a service course, there is no reason that the intrinsic excitement and potential of chemistry cannot be the focal point of the text and the course. We emphasize the positive aspects of chemistry and its relationship to students' lives, which requires bringing in applications early and often.

Unfortunately, one cannot assume that students in such courses today are highly motivated to study chemistry for its own sake. The explicit discussion of biological, environmental, and materials issues from a chemical perspective is intended to motivate the students and help them appreciate the relevance of chemistry to their lives. Material that has traditionally been relegated to boxes, and thus perhaps perceived as peripheral by the students, has been incorporated into the text to serve as a learning tool.

To begin the discussion of chemistry rapidly, the traditional first chapter introducing units, significant figures, conversion factors, dimensional analysis, and so on, has been reorganized. The material has been placed in the chapters where the relevant concepts are first introduced, thus providing three advantages: it eliminates the tedium of the traditional approach, which introduces mathematical operations at the outset, and thus avoids the perception that chemistry is a mathematics course; it avoids the early introduction of operations such as logarithms and exponents, which are typically not encountered again for several chapters and may easily be forgotten when they are needed; and

third, it provides a review for those students who have already had relatively sophisticated high school chemistry and math courses, although the sections are designed primarily for students unfamiliar with the topic.

Our specific objectives include the following:

1. To write the text at a level suitable for science majors, but using a less formal writing style that will appeal to modern students.
2. To produce a *truly* integrated text that gives the student who takes only a single year of chemistry an overview of the most important subdisciplines of chemistry, including organic, inorganic, biological, materials, environmental, and nuclear chemistry, thus emphasizing unifying concepts.
3. To introduce fundamental concepts in the first two-thirds of the chapter, then applications relevant to the health sciences or engineers. This provides a flexible text that can be tailored to the specific needs and interests of the audience.
4. To ensure the accuracy of the material presented, which is enhanced by the author's breadth of professional experience and experience as active chemical researchers.
5. To produce a spare, clean, uncluttered text that is less distracting to the student, where each piece of art serves as a pedagogical device.
6. To introduce the distinction between ionic and covalent bonding and reactions early in the text, and to continue to build on this foundation in the subsequent discussion, while emphasizing the relationship between structure and reactivity.
7. To utilize established pedagogical devices to maximize students' ability to learn directly from the text. These include copious worked examples in the text, problem-solving strategies, and similar unworked exercises with solutions. End-of-chapter problems are designed to ensure that students have grasped major concepts in addition to testing their ability to solve numerical problems. Problems emphasizing applications are drawn from many disciplines.
8. To emphasize an intuitive and predictive approach to problem solving that relies on a thorough understanding of key concepts and recognition of important patterns rather than on memorization. Many patterns are indicated throughout the text as notes in the margin.

The text is organized by units that discuss introductory concepts, atomic and molecular structure, the states of matter, kinetics and equilibria, and descriptive inorganic chemistry. The text breaks the traditional chapter on liquids and solids into two to expand the coverage of important topics such as semiconductors and superconductors, polymers, and engineering materials.

In summary, this text represents a step in the evolution of the general chemistry text toward one that reflects the increasing overlap between chemistry and other disciplines. Most importantly, the text discusses exciting and relevant aspects of biological, environmental, and materials science that are usually relegated to the last few chapters, and it provides a format that allows the instructor to tailor the emphasis to the needs of the class. By the end of **Chapter 6 "The Structure of Atoms"**, the student will have already been introduced to environmental topics such as acid rain, the ozone layer, and periodic extinctions, and to biological topics such as antibiotics and the caloric content of foods. Nonetheless, the new material is presented in such a way as to minimally perturb the traditional sequence of topics in a first-year course, making the adaptation easier for instructors.

Chapter 1

Introduction to Chemistry

As you begin your study of college chemistry, those of you who do not intend to become professional chemists may well wonder why you need to study chemistry. You will soon discover that a basic understanding of chemistry is useful in a wide range of disciplines and career paths. You will also discover that an understanding of chemistry helps you make informed decisions about many issues that affect you, your community, and your world. A major goal of this text is to demonstrate the importance of chemistry in your daily life and in our collective understanding of both the physical world we occupy and the biological realm of which we are a part. The objectives of this chapter are twofold: (1) to introduce the breadth, the importance, and some of the challenges of modern chemistry and (2) to present some of the fundamental concepts and definitions you will need to understand how chemists think and work.

1.1 Chemistry in the Modern World

LEARNING OBJECTIVE

1. To recognize the breadth, depth, and scope of chemistry.

Chemistry is the study of matter and the changes that material substances undergo. Of all the scientific disciplines, it is perhaps the most extensively connected to other fields of study. Geologists who want to locate new mineral or oil deposits use chemical techniques to analyze and identify rock samples. Oceanographers use chemistry to track ocean currents, determine the flux of nutrients into the sea, and measure the rate of exchange of nutrients between ocean layers. Engineers consider the relationships between the structures and the properties of substances when they specify materials for various uses. Physicists take advantage of the properties of substances to detect new subatomic particles. Astronomers use chemical signatures to determine the age and distance of stars and thus answer questions about how stars form and how old the universe is. The entire subject of environmental science depends on chemistry to explain the origin and impacts of phenomena such as air pollution, ozone layer depletion, and global warming. The disciplines that focus on living organisms and their interactions with the physical world rely heavily on biochemistry, the application of chemistry to the study of biological processes. A living cell contains a large collection of complex molecules that carry out thousands of chemical reactions, including those that are necessary for

the cell to reproduce. Biological phenomena such as vision, taste, smell, and movement result from numerous chemical reactions. Fields such as medicine, pharmacology, nutrition, and toxicology focus specifically on how the chemical substances that enter our bodies interact with the chemical components of the body to maintain our health and well-being. For example, in the specialized area of sports medicine, a knowledge of chemistry is needed to understand why muscles get sore after exercise as well as how prolonged exercise produces the euphoric feeling known as “runner’s high.”

Examples of the practical applications of chemistry are everywhere ([Figure 1.1 "Chemistry in Everyday Life"](#)).

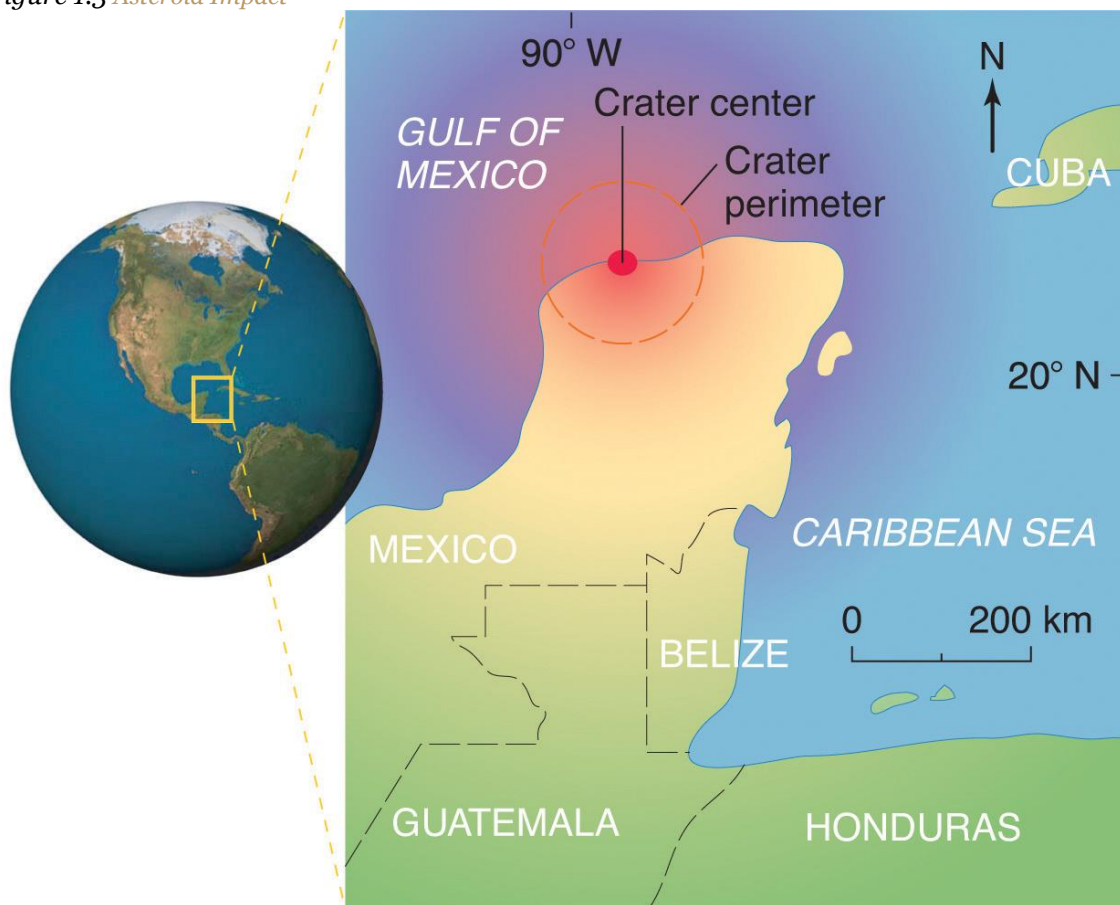
Engineers need to understand the chemical properties of the substances when designing biologically compatible implants for joint replacements or designing roads, bridges, buildings, and nuclear reactors that do not collapse because of weakened structural materials such as steel and cement. Archaeology and paleontology rely on chemical techniques to date bones and artifacts and identify their origins. Although law is not normally considered a field related to chemistry, forensic scientists use chemical methods to analyze blood, fibers, and other evidence as they investigate crimes. In particular, DNA matching—comparing biological samples of genetic material to see whether they could have come from the same person—has been used to solve many high-profile criminal cases as well as clear innocent people who have been wrongly accused or convicted. Forensics is a rapidly growing area of applied chemistry. In addition, the proliferation of chemical and biochemical innovations in industry is producing rapid growth in the area of patent law. Ultimately, the dispersal of information in all the fields in which chemistry plays a part requires experts who are able to explain complex chemical issues to the public through television, print journalism, the Internet, and popular books.

By this point, it shouldn’t surprise you to learn that chemistry was essential in explaining a pivotal event in the history of Earth: the disappearance of the dinosaurs. Although dinosaurs ruled Earth for more than 150 million years, fossil evidence suggests that they became extinct rather abruptly approximately 66 million years ago. Proposed explanations for their extinction have ranged from an epidemic caused by some deadly microbe or virus to more gradual phenomena such as massive climate changes. In 1978 Luis Alvarez (a Nobel Prize–winning physicist), the geologist Walter Alvarez (Luis’s son), and their coworkers discovered a thin layer of sedimentary rock formed 66 million years ago that contained unusually high concentrations of iridium, a rather rare metal (part (a) in [Figure 1.2 "Evidence for the Asteroid Impact That May Have Caused the Extinction of the Dinosaurs"](#)). This layer was deposited at about the time dinosaurs disappeared from the fossil record. Although iridium is very rare in most rocks,

accounting for only 0.0000001% of Earth's crust, it is much more abundant in comets and asteroids. Because corresponding samples of rocks at sites in Italy and Denmark contained high iridium concentrations, the Alvarezes suggested that the impact of a large asteroid with Earth led to the extinction of the dinosaurs. When chemists analyzed additional samples of 66-million-year-old sediments from sites around the world, all were found to contain high levels of iridium. In addition, small grains of quartz in most of the iridium-containing layers exhibit microscopic cracks characteristic of high-intensity shock waves (part (b) in Figure 1.2 "Evidence for the Asteroid Impact That May Have Caused the Extinction of the Dinosaurs"). These grains apparently originated from terrestrial rocks at the impact site, which were pulverized on impact and blasted into the upper atmosphere before they settled out all over the world.

Scientists calculate that a collision of Earth with a stony asteroid about 10 kilometers (6 miles) in diameter, traveling at 25 kilometers per second (about 56,000 miles per hour), would almost instantaneously release energy equivalent to the explosion of about 100 million megatons of TNT (trinitrotoluene). This is more energy than that stored in the entire nuclear arsenal of the world. The energy released by such an impact would set fire to vast areas of forest, and the smoke from the fires and the dust created by the impact would block the sunlight for months or years, eventually killing virtually all green plants and most organisms that depend on them. This could explain why about 70% of *all* species—not just dinosaurs—disappeared at the same time. Scientists also calculate that this impact would form a crater at least 125 kilometers (78 miles) in diameter. Recently, satellite images from a Space Shuttle mission confirmed that a huge asteroid or comet crashed into Earth's surface across the Yucatan's northern tip in the Gulf of Mexico 65 million years ago, leaving a partially submerged crater 180 kilometers (112 miles) in diameter (Figure 1.3 "Asteroid Impact"). Thus simple chemical measurements of the abundance of one element in rocks led to a new and dramatic explanation for the extinction of the dinosaurs. Though still controversial, this explanation is supported by additional evidence, much of it chemical.

Figure 1.3 Asteroid Impact



The location of the asteroid impact crater near what is now the tip of the Yucatan Peninsula in Mexico.

This is only one example of how chemistry has been applied to an important scientific problem. Other chemical applications and explanations that we will discuss in this text include how astronomers determine the distance of galaxies and how fish can survive in subfreezing water under polar ice sheets. We will also consider ways in which chemistry affects our daily lives: the addition of iodine to table salt; the development of more effective drugs to treat diseases such as cancer, AIDS (acquired immunodeficiency syndrome), and arthritis; the retooling of industry to use nonchlorine-containing refrigerants, propellants, and other chemicals to preserve Earth's ozone layer; the use of modern materials in engineering; current efforts to control the problems of acid rain and global warming; and the awareness that our bodies require small amounts of some chemical substances that are toxic when ingested in larger doses. By the time you finish this text, you will be able to discuss these kinds of topics knowledgeably, either as a

beginning scientist who intends to spend your career studying such problems or as an informed observer who is able to participate in public debates that will certainly arise as society grapples with scientific issues.

Summary

Chemistry is the study of matter and the changes material substances undergo. It is essential for understanding much of the natural world and central to many other scientific disciplines, including astronomy, geology, paleontology, biology, and medicine.

KEY TAKEAWAY

- An understanding of chemistry is essential for understanding much of the natural world and is central to many other disciplines.

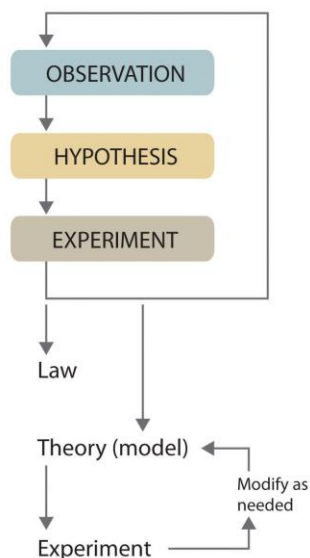
1.2 The Scientific Method

LEARNING OBJECTIVE

1. To identify the components of the scientific method.

Scientists search for answers to questions and solutions to problems by using a procedure called the scientific method. This procedure consists of making *observations*, formulating *hypotheses*, and designing *experiments*, which in turn lead to additional observations, hypotheses, and experiments in repeated cycles ([Figure 1.4 "The Scientific Method"](#)).

Figure 1.4 The Scientific Method



As depicted in this flowchart, the scientific method consists of making observations, formulating hypotheses, and designing experiments. A scientist may enter the cycle at any point.

Observations can be qualitative or quantitative. *Qualitative observations* describe properties or occurrences in ways that do not rely on numbers. Examples of qualitative observations include the following: the outside air temperature is cooler during the winter season, table salt is a crystalline solid, sulfur crystals are yellow, and dissolving a penny in dilute nitric acid forms a blue solution and a brown gas. *Quantitative observations* are measurements, which by definition consist of both a *number* and a *unit*. Examples of quantitative observations include the following: the melting point of crystalline sulfur is 115.21 degrees Celsius, and 35.9 grams of table salt—whose chemical name is sodium chloride—dissolve in 100 grams of water at 20 degrees Celsius. For the question of the dinosaurs' extinction, the initial observation was quantitative: iridium concentrations in sediments dating to 66 million years ago were 20–160 times higher than normal.

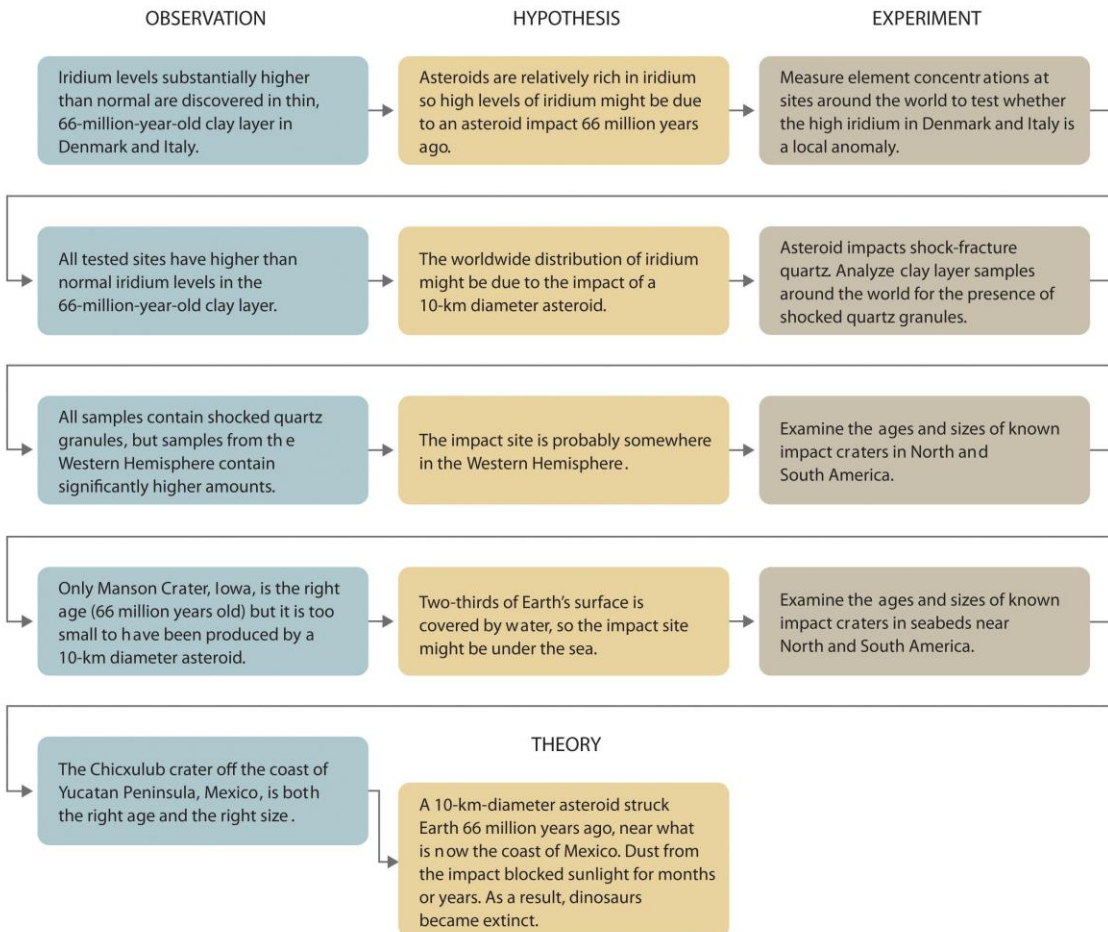
After deciding to learn more about an observation or a set of observations, scientists generally begin an investigation by forming a hypothesis, a tentative explanation for the observation(s). The hypothesis may not be correct, but it puts the scientist's understanding of the system being studied into a form that can be tested. For example, the observation that we experience alternating periods of light and darkness corresponding to observed movements of the sun, moon, clouds, and shadows is consistent with either of two hypotheses: (1) Earth rotates on its axis every 24 hours, alternately exposing one side to the sun, or (2) the sun revolves around Earth every 24 hours. Suitable experiments can be designed to choose between these two alternatives. For the disappearance of the dinosaurs, the hypothesis was that the impact of a large extraterrestrial object caused their extinction. Unfortunately (or perhaps fortunately), this hypothesis does not lend itself to direct testing by any obvious experiment, but scientists can collect additional data that either support or refute it.

After a hypothesis has been formed, scientists conduct experiments to test its validity. Experiments are systematic observations or measurements, preferably made under *controlled* conditions—that is, under conditions in which a single variable changes. For example, in our extinction scenario, iridium concentrations were measured worldwide and compared. A properly designed and executed experiment enables a scientist to determine whether the original hypothesis is valid. Experiments often demonstrate that the hypothesis is incorrect or that it must be modified. More experimental data are then collected and analyzed, at which point a scientist may begin to think that the results are sufficiently reproducible (i.e., dependable) to merit being summarized in a law, a verbal or mathematical description of a phenomenon that allows for general predictions. A law simply says *what* happens; it does not address the question of *why*. One example of a law, the law of definite proportions, which was discovered by the French scientist Joseph Proust (1754–1826), states that a chemical substance always contains the same proportions of

elements by mass. Thus sodium chloride (table salt) always contains the same proportion by mass of sodium to chlorine, in this case 39.34% sodium and 60.66% chlorine by mass, and sucrose (table sugar) is always 42.11% carbon, 6.48% hydrogen, and 51.41% oxygen by mass.^[1] (For a review of common units of measurement, see Essential Skills 1 in Section 1.9 "Essential Skills 1".) The law of definite proportions should seem obvious—we would expect the composition of sodium chloride to be consistent—but the head of the US Patent Office did not accept it as a fact until the early 20th century.

Whereas a law states only *what* happens, a theory attempts to explain *why* nature behaves as it does. Laws are unlikely to change greatly over time unless a major experimental error is discovered. In contrast, a theory, by definition, is incomplete and imperfect, evolving with time to explain new facts as they are discovered. The theory developed to explain the extinction of the dinosaurs, for example, is that Earth occasionally encounters small- to medium-sized asteroids, and these encounters may have unfortunate implications for the continued existence of most species. This theory is by no means proven, but it is consistent with the bulk of evidence amassed to date. Figure 1.5 "A Summary of How the Scientific Method Was Used in Developing the Asteroid Impact Theory to Explain the Disappearance of the Dinosaurs from Earth" summarizes the application of the scientific method in this case.

Figure 1.5 A Summary of How the Scientific Method Was Used in Developing the Asteroid Impact Theory to Explain the Disappearance of the Dinosaurs from Earth



1. Classify each statement as a law, a theory, an experiment, a hypothesis, a qualitative observation, or a quantitative observation.

a. Ice always floats on liquid water.

b. Birds evolved from dinosaurs.

c. Hot air is less dense than cold air, probably because the components of hot air are moving more rapidly.

d. When 10 g of ice were added to 100 mL of water at 25°C, the temperature of the water decreased to 15.5°C after the ice melted.

e. The ingredients of Ivory soap were analyzed to see whether it really is 99.44% pure, as advertised.

2. **Given:** components of the scientific method

Asked for: statement classification

Strategy:

Refer to the definitions in this section to determine which category best describes each statement.

Solution:

- a. This is a general statement of a relationship between the properties of liquid and solid water, so it is a law.
- b. This is a possible explanation for the origin of birds, so it is a hypothesis.
- c. This is a statement that tries to explain the relationship between the temperature and the density of air based on fundamental principles, so it is a theory.
- d. The temperature is measured before and after a change is made in a system, so these are quantitative observations.
- e. This is an analysis designed to test a hypothesis (in this case, the manufacturer's claim of purity), so it is an experiment.

3) Exercise

Classify each statement as a law, a theory, an experiment, a hypothesis, a qualitative observation, or a quantitative observation.

- a. Measured amounts of acid were added to a Roloids tablet to see whether it really "consumes 47 times its weight in excess stomach acid."
- b. Heat always flows from hot objects to cooler ones, not in the opposite direction.
- c. The universe was formed by a massive explosion that propelled matter into a vacuum.
- d. Michael Jordan is the greatest pure shooter ever to play professional basketball.
- e. Limestone is relatively insoluble in water but dissolves readily in dilute acid with the evolution of a gas.
- f. Gas mixtures that contain more than 4% hydrogen in air are potentially explosive.

Answers:

- a. experiment
- b. laws
- c. theory

- d. hypothesis
- e. qualitative observation
- f. quantitative observation

Because scientists can enter the cycle shown in Figure 1.4 "The Scientific Method" at any point, the actual application of the scientific method to different topics can take many different forms. For example, a scientist may start with a hypothesis formed by reading about work done by others in the field, rather than by making direct observations.

It is important to remember that scientists have a tendency to formulate hypotheses in familiar terms simply because it is difficult to propose something that has never been encountered or imagined before. As a result, scientists sometimes discount or overlook unexpected findings that disagree with the basic assumptions behind the hypothesis or theory being tested. Fortunately, truly important findings are immediately subject to independent verification by scientists in other laboratories, so science is a self-correcting discipline. When the Alvarezes originally suggested that an extraterrestrial impact caused the extinction of the dinosaurs, the response was almost universal skepticism and scorn. In only 20 years, however, the persuasive nature of the evidence overcame the skepticism of many scientists, and their initial hypothesis has now evolved into a theory that has revolutionized paleontology and geology.

In Section 1.3 "A Description of Matter", we begin our discussion of chemistry with a description of *matter*. This discussion is followed by a summary of some of the pioneering discoveries that led to our present understanding of the structure of the fundamental unit of chemistry: the *atom*.

Summary

Chemists expand their knowledge by making observations, carrying out **experiments**, and testing **hypotheses** to develop **laws** to summarize their results and **theories** to explain them. In doing so, they are using the **scientific method**.

KEY TAKEAWAY

- Chemists expand their knowledge with the scientific method.
 - [1] You will learn in Chapter 12 "Solids" that some solid compounds do not strictly obey the law of definite proportions.

1.3 A Description of Matter

LEARNING OBJECTIVE

1. To classify matter.

Chemists study the structures, physical properties, and chemical properties of material substances. These consist of matter, which is anything that occupies space and has mass. Gold and iridium are matter, as are peanuts, people, and postage stamps. Smoke, smog, and laughing gas are matter. Energy, light, and sound, however, are not matter; ideas and emotions are also not matter.

The mass of an object is the quantity of matter it contains. Do not confuse an object's mass with its weight, which is a force caused by the gravitational attraction that operates on the object. Mass is a fundamental property of an object that does not depend on its location.^[1] Weight, on the other hand, depends on the location of an object. An astronaut whose mass is 95 kg weighs about 210 lb on Earth but only about 35 lb on the moon because the gravitational force he or she experiences on the moon is approximately one-sixth the force experienced on Earth. For practical purposes, weight and mass are often used interchangeably in laboratories. Because the force of gravity is considered to be the same everywhere on Earth's surface, 2.2 lb (a weight) equals 1.0 kg (a mass), regardless of the location of the laboratory on Earth.

Under normal conditions, there are three distinct *states of matter*: solids, liquids, and gases (Figure 1.6 "The Three States of Matter"). Solids are relatively rigid and have fixed shapes and volumes. A rock, for example, is a solid. In contrast, liquids have fixed volumes but flow to assume the shape of their containers, such as a beverage in a can. Gases, such as air in an automobile tire, have neither fixed shapes nor fixed volumes and expand to completely fill their containers. Whereas the volume of gases strongly depends on their temperature and pressure (the amount of force exerted on a given area), the volumes of liquids and solids are virtually independent of temperature and pressure. Matter can often change from one physical state to another in a process called a physical change. For example, liquid water can be heated to form a gas called steam, or steam can be cooled to form liquid water. However, such changes of state do not affect the chemical composition of the substance.

Pure Substances and Mixtures

A *pure chemical substance* is any matter that has a fixed chemical composition and characteristic properties. Oxygen, for example, is a pure chemical substance that is a colorless, odorless gas at 25°C. Very few samples of matter consist of pure substances; instead, most are mixtures, which are combinations of two or more pure substances in variable proportions in which the individual substances retain their identity. Air, tap water, milk, blue cheese, bread, and dirt are all mixtures. If all portions of a material are in the same state, have no visible boundaries, and are uniform throughout, then the material is homogeneous. Examples of homogeneous mixtures are the air we breathe

and the tap water we drink. Homogeneous mixtures are also called *solutions*. Thus air is a solution of nitrogen, oxygen, water vapor, carbon dioxide, and several other gases; tap water is a solution of small amounts of several substances in water. The specific compositions of both of these solutions are not fixed, however, but depend on both source and location; for example, the composition of tap water in Boise, Idaho, is *not* the same as the composition of tap water in Buffalo, New York. Although most solutions we encounter are liquid, solutions can also be solid. The gray substance still used by some dentists to fill tooth cavities is a complex solid solution that contains 50% mercury and 50% of a powder that contains mostly silver, tin, and copper, with small amounts of zinc and mercury. Solid solutions of two or more metals are commonly called *alloys*.

If the composition of a material is not completely uniform, then it is heterogeneous (e.g., chocolate chip cookie dough, blue cheese, and dirt). Mixtures that appear to be homogeneous are often found to be heterogeneous after microscopic examination. Milk, for example, appears to be homogeneous, but when examined under a microscope, it clearly consists of tiny globules of fat and protein dispersed in water (Figure 1.7 "A Heterogeneous Mixture"). The components of heterogeneous mixtures can usually be separated by simple means. Solid-liquid mixtures such as sand in water or tea leaves in tea are readily separated by *filtration*, which consists of passing the mixture through a barrier, such as a strainer, with holes or pores that are smaller than the solid particles. In principle, mixtures of two or more solids, such as sugar and salt, can be separated by microscopic inspection and sorting. More complex operations are usually necessary, though, such as when separating gold nuggets from river gravel by panning. First solid material is filtered from river water; then the solids are separated by inspection. If gold is embedded in rock, it may have to be isolated using chemical methods.

Homogeneous mixtures (solutions) can be separated into their component substances by physical processes that rely on differences in some physical property, such as differences in their boiling points. Two of these separation methods are distillation and crystallization. Distillation makes use of differences in *volatility*, a measure of how easily a substance is converted to a gas at a given temperature. Figure 1.8 "The Distillation of a Solution of Table Salt in Water" shows a simple distillation apparatus for separating a mixture of substances, at least one of which is a liquid. The most volatile component boils first and is condensed back to a liquid in the water-cooled condenser, from which it flows into the receiving flask. If a solution of salt and water is distilled, for example, the more volatile component, pure water, collects in the receiving flask, while the salt remains in the distillation flask.

Mixtures of two or more liquids with different boiling points can be separated with a more complex distillation apparatus. One example is the refining of crude petroleum into a range of useful products: aviation fuel, gasoline,

kerosene, diesel fuel, and lubricating oil (in the approximate order of decreasing volatility). Another example is the distillation of alcoholic spirits such as brandy or whiskey. This relatively simple procedure caused more than a few headaches for federal authorities in the 1920s during the era of Prohibition, when illegal stills proliferated in remote regions of the United States.

Crystallization separates mixtures based on differences in *solubility*, a measure of how much solid substance remains dissolved in a given amount of a specified liquid. Most substances are more soluble at higher temperatures, so a mixture of two or more substances can be dissolved at an elevated temperature and then allowed to cool slowly. Alternatively, the liquid, called the *solvent*, may be allowed to evaporate. In either case, the least soluble of the dissolved substances, the one that is least likely to remain in solution, usually forms crystals first, and these crystals can be removed from the remaining solution by filtration. **Figure 1.9 "The Crystallization of Sodium Acetate from a Concentrated Solution of Sodium Acetate in Water"** dramatically illustrates the process of crystallization.

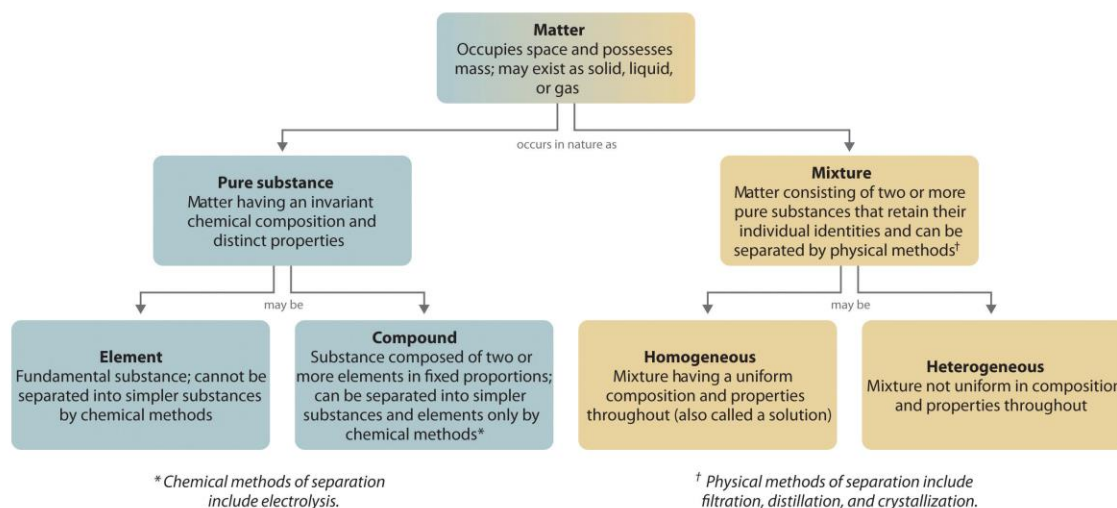
Most mixtures can be separated into pure substances, which may be either elements or compounds. An element, such as gray, metallic sodium, is a substance that cannot be broken down into simpler ones by chemical changes; a compound, such as white, crystalline sodium chloride, contains two or more elements and has chemical and physical properties that are usually different from those of the elements of which it is composed. With only a few exceptions, a particular compound has the same elemental composition (the same elements in the same proportions) regardless of its source or history. The chemical composition of a substance is altered in a process called a chemical change. The conversion of two or more elements, such as sodium and chlorine, to a chemical compound, sodium chloride, is an example of a chemical change, often called a chemical reaction. Currently, about 115 elements are known, but millions of chemical compounds have been prepared from these 115 elements. The known elements are listed in the periodic table (see **Chapter 32 "Appendix H: Periodic Table of Elements"**).

In general, a reverse chemical process breaks down compounds into their elements. For example, water (a compound) can be decomposed into hydrogen and oxygen (both elements) by a process called *electrolysis*. In electrolysis, electricity provides the energy needed to separate a compound into its constituent elements (**Figure 1.10 "The Decomposition of Water to Hydrogen and Oxygen by Electrolysis"**). A similar technique is used on a vast scale to obtain pure aluminum, an element, from its ores, which are mixtures of compounds. Because a great deal of energy is required for electrolysis, the cost of electricity is by far the greatest expense incurred in manufacturing pure aluminum. Thus recycling aluminum is both cost-effective and ecologically sound.

Figure 1.10 The Decomposition of Water to Hydrogen and Oxygen by Electrolysis

The overall organization of matter and the methods used to separate mixtures are summarized in Figure 1.11

"Relationships between the Types of Matter and the Methods Used to Separate Mixtures".



EXAMPLE 2

1. Identify each substance as a compound, an element, a heterogeneous mixture, or a homogeneous mixture (solution).

- filtered tea
- freshly squeezed orange juice
- a compact disc
- aluminum oxide, a white powder that contains a 2:3 ratio of aluminum and oxygen atoms
- selenium

2, **Given:** a chemical substance

Asked for: its classification

Strategy:

A Decide whether a substance is chemically pure. If it is pure, the substance is either an element or a compound. If a substance can be separated into its elements, it is a compound.

B If a substance is not chemically pure, it is either a heterogeneous mixture or a homogeneous mixture. If its composition is uniform throughout, it is a homogeneous mixture.

Solution:

- a. **A** Tea is a solution of compounds in water, so it is not chemically pure. It is usually separated from tea leaves by filtration. **B** Because the composition of the solution is uniform throughout, it is a homogeneous mixture.
- b. **A** Orange juice contains particles of solid (pulp) as well as liquid; it is not chemically pure. **B** Because its composition is not uniform throughout, orange juice is a heterogeneous mixture.
- c. **A** A compact disc is a solid material that contains more than one element, with regions of different compositions visible along its edge. Hence a compact disc is not chemically pure. **B** The regions of different composition indicate that a compact disc is a heterogeneous mixture.
- d. **A** Aluminum oxide is a single, chemically pure compound.
- e. **A** Selenium is one of the known elements.

3. Exercise

Identify each substance as a compound, an element, a heterogeneous mixture, or a homogeneous mixture (solution).

- a. white wine
- b. mercury
- c. ranch-style salad dressing
- d. table sugar (sucrose)

Answers:

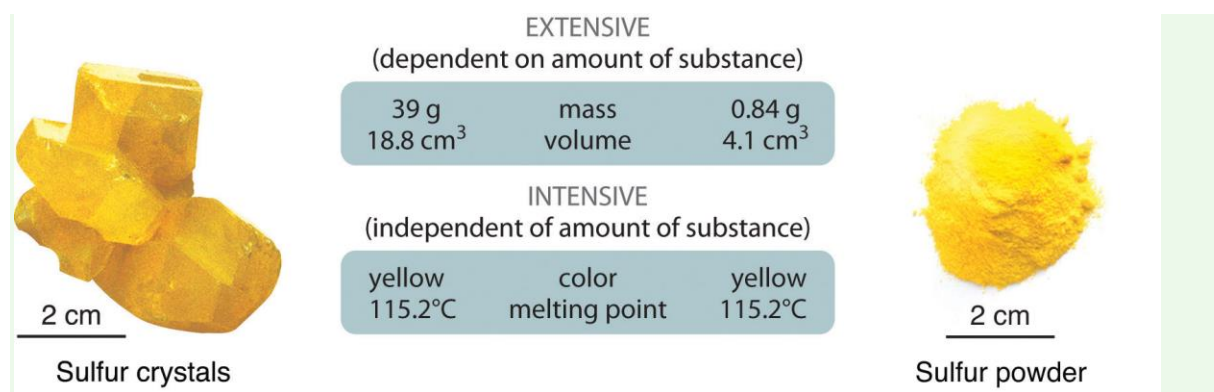
- a. solution
- b. element
- c. heterogeneous mixture
- d. compound

Properties of Matter

All matter has physical and chemical properties. Physical properties are characteristics that scientists can measure without changing the composition of the sample under study, such as mass, color, and volume (the amount of space occupied by a sample). Chemical properties describe the characteristic ability of a substance to react to form new substances; they include its flammability and susceptibility to corrosion. All samples of a pure substance have the same chemical and physical properties. For example, pure copper is always a reddish-brown solid (a physical property) and always dissolves in dilute nitric acid to produce a blue solution and a brown gas (a chemical property).

Physical properties can be extensive or intensive. Extensive properties vary with the amount of the substance and include mass, weight, and volume. Intensive properties, in contrast, do not depend on the amount of the substance; they include color, melting point, boiling point, electrical conductivity, and physical state at a given temperature. For example, elemental sulfur is a yellow crystalline solid that does not conduct electricity and has a melting point of 115.2°C , no matter what amount is examined (Figure 1.12 "The Difference between Extensive and Intensive Properties of Matter"). Scientists commonly measure intensive properties to determine a substance's identity, whereas extensive properties convey information about the amount of the substance in a sample.

Figure 1.12 The Difference between Extensive and Intensive Properties of Matter



Because they differ in size, the two samples of sulfur have different extensive properties, such as mass and volume. In contrast, their intensive properties, including color, melting point, and electrical conductivity, are identical.

Although mass and volume are both extensive properties, their ratio is an important intensive property called density (d). Density is defined as mass per unit volume and is usually expressed in grams per cubic

centimeter (g/cm³). As mass increases in a given volume, density also increases. For example, lead, with its greater mass, has a far greater density than the same volume of air, just as a brick has a greater density than the same volume of Styrofoam. At a given temperature and pressure, the density of a pure substance is a constant:

Equation 1.1

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

Pure water, for example, has a density of 0.998 g/cm³ at 25°C.

The average densities of some common substances are in Table 1.1 "Densities of Common Substances". Notice that corn oil has a lower mass to volume ratio than water. This means that when added to water, corn oil will "float."

Example 3 shows how density measurements can be used to identify pure substances.

Table 1.1 Densities of Common Substances

Substance	Density at 25°C (g/cm ³)
blood	1.035
body fat	0.918
whole milk	1.030
corn oil	0.922
mayonnaise	0.910
honey	1.420

EXAMPLE 3

The densities of some common liquids are in Table 1.2 "Densities of Liquids in Example 3". Imagine you have five bottles containing colorless liquids (labeled A–E). You must identify them by measuring the density of each. Using a pipette, a laboratory instrument for accurately measuring and transferring liquids, you carefully measure 25.00 mL of each liquid into five beakers of known mass (1 mL = 1 cm³). You then weigh each sample on a laboratory balance. Use the tabulated data to calculate the density of each sample. Based solely on your results, can you unambiguously identify all five liquids? ^[2]

Masses of samples: A, 17.72 g; B, 19.75 g; C, 24.91 g; D, 19.65 g; E, 27.80 g

TABLE 1.2 DENSITIES OF LIQUIDS IN EXAMPLE 3

Substance	Density at 25°C (g/cm ³)
water	0.998

Substance	Density at 25°C (g/cm ³)
ethanol (the alcohol in beverages)	0.789
methanol (wood alcohol)	0.792
ethylene glycol (used in antifreeze)	1.113
diethyl ether ("ether"; once widely used as an anesthetic)	0.708
isopropanol (rubbing alcohol)	0.785

Given: volume and mass

Asked for: density

Strategy:

A Calculate the density of each liquid from the volumes and masses given.

B Check to make sure that your answer makes sense.

C Compare each calculated density with those given in Table 1.2 "Densities of Liquids in Example 3". If the calculated density of a liquid is not significantly different from that of one of the liquids given in the table, then the unknown liquid is most likely the corresponding liquid.

D If none of the reported densities corresponds to the calculated density, then the liquid cannot be unambiguously identified.

Solution:

A Density is mass per unit volume and is usually reported in grams per cubic centimeter (or grams per milliliter because 1 mL = 1 cm³). The masses of the samples are given in grams, and the volume of all the samples is 25.00 mL (= 25.00 cm³). The density of each sample is calculated by dividing the mass by its volume (Equation 1.1). The density of sample A, for example, is

$$17.72\text{g}/25.00\text{cm}^3 = 0.7088\text{ g/cm}^3$$

Both the volume and the mass are given to four significant figures, so four significant figures are permitted in the result. (See Essential Skills 1, Section 1.9 "Essential Skills 1", for a discussion of significant figures.)

The densities of the other samples (in grams per cubic centimeter) are as follows: B, 0.7900; C, 0.9964; D, 0.7860; and E, 1.112.

B Except for sample E, the calculated densities are slightly less than 1 g/cm³. This makes sense because the masses (in grams) of samples A–D are all slightly less than the volume of the samples, 25.00 mL. In

contrast, the mass of sample *E* is slightly greater than 25 g, so its density must be somewhat greater than 1 g/cm³.

C Comparing these results with the data given in Table 1.2 "Densities of Liquids in Example 3" shows that sample *A* is probably diethyl ether (0.708 g/cm³ and 0.7088 g/cm³ are not substantially different), sample *C* is probably water (0.998 g/cm³ in the table versus 0.9964 g/cm³ measured), and sample *E* is probably ethylene glycol (1.113 g/cm³ in the table versus 1.112 g/cm³ measured).

D Samples *B* and *D* are more difficult to identify for two reasons: (1) Both have similar densities (0.7900 and 0.7860 g/cm³), so they may or may not be chemically identical. (2) Within experimental error, the measured densities of *B* and *D* are indistinguishable from the densities of ethanol (0.789 g/cm³), methanol (0.792 g/cm³), and isopropanol (0.785 g/cm³). Thus some property other than density must be used to identify each sample.

Exercise

Given the volumes and masses of five samples of compounds used in blending gasoline, together with the densities of several chemically pure liquids, identify as many of the samples as possible.

Sample	Volume (mL)	Mass (g)
<i>A</i>	337	250.0
<i>B</i>	972	678.1
<i>C</i>	243	190.9
<i>D</i>	119	103.2
<i>E</i>	499	438.7
Substance		Density (g/cm ³)
benzene		0.8787
toluene		0.8669
<i>m</i> -xylene		0.8684
isooctane		0.6979
methyl <i>t</i> -butyl ether		0.7405
<i>t</i> -butyl alcohol		0.7856

Answer: *A*, methyl *t*-butyl ether; *B*, isooctane; *C*, *t*-butyl alcohol; *D*, toluene or *m*-xylene; *E*, benzene

Summary

Matter is anything that occupies space and has **mass**. The three states of matter are **solid**, **liquid**, and **gas**. A **physical change** involves the conversion of a substance from one state of matter to another, without changing its chemical composition. Most matter consists of **mixtures** of pure substances, which can be **homogeneous** (uniform in composition) or **heterogeneous** (different regions possess different compositions and properties). Pure substances can be either chemical compounds or elements. **Compounds** can be broken down into elements by chemical reactions, but **elements** cannot be separated into simpler substances by chemical means. The properties of substances can be classified as either physical or chemical. Scientists can observe **physical properties** without changing the composition of the substance, whereas **chemical properties** describe the tendency of a substance to undergo **chemical changes** (chemical reactions) that change its chemical composition. Physical properties can be intensive or extensive. **Intensive properties** are the same for all samples; do not depend on sample size; and include, for example, color, physical state, and melting and boiling points. **Extensive properties** depend on the amount of material and include mass and volume. The ratio of two extensive properties, mass and volume, is an important intensive property called **density**.

KEY TAKEAWAY

- Matter can be classified according to physical and chemical properties.

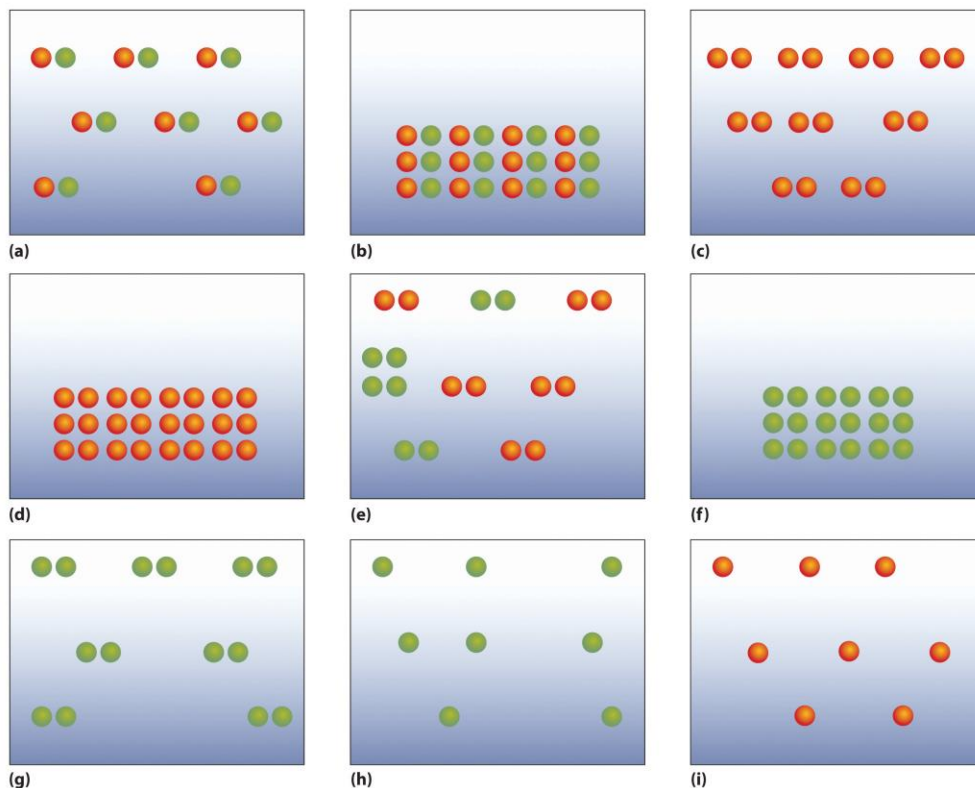
CONCEPTUAL PROBLEMS

Please be sure you are familiar with the topics discussed in Essential Skills 1 (Section 1.9 "Essential Skills 1") before proceeding to the Conceptual Problems.

1. What is the difference between mass and weight? Is the mass of an object on Earth the same as the mass of the same object on Jupiter? Why or why not?
2. Is it accurate to say that a substance with a mass of 1 kg weighs 2.2 lb? Why or why not?
3. What factor must be considered when reporting the weight of an object as opposed to its mass?
4. Construct a table with the headings "Solid," "Liquid," and "Gas." For any given substance, state what you expect for each of the following:
 - a. the relative densities of the three phases
 - b. the physical shapes of the three phases
 - c. the volumes for the same mass of compound
 - d. the sensitivity of the volume of each phase to changes in temperature

- e. the sensitivity of the volume to changes in pressure
5. Classify each substance as homogeneous or heterogeneous and explain your reasoning.
- a. platinum
 - b. a carbonated beverage
 - c. bronze
 - d. wood
 - e. natural gas
 - f. Styrofoam
6. Classify each substance as homogeneous or heterogeneous and explain your reasoning.
- a. snowflakes
 - b. gasoline
 - c. black tea
 - d. plastic wrap
 - e. blood
 - f. water containing ice cubes
7. Classify each substance as a pure substance or a mixture and explain your reasoning.
- a. seawater
 - b. coffee
 - c. 14-karat gold
 - d. diamond
 - e. distilled water
8. Classify each substance as a pure substance or a mixture.
- a. cardboard
 - b. caffeine
 - c. tin
 - d. a vitamin tablet
 - e. helium gas
9. Classify each substance as an element or a compound.
- a. sugar

- b. silver
 - c. rust
 - d. rubbing alcohol
 - e. copper
10. Classify each substance as an element or a compound.
- a. water
 - b. iron
 - c. hydrogen gas
 - d. glass
 - e. nylon
11. What techniques could be used to separate each of the following?
- a. sugar and water from an aqueous solution of sugar
 - b. a mixture of sugar and sand
 - c. a heterogeneous mixture of solids with different solubilities
12. What techniques could be used to separate each of the following?
- a. solid calcium chloride from a solution of calcium chloride in water
 - b. the components of a solution of vinegar in water
 - c. particulates from water in a fish tank
13. Match each separation technique in (a) with the physical/chemical property that each takes advantage of in (b).
- a. crystallization, distillation, filtration
 - b. volatility, physical state, solubility
14. The following figures illustrate the arrangement of atoms in some samples of matter. Which figures are related by a physical change? By a chemical change?



15. Classify each statement as an extensive property or an intensive property.

- Carbon, in the form of diamond, is one of the hardest known materials.
- A sample of crystalline silicon, a grayish solid, has a mass of 14.3 g.
- Germanium has a density of 5.32 g/cm^3 .
- Gray tin converts to white tin at 13.2°C .
- Lead is a bluish-white metal.

16. Classify each statement as a physical property or a chemical property.

- Fluorine etches glass.
- Chlorine interacts with moisture in the lungs to produce a respiratory irritant.
- Bromine is a reddish-brown liquid.
- Iodine has a density of 11.27 g/L at 0°C .

NUMERICAL PROBLEMS

Please be sure you are familiar with the topics discussed in Essential Skills 1 (Section 1.9 "Essential Skills 1") before proceeding to the Numerical Problems.

1. If a person weighs 176 lb on Earth, what is his or her mass on Mars, where the force of gravity is 37% of that on Earth?
2. If a person weighs 135 lb on Earth, what is his or her mass on Jupiter, where the force of gravity is 236% of that on Earth?
3. Calculate the volume of 10.00 g of each element and then arrange the elements in order of decreasing volume. The numbers in parentheses are densities.
 - a. copper (8.92 g/cm³)
 - b. calcium (1.54 g/cm³)
 - c. titanium (4.51 g/cm³)
 - d. iridium (22.85 g/cm³)
4. Given 15.00 g of each element, calculate the volume of each and then arrange the elements in order of increasing volume. The numbers in parentheses are densities.
 - a. gold (19.32 g/cm³)
 - b. lead (11.34 g/cm³)
 - c. iron (7.87 g/cm³)
 - d. sulfur (2.07 g/cm³)
5. A silver bar has dimensions of 10.00 cm × 4.00 cm × 1.50 cm, and the density of silver is 10.49 g/cm³. What is the mass of the bar?
6. Platinum has a density of 21.45 g/cm³. What is the mass of a platinum bar measuring 3.00 cm × 1.50 cm × 0.500 cm?
7. Complete the following table.

Density (g/cm ³)	Mass (g)	Volume (cm ³)	Element
3.14	79.904		Br
3.51		3.42	C
	39.1	45.5	K
11.34	207.2		Pb
	107.868	10.28	Ag
6.51		14.0	Zr

8. Gold has a density of 19.30 g/cm^3 . If a person who weighs 85.00 kg ($1 \text{ kg} = 1000 \text{ g}$) were given his or her weight in gold, what volume (in cm^3) would the gold occupy? Are we justified in using the SI unit of mass for the person's weight in this case?
9. An irregularly shaped piece of magnesium with a mass of 11.81 g was dropped into a graduated cylinder partially filled with water. The magnesium displaced 6.80 mL of water. What is the density of magnesium?
10. The density of copper is 8.92 g/cm^3 . If a 10.00 g sample is placed in a graduated cylinder that contains 15.0 mL of water, what is the total volume that would be occupied?
11. At 20°C , the density of fresh water is 0.9982 kg/m^3 , and the density of seawater is 1.025 kg/m^3 . Will a ship float higher in fresh water or in seawater? Explain your reasoning.

ANSWERS

1. Unlike weight, mass does not depend on location. The mass of the person is therefore the same on Earth and Mars: $176 \text{ lb} \div 2.2 \text{ lb/kg} = 80 \text{ kg}$.
- 2: a. Cu: 1.12 cm^3
b. Ca: 6.49 cm^3
c. Ti: 2.22 cm^3
d. Ir: 0.4376 cm^3
Volume decreases: $\text{Ca} > \text{Ti} > \text{Cu} > \text{Ir}$

[1] In physical terms, the mass of an object is directly proportional to the force required to change its speed or direction. A more detailed discussion of the differences between weight and mass and the units used to measure them is included in Essential Skills 1 (Section 1.9 "Essential Skills 1").

[2] If necessary, review the use of significant figures in calculations in Essential Skills 1 (Section 1.9 "Essential Skills 1") prior to working this example.

1.4 A Brief History of Chemistry

LEARNING OBJECTIVE

1. To understand the development of the atomic model.

It was not until the era of the ancient Greeks that we have any record of how people tried to explain the chemical changes they observed and used. At that time, natural objects were thought to consist of only four basic elements: earth, air, fire, and water. Then, in the fourth century BC, two Greek philosophers, Democritus and Leucippus, suggested that matter was not infinitely divisible into smaller particles but instead consisted of fundamental, indivisible particles called atoms. Unfortunately, these early philosophers did not have the technology to test their hypothesis. They would have been unlikely to do so in any case because the ancient Greeks did not conduct experiments or use the scientific method. They believed that the nature of the universe could be discovered by rational thought alone.

Over the next two millennia, *alchemists*, who engaged in a form of chemistry and speculative philosophy during the Middle Ages and Renaissance, achieved many advances in chemistry. Their major goal was to convert certain elements into others by a process they called transmutation (Figure 1.13 "An Alchemist at Work"). In particular, alchemists wanted to find a way to transform cheaper metals into gold. Although most alchemists did not approach chemistry systematically and many appear to have been outright frauds, alchemists in China, the Arab kingdoms, and medieval Europe made major contributions, including the discovery of elements such as quicksilver (mercury) and the preparation of several strong acids.

Modern Chemistry

The 16th and 17th centuries saw the beginnings of what we now recognize as modern chemistry. During this period, great advances were made in *metallurgy*, the extraction of metals from ores, and the first systematic quantitative experiments were carried out. In 1661, the Englishman Robert Boyle (1627–91) published *The Sceptical Chymist*, which described the relationship between the pressure and the volume of air. More important, Boyle defined an element as a substance that cannot be broken down into two or more simpler substances by chemical means. This led to the identification of a large number of elements, many of which were metals. Ironically, Boyle himself never thought that metals were elements.

In the 18th century, the English clergyman Joseph Priestley (1733–1804) discovered oxygen gas and found that many carbon-containing materials burn vigorously in an oxygen atmosphere, a process called combustion. Priestley also discovered that the gas produced by fermenting beer, which we now

know to be carbon dioxide, is the same as one of the gaseous products of combustion. Priestley's studies of this gas did not continue as he would have liked, however. After he fell into a vat of fermenting beer, brewers prohibited him from working in their factories. Although Priestley did not understand its identity, he found that carbon dioxide dissolved in water to produce seltzer water. In essence, he may be considered the founder of the multibillion-dollar carbonated soft drink industry.

Joseph Priestley (1733–1804)

Priestley was a political theorist and a leading Unitarian minister. He was appointed to Warrington Academy in Lancashire, England, where he developed new courses on history, science, and the arts. During visits to London, Priestley met the leading men of science, including Benjamin Franklin, who encouraged Priestley's interest in electricity. Priestley's work on gases began while he was living next to a brewery in Leeds, where he noticed "fixed air" bubbling out of vats of fermenting beer and ale. His scientific discoveries included the relationship between electricity and chemical change, 10 new "airs," and observations that led to the discovery of photosynthesis. Due to his support for the principles of the French Revolution, Priestley's house, library, and laboratory were destroyed by a mob in 1791. He and his wife emigrated to the United States in 1794 to join their three sons, who had previously emigrated to Pennsylvania. Priestley never returned to England and died in his new home in Pennsylvania.

Despite the pioneering studies of Priestley and others, a clear understanding of combustion remained elusive. In the late 18th century, however, the French scientist Antoine Lavoisier (1743–94) showed that combustion is the reaction of a carbon-containing substance with oxygen to form carbon dioxide and water and that life depends on a similar reaction, which today we call *respiration*. Lavoisier also wrote the first modern chemistry text and is widely regarded as the father of modern chemistry. His most important contribution was the law of conservation of mass, which states that in any chemical reaction, the mass of the substances that react equals the mass of the products that are formed. That is, in a chemical reaction, mass is neither lost nor destroyed. Unfortunately, Lavoisier invested in a private corporation that collected taxes for the Crown, and royal tax collectors were not popular during the French Revolution. He was executed on the guillotine at age 51, prematurely terminating his contributions to chemistry.

The Atomic Theory of Matter

In 1803, the English schoolteacher John Dalton (1766–1844) expanded Proust's development of the **law of definite proportions** (Section 1.2 "The Scientific Method") and Lavoisier's findings on the conservation of mass in chemical reactions to propose that elements consist of indivisible particles that he called *atoms* (taking the term from Democritus and Leucippus). Dalton's *atomic theory of matter* contains four fundamental hypotheses:

1. All matter is composed of tiny indivisible particles called atoms.
2. All atoms of an element are identical in mass and chemical properties, whereas atoms of different elements differ in mass and fundamental chemical properties.
3. A chemical compound is a substance that always contains the same atoms in the same ratio.
4. In chemical reactions, atoms from one or more compounds or elements redistribute or rearrange in relation to other atoms to form one or more new compounds. *Atoms themselves do not undergo a change of identity in chemical reactions.*

This last hypothesis suggested that the alchemists' goal of transmuting other elements to gold was impossible, at least through chemical reactions. We now know that Dalton's atomic theory is essentially correct, with four minor modifications:

1. Not all atoms of an element must have precisely the same mass.
2. Atoms of one element can be transformed into another through nuclear reactions.
3. The compositions of many solid compounds are somewhat variable.
4. Under certain circumstances, some atoms can be divided (split into smaller particles).

These modifications illustrate the effectiveness of the scientific method; later experiments and observations were used to refine Dalton's original theory.

The Law of Multiple Proportions

Despite the clarity of his thinking, Dalton could not use his theory to determine the elemental compositions of chemical compounds because he had no reliable scale of atomic masses; that is, he did not know the relative masses of elements such as carbon and oxygen. For example, he knew that the gas we now call carbon monoxide contained carbon and oxygen in the ratio 1:1.33 by mass, and a second compound, the gas we call carbon dioxide, contained carbon and oxygen in the ratio 1:2.66 by mass. Because $2.66/1.33 = 2.00$, the second compound contained twice as many oxygen atoms per carbon atom

as did the first. But what was the correct formula for each compound? If the first compound consisted of particles that contain one carbon atom and one oxygen atom, the second must consist of particles that contain one carbon atom and two oxygen atoms. If the first compound had two carbon atoms and one oxygen atom, the second must have two carbon atoms and two oxygen atoms. If the first had one carbon atom and two oxygen atoms, the second would have one carbon atom and four oxygen atoms, and so forth. Dalton had no way to distinguish among these or more complicated alternatives. However, these data led to a general statement that is now known as the law of multiple proportions: when two elements form a series of compounds, the ratios of the masses of the second element that are present per gram of the first element can almost always be expressed as the ratios of integers. (The same law holds for mass ratios of compounds forming a series that contains more than two elements.) Example 4 shows how the law of multiple proportions can be applied to determine the identity of a compound.

EXAMPLE 4

A chemist is studying a series of simple compounds of carbon and hydrogen. The following table lists the masses of hydrogen that combine with 1 g of carbon to form each compound.

Compound	Mass of Hydrogen (g)
<i>A</i>	0.0839
<i>B</i>	0.1678
<i>C</i>	0.2520
<i>D</i>	

- Determine whether these data follow the law of multiple proportions.
- Calculate the mass of hydrogen that would combine with 1 g of carbon to form *D*, the fourth compound in the series.

Given: mass of hydrogen per gram of carbon for three compounds

Asked for:

- ratios of masses of hydrogen to carbon
- mass of hydrogen per gram of carbon for fourth compound in series

Strategy:

A Select the lowest mass to use as the denominator and then calculate the ratio of each of the other masses to that mass. Include other ratios if appropriate.

B If the ratios are small whole integers, the data follow the law of multiple proportions.

C Decide whether the ratios form a numerical series. If so, then determine the next member of that series and predict the ratio corresponding to the next compound in the series.

D Use proportions to calculate the mass of hydrogen per gram of carbon in that compound.

Solution:

A Compound A has the lowest mass of hydrogen, so we use it as the denominator. The ratios of the remaining masses of hydrogen, B and C, that combine with 1 g of carbon are as follows:

$$C/A = 0.2520\text{g}/0.0839\text{g} = 3.00 = 3/1$$

$$B/A = 0.1678\text{g}/0.0839\text{g} = 2.00 = 2/1$$

$$C/B = 0.2520\text{g}/0.1678\text{g} = 1.502 = 3/2$$

B The ratios of the masses of hydrogen that combine with 1 g of carbon are indeed composed of small whole integers (3/1, 2/1, 3/2), as predicted by the law of multiple proportions.

C The ratios B/A and C/A form the series 2/1, 3/1, so the next member of the series should be D/A = 4/1.

D Thus, if compound D exists, it would be formed by combining $4 \times 0.0839 \text{ g} = 0.336 \text{ g}$ of hydrogen with 1 g of carbon. Such a compound does exist; it is *methane*, the major constituent of natural gas.

Exercise

Four compounds containing only sulfur and fluorine are known. The following table lists the masses of fluorine that combine with 1 g of sulfur to form each compound.

Compound	Mass of Fluorine (g)
A	3.54
B	2.96
C	2.36
D	0.59

a. Determine the ratios of the masses of fluorine that combine with 1 g of sulfur in these compounds. Are these data consistent with the law of multiple proportions?

b. Calculate the mass of fluorine that would combine with 1 g of sulfur to form the next two compounds in the series: E and F.

Answer:

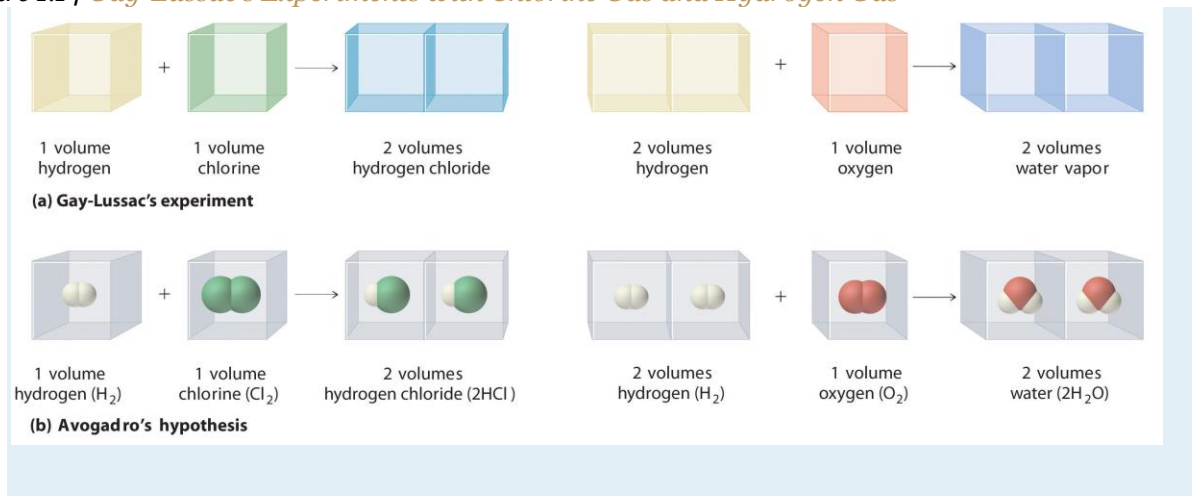
a. $A/D = 6.0$ or $6/1$; $B/D \approx 5.0$, or $5/1$; $C/D = 4.0$, or $4/1$; yes

- b. Ratios of 3.0 and 2.0 give 1.8 g and 1.2 g of fluorine/gram of sulfur, respectively. (Neither of these compounds is yet known.)

Avogadro's Hypothesis

In a further attempt to establish the formulas of chemical compounds, the French chemist Joseph Gay-Lussac (1778–1850) carried out a series of experiments using volume measurements. Under conditions of constant temperature and pressure, he carefully measured the volumes of gases that reacted to make a given chemical compound, together with the volumes of the products if they were gases. Gay-Lussac found, for example, that one volume of chlorine gas always reacted with one volume of hydrogen gas to produce two volumes of hydrogen chloride gas. Similarly, one volume of oxygen gas always reacted with two volumes of hydrogen gas to produce two volumes of water vapor (part (a) in Figure 1.14 "Gay-Lussac's Experiments with Chlorine Gas and Hydrogen Gas").

Figure 1.14 *Gay-Lussac's Experiments with Chlorine Gas and Hydrogen Gas*



(a) One volume of chlorine gas reacted with one volume of hydrogen gas to produce two volumes of hydrogen chloride gas, and one volume of oxygen gas reacted with two volumes of hydrogen gas to produce two volumes of water vapor. (b) A summary of Avogadro's hypothesis, which interpreted Gay-Lussac's results in terms of atoms. Note that the simplest way for two molecules of hydrogen chloride to be produced is if hydrogen and chlorine each consist of molecules that contain two atoms of the element.

Gay-Lussac's results did not by themselves reveal the formulas for hydrogen chloride and water. The Italian chemist Amadeo Avogadro (1776–1856) developed the key insight that led to the exact formulas. He proposed that when gases are measured at the same temperature and pressure, *equal volumes of different gases contain equal numbers*

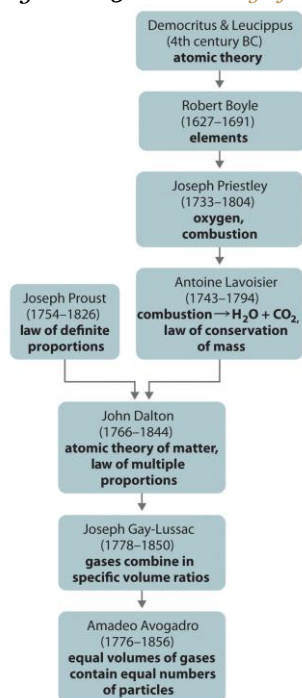
of gas particles. Avogadro's hypothesis, which explained Gay-Lussac's results, is summarized here and in part

(b) in Figure 1.14 "Gay-Lussac's Experiments with Chlorine Gas and Hydrogen Gas":

One volume (or particle) of hydrogen	+	one volume (or particle) of chlorine	====>	two volumes (or particles) of hydrogen chloride

If Dalton's theory of atoms was correct, then each particle of hydrogen or chlorine had to contain *at least two atoms* of hydrogen or chlorine because two particles of hydrogen chloride were produced. The simplest—but not the only—explanation was that hydrogen and chlorine contained two atoms each (i.e., they were *diatomic*) and that hydrogen chloride contained one atom each of hydrogen and chlorine. Applying this reasoning to Gay-Lussac's results with hydrogen and oxygen leads to the conclusion that water contains two hydrogen atoms per oxygen atom. Unfortunately, because no data supported Avogadro's hypothesis that equal volumes of gases contained equal numbers of particles, his explanations and formulas for simple compounds were not generally accepted for more than 50 years. Dalton and many others continued to believe that water particles contained one hydrogen atom and one oxygen atom, rather than two hydrogen atoms and one oxygen atom. The historical development of the concept of the atom is summarized in Figure 1.15 "A Summary of the Historical Development of the Concept of the Atom".

Figure 1.15 A Summary of the Historical Development of the Concept of the Atom



Summary

The ancient Greeks first proposed that matter consisted of fundamental particles called **atoms**.

Chemistry took its present scientific form in the 18th century, when careful quantitative experiments by Lavoisier, Proust, and Dalton resulted in the law of definite proportions, the **law of conservation of mass**, and the **law of multiple proportions**, which laid the groundwork for Dalton's atomic theory of matter. In particular, Avogadro's hypothesis provided the first link between the macroscopic properties of a substance (in this case, the volume of a gas) and the number of atoms or molecules present.

KEY TAKEAWAY

- The development of the atomic model relied on the application of the scientific method over several centuries.

CONCEPTUAL PROBLEMS

1. Define *combustion* and discuss the contributions made by Priestley and Lavoisier toward understanding a combustion reaction.
2. Chemical engineers frequently use the concept of "mass balance" in their calculations, in which the mass of the reactants must equal the mass of the products. What law supports this practice?
3. Does the law of multiple proportions apply to both mass ratios and atomic ratios? Why or why not?
4. What are the four hypotheses of the atomic theory of matter?
5. Much of the energy in France is provided by nuclear reactions. Are such reactions consistent with Dalton's hypotheses? Why or why not?
6. Does 1 L of air contain the same number of particles as 1 L of nitrogen gas? Explain your answer.

NUMERICAL PROBLEMS

Please be sure you are familiar with the topics discussed in Essential Skills 1 (Section 1.9 "Essential Skills 1") before proceeding to the Numerical Problems.

1. One of the minerals found in soil has an Al:Si:O atomic ratio of 0.2:0.2:0.5. Is this consistent with the law of multiple proportions? Why or why not? Is the ratio of elements consistent with Dalton's atomic theory of matter?
2. Nitrogen and oxygen react to form three different compounds that contain 0.571 g, 1.143 g, and 2.285 g of oxygen/gram of nitrogen, respectively. Is this consistent with the law of multiple proportions? Explain your answer.

3. Three binary compounds of vanadium and oxygen are known. The following table gives the masses of oxygen that combine with 10.00 g of vanadium to form each compound.

Compound	Mass of Oxygen (g)
<i>A</i>	4.71
<i>B</i>	6.27
<i>C</i>	

- a. Determine the ratio of the masses of oxygen that combine with 3.14 g of vanadium in compounds *A* and *B*.
- b. Predict the mass of oxygen that would combine with 3.14 g of vanadium to form the third compound in the series.
4. Three compounds containing titanium, magnesium, and oxygen are known. The following table gives the masses of titanium and magnesium that react with 5.00 g of oxygen to form each compound.

Compound	Mass of Titanium (g)	Mass of Magnesium (g)
<i>A</i>	4.99	2.53
<i>B</i>	3.74	3.80
<i>C</i>		

- a. Determine the ratios of the masses of titanium and magnesium that combine with 5.00 g of oxygen in these compounds.
- b. Predict the masses of titanium and magnesium that would combine with 5.00 g of oxygen to form another possible compound in the series: *C*.

1.5 The Atom

LEARNING OBJECTIVE

1. To become familiar with the components and structure of the atom.

To date, about 115 different elements have been discovered; by definition, each is chemically unique. To understand why they are unique, you need to understand the structure of the atom (the fundamental, individual particle of an element) and the characteristics of its components.

Atoms consist of electrons, protons, and neutrons.^[1] Some properties of these subatomic particles are summarized in Table 1.3 "Properties of Subatomic Particles*", which illustrates three important points.

1. Electrons and protons have electrical charges that are identical in magnitude but opposite in sign. We usually assign *relative* charges of -1 and $+1$ to the electron and proton, respectively.
2. Neutrons have approximately the same mass as protons but no charge. They are electrically neutral.
3. The mass of a proton or a neutron is about 1836 times greater than the mass of an electron. Protons and neutrons constitute by far the bulk of the mass of atoms.

The discovery of the electron and the proton was crucial to the development of the modern model of the atom and provides an excellent case study in the application of the scientific method. In fact, the elucidation of the atom's structure is one of the greatest detective stories in the history of science.

Table 1.3 Properties of Subatomic Particles*

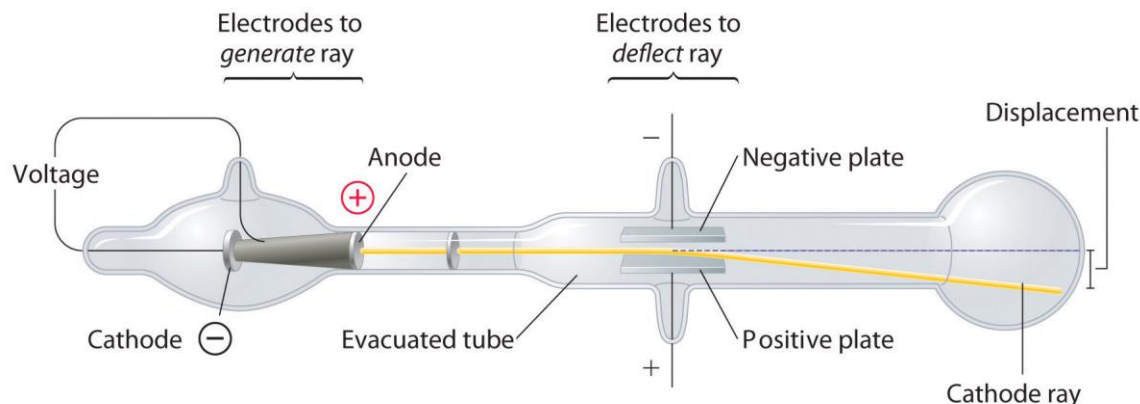
Particle	Mass (g)	Atomic Mass (amu)	Electrical Charge (coulombs)	Relative Charge
electron	9.109×10^{-28}	0.0005486	-1.602×10^{-19}	-1
proton	1.673×10^{-24}	1.007276	$+1.602 \times 10^{-19}$	$+1$
neutron	1.675×10^{-24}	1.008665	0	0
* For a review of using scientific notation and units of measurement, see Essential Skills 1 (Section 1.9 "Essential Skills 1").				

The Electron

Long before the end of the 19th century, it was well known that applying a high voltage to a gas contained at low pressure in a sealed tube (called a gas discharge tube) caused electricity to flow through the gas, which then emitted light (Figure 1.16 "A Gas Discharge Tube Producing Cathode Rays"). Researchers trying to understand this phenomenon found that an unusual form of energy was also emitted from the *cathode*, or negatively charged electrode; hence this form of energy was called *cathode rays*. In 1897, the British physicist J. J. Thomson (1856–1940) proved that atoms were not the ultimate form of matter. He demonstrated that cathode rays could be deflected, or bent, by magnetic or electric fields, which indicated that cathode rays consist of charged particles (Figure 1.17 "Deflection of Cathode Rays by an Electric Field"). More important, by measuring the extent of the deflection of the cathode rays in magnetic or electric fields of various strengths, Thomson was able to calculate the *mass-to-charge ratio* of the particles. These particles were emitted by the negatively charged cathode and repelled by the negative terminal of an electric field. Because like charges repel each other and opposite charges attract, Thomson concluded that the particles had a net negative charge; we now call these particles **electrons**. Most important for

chemistry, Thomson found that the mass-to-charge ratio of cathode rays was independent of the nature of the metal electrodes or the gas, which suggested that electrons were fundamental components of all atoms.

Figure 1.17 *Deflection of Cathode Rays by an Electric Field*



As the cathode rays travel toward the right, they are deflected toward the positive electrode (+), demonstrating that they are negatively charged.

Subsequently, the American scientist Robert Millikan (1868–1953) carried out a series of experiments using electrically charged oil droplets, which allowed him to calculate the charge on a single electron. With this information and Thomson’s mass-to-charge ratio, Millikan determined the mass of an electron.

Mass/Charge(crossed-out) x charge (crossed out) = m_e

It was at this point that two separate lines of investigation began to converge, both aimed at determining how and why matter emits energy.

Radioactivity

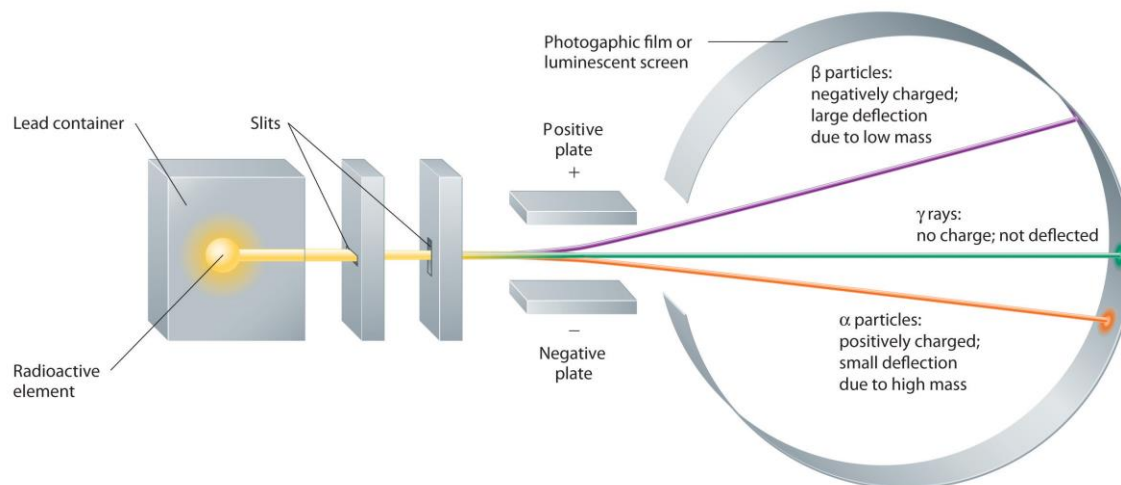
The second line of investigation began in 1896, when the French physicist Henri Becquerel (1852–1908) discovered that certain minerals, such as uranium salts, emitted a new form of energy. Becquerel’s work was greatly extended by Marie Curie (1867–1934) and her husband, Pierre (1854–1906); all three shared the Nobel Prize in Physics in 1903. Marie Curie coined the term radioactivity (from the Latin *radius*, meaning “ray”) to describe the emission of energy rays by matter. She found that one particular uranium ore, pitchblende, was substantially more radioactive than most, which suggested that it contained one or more highly radioactive impurities. Starting with several tons of pitchblende, the Curies isolated two new radioactive elements after months of work: polonium, which was named for Marie’s native Poland, and radium, which was named for its intense radioactivity. Pierre Curie carried a vial of radium in his coat pocket to demonstrate its greenish glow, a habit that caused him to become ill from radiation poisoning

well before he was run over by a horse-drawn wagon and killed instantly in 1906. Marie Curie, in turn, died of what was almost certainly radiation poisoning.

Building on the Curies' work, the British physicist Ernest Rutherford (1871–1937) performed decisive experiments that led to the modern view of the structure of the atom. While working in Thomson's laboratory shortly after Thomson discovered the electron, Rutherford showed that compounds of uranium and other elements emitted at least two distinct types of radiation. One was readily absorbed by matter and seemed to consist of particles that had a positive charge and were massive compared to electrons. Because it was the first kind of radiation to be discovered, Rutherford called these substances *α particles*. Rutherford also showed that the particles in the second type of radiation, *β particles*, had the same charge and mass-to-charge ratio as Thomson's electrons; they are now known to be high-speed electrons. A third type of radiation, *γ rays*, was discovered somewhat later and found to be similar to a lower-energy form of radiation called x-rays, now used to produce images of bones and teeth.

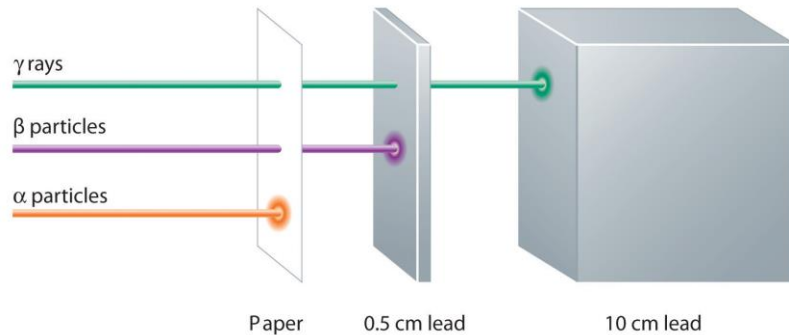
These three kinds of radiation— *α particles*, *β particles*, and *γ rays*—are readily distinguished by the way they are deflected by an electric field and by the degree to which they penetrate matter. As Figure 1.18 "Effect of an Electric Field on *α Particles*, *β Particles*, and *γ Rays*" illustrates, *α particles* and *β particles* are deflected in opposite directions; *α particles* are deflected to a much lesser extent because of their higher mass-to-charge ratio. In contrast, *γ rays* have no charge, so they are not deflected by electric or magnetic fields. Figure 1.19 "Relative Penetrating Power of the Three Types of Radiation" shows that *α particles* have the least penetrating power and are stopped by a sheet of paper, whereas *β particles* can pass through thin sheets of metal but are absorbed by lead foil or even thick glass. In contrast, *γ -rays* can readily penetrate matter; thick blocks of lead or concrete are needed to stop them.

Figure 1.18 *Effect of an Electric Field on α Particles, β Particles, and γ Rays*



A negative electrode deflects negatively charged β particles, whereas a positive electrode deflects positively charged α particles. Uncharged γ rays are unaffected by an electric field. (Relative deflections are not shown to scale.)

Figure 1.19 *Relative Penetrating Power of the Three Types of Radiation*

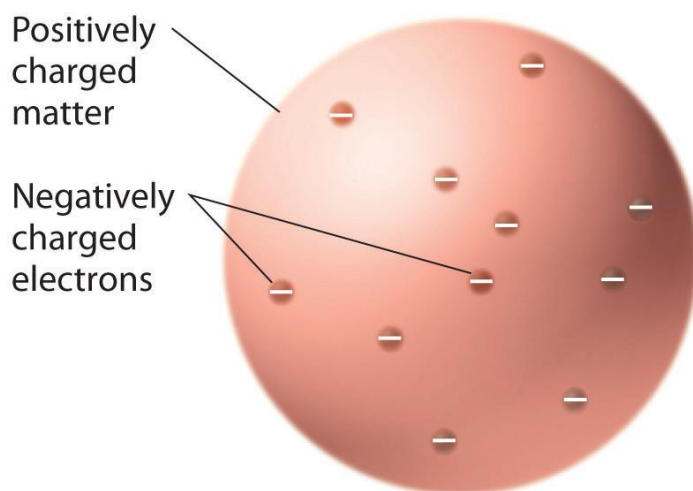


A sheet of paper stops comparatively massive α particles, whereas β particles easily penetrate paper but are stopped by a thin piece of lead foil. Uncharged γ rays penetrate the paper and lead foil; a much thicker piece of lead or concrete is needed to absorb them.

The Atomic Model

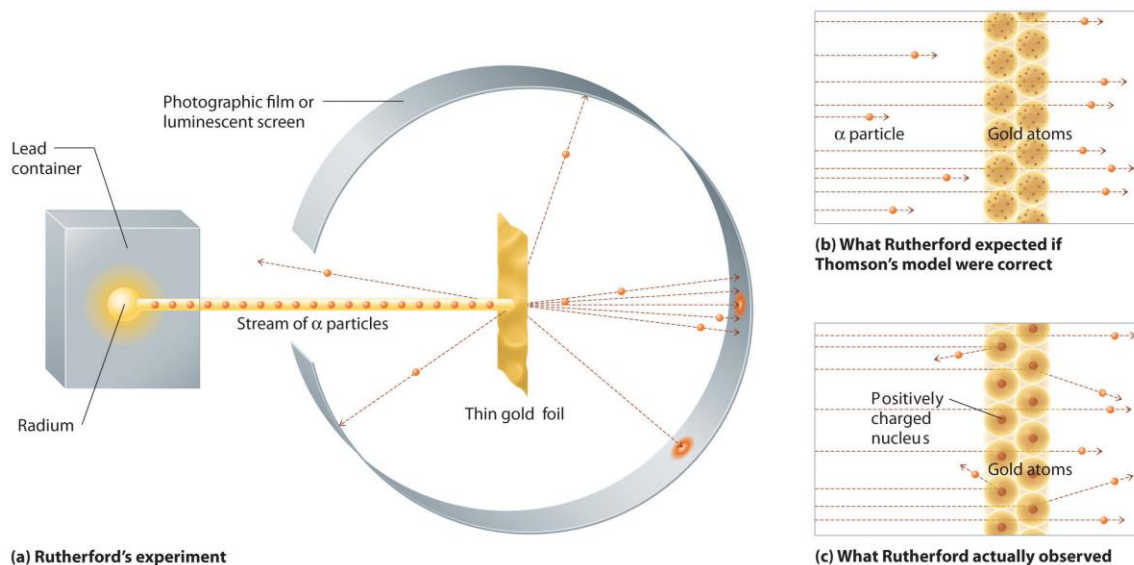
Once scientists concluded that all matter contains negatively charged electrons, it became clear that atoms, which are electrically neutral, must also contain positive charges to balance the negative ones. Thomson proposed that the electrons were embedded in a uniform sphere that contained both the positive charge and most of the mass of the atom, much like raisins in plum pudding or chocolate chips in a cookie (Figure 1.20 "Thomson's Plum Pudding or Chocolate Chip Cookie Model of the Atom").

Figure 1.20 *Thomson's Plum Pudding or Chocolate Chip Cookie Model of the Atom*



In a single famous experiment, however, Rutherford showed unambiguously that Thomson's model of the atom was impossible. Rutherford aimed a stream of α particles at a very thin gold foil target (part (a) in Figure 1.21 "A Summary of Rutherford's Experiments") and examined how the α particles were scattered by the foil. Gold was chosen because it could be easily hammered into extremely thin sheets with a thickness that minimized the number of atoms in the target. If Thomson's model of the atom were correct, the positively charged α particles should crash through the uniformly distributed mass of the gold target like cannonballs through the side of a wooden house. They might be moving a little slower when they emerged, but they should pass essentially straight through the target (part (b) in Figure 1.21 "A Summary of Rutherford's Experiments"). To Rutherford's amazement, a small fraction of the α particles were deflected at large angles, and some were reflected directly back at the source (part (c) in Figure 1.21 "A Summary of Rutherford's Experiments"). According to Rutherford, "It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you."

Figure 1.21 *A Summary of Rutherford's Experiments*



(a) A representation of the apparatus Rutherford used to detect deflections in a stream of α particles aimed at a thin gold foil target. The particles were produced by a sample of radium. (b) If Thomson's model of the atom were correct, the α particles should have passed straight through the gold foil. (c) But a small number of α particles were deflected in various directions, including right back at the source. This could be true only if the positive charge were

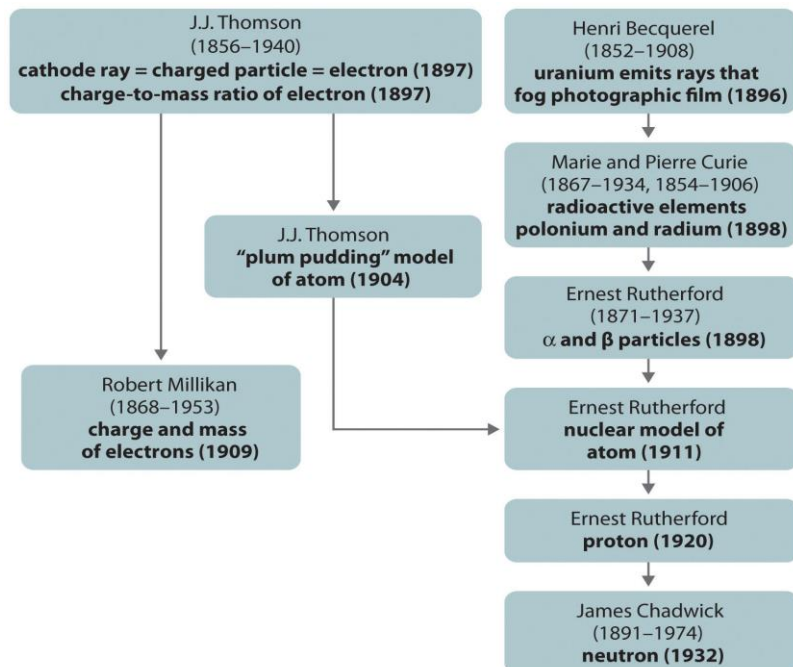
much more massive than the α particle. It suggested that the mass of the gold atom is concentrated in a very small region of space, which he called the nucleus.

Rutherford's results were *not* consistent with a model in which the mass and positive charge are distributed uniformly throughout the volume of an atom. Instead, they strongly suggested that both the mass and positive charge are concentrated in a tiny fraction of the volume of an atom, which Rutherford called the nucleus. It made sense that a small fraction of the α particles collided with the dense, positively charged nuclei in either a glancing fashion, resulting in large deflections, or almost head-on, causing them to be reflected straight back at the source.

Although Rutherford could not explain why repulsions between the positive charges in nuclei that contained more than one positive charge did not cause the nucleus to disintegrate, he reasoned that repulsions between negatively charged electrons would cause the electrons to be uniformly distributed throughout the atom's volume.^[2] For this and other insights, Rutherford was awarded the Nobel Prize in Chemistry in 1908. Unfortunately, Rutherford would have preferred to receive the Nobel Prize in Physics because he thought that physics was superior to chemistry. In his opinion, "All science is either physics or stamp collecting." (The authors of this text do *not* share Rutherford's view!) Subsequently, Rutherford established that the nucleus of the hydrogen atom was a positively charged particle, for which he coined the name *proton* in 1920. He also suggested that the nuclei of elements other than hydrogen must contain electrically neutral particles with approximately the same mass as the proton. The neutron, however, was not discovered until 1932, when James Chadwick (1891–1974, a student of Rutherford; Nobel Prize in Physics, 1935) discovered it. As a result of Rutherford's work, it became clear that an α particle contains two protons and neutrons and is therefore simply the nucleus of a helium atom.

The historical development of the different models of the atom's structure is summarized in Figure 1.22 "A Summary of the Historical Development of Models of the Components and Structure of the Atom". Rutherford's model of the atom is essentially the same as the modern one, except that we now know that electrons are *not* uniformly distributed throughout an atom's volume. Instead, they are distributed according to a set of principles described in Chapter 6 "The Structure of Atoms". Figure 1.23 "The Evolution of Atomic Theory, as Illustrated by Models of the Oxygen Atom" shows how the model of the atom has evolved over time from the indivisible unit of Dalton to the modern view taught today.

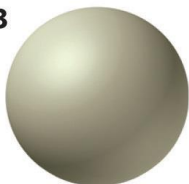
Figure 1.22 A Summary of the Historical Development of Models of the Components and Structure of the Atom



The dates in parentheses are the years in which the key experiments were performed.

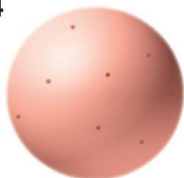
Figure 1.23 The Evolution of Atomic Theory, as Illustrated by Models of the Oxygen Atom

1803



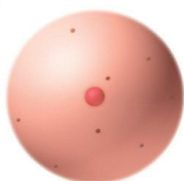
Dalton proposes the indivisible unit of an element is the atom.

1904



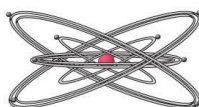
Thomson discovers electrons, believed to reside within a sphere of uniform positive charge (the plum pudding model).

1911



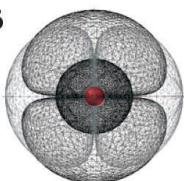
Rutherford demonstrates the existence of a positively charged nucleus that contains nearly all the mass of an atom.

1913



Bohr proposes fixed circular orbits around the nucleus for electrons.

1926



In the current model of the atom, electrons occupy regions of space (orbitals) around the nucleus determined by their energies.

Bohr's model and the current model are described in Chapter 6 "The Structure of Atoms".

Summary

Atoms, the smallest particles of an element that exhibit the properties of that element, consist of negatively charged **electrons** around a central **nucleus** composed of more massive positively charged **protons** and electrically neutral **neutrons**. **Radioactivity** is the emission of energetic particles and rays (radiation) by some substances. Three important kinds of radiation are α particles (helium nuclei), β particles (electrons traveling at high speed), and γ rays (similar to x-rays but higher in energy).

KEY TAKEAWAY

- The atom consists of discrete particles that govern its chemical and physical behavior.

CONCEPTUAL PROBLEMS

1. Describe the experiment that provided evidence that the proton is positively charged.
2. What observation led Rutherford to propose the existence of the neutron?
3. What is the difference between Rutherford's model of the atom and the model chemists use today?
4. If cathode rays are not deflected when they pass through a region of space, what does this imply about the presence or absence of a magnetic field perpendicular to the path of the rays in that region?
5. Describe the outcome that would be expected from Rutherford's experiment if the charge on α particles had remained the same but the nucleus were negatively charged. If the nucleus were neutral, what would have been the outcome?
6. Describe the differences between an α particle, a β particle, and a γ ray. Which has the greatest ability to penetrate matter?

NUMERICAL PROBLEMS

Please be sure you are familiar with the topics discussed in Essential Skills 1 (Section 1.9 "Essential Skills 1") before proceeding to the Numerical Problems.

1. Using the data in Table 1.3 "Properties of Subatomic Particles*" and the periodic table (see Chapter 32 "Appendix H: Periodic Table of Elements"), calculate the percentage of the mass of a silicon atom that is due to
 - a. electrons.
 - b. protons.
2. Using the data in Table 1.3 "Properties of Subatomic Particles*" and the periodic table (see Chapter 32 "Appendix H: Periodic Table of Elements"), calculate the percentage of the mass of a helium atom that is due to
 - a. electrons.
 - b. protons.
3. The radius of an atom is approximately 10^4 times larger than the radius of its nucleus. If the radius of the nucleus were 1.0 cm, what would be the radius of the atom in centimeters? in miles?
4. The total charge on an oil drop was found to be 3.84×10^{-18} coulombs. What is the total number of electrons contained in the drop?

[1] This is an oversimplification that ignores the other subatomic particles that have been discovered, but it is sufficient for our discussion of chemical principles.

[2] Today we know that *strong nuclear forces*, which are much stronger than electrostatic interactions, hold the protons and the neutrons together in the nucleus.

1.6 Isotopes and Atomic Masses

LEARNING OBJECTIVE

1. To know the meaning of isotopes and atomic masses.

Rutherford's nuclear model of the atom helped explain why atoms of different elements exhibit different chemical behavior. The identity of an element is defined by its atomic number (Z), the number of protons in the nucleus of an atom of the element. *The atomic number is therefore different for each element.* The known elements are arranged in order of increasing Z in the periodic table (Figure 1.24 "The Periodic Table Showing the Elements in Order of Increasing "; also see Chapter 32 "Appendix H: Periodic Table of Elements"),^[1] in which each element is assigned a unique one-, two-, or three-letter symbol. The names of the elements are listed in the periodic table, along with their symbols, atomic numbers, and atomic masses. The chemistry of each element is determined by its number of protons and electrons. In a neutral atom, the number of electrons equals the number of protons.

Figure 1.24 *The Periodic Table Showing the Elements in Order of Increasing Z*

The periodic table is organized into periods (rows) and groups (columns). The main group elements are highlighted in the top left and top right. The transition elements are in the center. The Lanthanides and Actinides are shown at the bottom.

As described in Section 1.7 "Introduction to the Periodic Table", the metals are on the bottom left in the periodic table, and the nonmetals are at the top right. The semimetals lie along a diagonal line separating the metals and nonmetals.

In most cases, the symbols for the elements are derived directly from each element's name, such as C for carbon, U for uranium, Ca for calcium, and Po for polonium. Elements have also been named for their properties [such as radium (Ra) for its radioactivity], for the native country of the scientist(s) who discovered them [polonium (Po) for Poland], for eminent scientists [curium (Cm) for the Curies], for gods and goddesses [selenium (Se) for the Greek goddess of the moon, Selene], and for other poetic or historical reasons. Some of the symbols used for elements that have been known since antiquity are derived from historical names that are no longer in use; only the symbols remain to remind us of their origin. Examples are Fe for iron, from the Latin *ferrum*; Na for sodium, from the Latin *natrium*; and W for tungsten, from the German *wolfram*. Examples are in Table 1.4 "Element Symbols Based on Names No Longer in Use". As you work through this text, you will encounter the names and symbols of the elements repeatedly, and much as you become familiar with characters in a play or a film, their names and symbols will become familiar.

Table 1.4 Element Symbols Based on Names No Longer in Use

Element	Symbol	Derivation	Meaning
antimony	Sb	<i>stibium</i>	Latin for "mark"
copper	With	<i>cuprum</i>	from <i>Cyprium</i> , Latin name for the island of Cyprus, the major source

Element	Symbol	Derivation	Meaning
			of copper ore in the Roman Empire
gold	To	<i>aurum</i>	Latin for "gold"
iron	Faith	<i>ferrum</i>	Latin for "iron"
lead	Pb	<i>plumbum</i>	Latin for "heavy"
mercury	Hg	<i>hydrargyrum</i>	Latin for "liquid silver"
potassium	K	<i>potassium</i>	from the Arabic <i>al-qili</i> , "alkali"
silver	Ag	<i>argentum</i>	Latin for "silver"
sodium	In	<i>sodium</i>	Latin for "sodium"
believe	Sn	<i>stannum</i>	Latin for "tin"
tungsten	In	<i>tungsten</i>	German for "wolf stone" because it interfered with the smelting of tin and was thought to devour the tin

Recall from Section 1.5 "The Atom" that the nuclei of most atoms contain neutrons as well as protons. Unlike protons, the number of neutrons is not absolutely fixed for most elements. Atoms that have *the same number of protons*, and hence the same atomic number, but *different numbers of neutrons* are called isotopes. All isotopes of an element have the same number of protons and electrons, which means they exhibit the same chemistry. The isotopes of an element differ only in their atomic mass, which is given by the mass number (A), the sum of the numbers of protons and neutrons.

The element carbon (C) has an atomic number of 6, which means that all neutral carbon atoms contain 6 protons and 6 electrons. In a typical sample of carbon-containing material, 98.89% of the carbon atoms also contain 6 neutrons, so each has a mass number of 12. An isotope of any element can be uniquely represented as X_ZA , where X is the atomic symbol of the element. The isotope of carbon that has 6 neutrons is the atomic symbol already, which is read as "carbon-12." Nevertheless, the value of Z is commonly included in the notation for *nuclear* reactions because these reactions involve changes in Z , as described in Chapter 20 "Nuclear Chemistry".

Mass number

Number of protons
and neutrons in atom

**Atomic symbol**

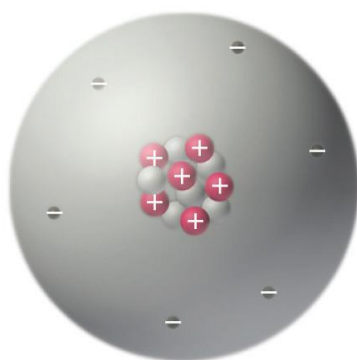
Abbreviation used
to represent atom
in chemical
formulas

Atomic number

Number of protons
in atom



6 protons 
6 neutrons 
6 electrons 



In with 8 neutrons and 6 protons. The nucleus of ^{14}C is not stable, however, but undergoes a slow radioactive decay that is the basis of the carbon-14 dating technique used in archaeology (see Chapter 14 "Chemical Kinetics"). Many elements other than carbon have more than one stable isotope; tin, for example, has 10 isotopes. The properties of some common isotopes are in Table 1.5 "Properties of Selected Isotopes".

Table 1.5 Properties of Selected Isotopes

Element	Symbol	Atomic Mass (amu)	Isotope Mass Number	Isotope Masses (amu)	Percent Abundances (%)
hydrogen	H	1.0079	1	1.007825	99.9855

Element	Symbol	Atomic Mass (amu)	Isotope Mass Number	Isotope Masses (amu)	Percent Abundances (%)
			2	2.014102	0.0115
boron	B	10.81	10	10.012937	19.91
			11	11.009305	80.09
carbon	C	12.011	12	12 (defined)	99.89
			13	13.003355	1.11
oxygen	The	15.9994	16	15.994915	99.757
			17	16.999132	0.0378
			18	17.999161	0.205
iron	Faith	55.845	54	53.939611	5.82
			56	55.934938	91.66
			57	56.935394	2.19
			58	57.933276	0.33
uranium	You	238.03	234	234.040952	0.0054
			235	235.043930	0.7204
			238	238.050788	99.274

Sources of isotope data: G. Audi et al., *Nuclear Physics A* 729 (2003): 337–676; J. C. Kotz and K. F. Purcell, *Chemistry and Chemical Reactivity*, 2nd ed., 1991.

EXAMPLE 5

An element with three stable isotopes has 82 protons. The separate isotopes contain 124, 125, and 126 neutrons. Identify the element and write symbols for the isotopes.

Given: number of protons and neutrons

Asked for: element and atomic symbol

Strategy:

A Refer to the periodic table (see Chapter 32 "Appendix H: Periodic Table of Elements") and use the number of protons to identify the element.

B Calculate the mass number of each isotope by adding together the numbers of protons and neutrons.

C Give the symbol of each isotope with the mass number as the superscript and the number of protons as the subscript, both written to the left of the symbol of the element.

Solution:

A The element with 82 protons (atomic number of 82) is lead: Pb.

B For the first isotope, $A = 82 \text{ protons} + 124 \text{ neutrons} = 206$. Similarly, $A = 82 + 125 = 207$ and $A = 82 + 126 = 208$ for the second and third isotopes, respectively. The symbols for these isotopes are ^{207}Pb , and ^{208}Pb .

Exercise

Identify the element with 35 protons and write the symbols for its isotopes with 44 and 46 neutrons.

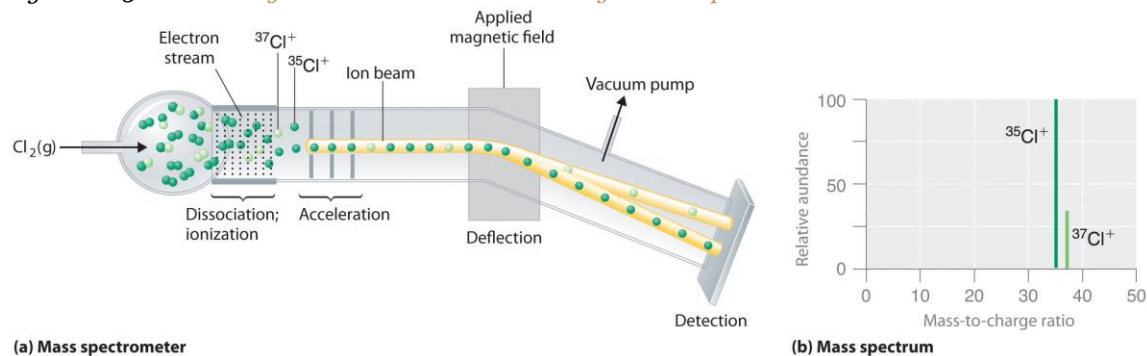
Answer: B3579r and B3581r or, more commonly, ^{79}Br and ^{81}Br .

Although the masses of the electron, the proton, and the neutron are known to a high degree of precision (Table 1.3 "Properties of Subatomic Particles*"), the mass of any given atom is not simply the sum of the masses of its electrons, protons, and neutrons. For example, the ratio of the masses of ^1H (hydrogen) and ^2H (deuterium) is actually 0.500384, rather than 0.49979 as predicted from the numbers of neutrons and protons present. Although the difference in mass is small, it is extremely important because it is the source of the huge amounts of energy released in nuclear reactions (Chapter 20 "Nuclear Chemistry").

Because atoms are much too small to measure individually and do not have a charge, there is no convenient way to accurately measure *absolute* atomic masses. Scientists can measure *relative* atomic masses very accurately, however, using an instrument called a *mass spectrometer*. The technique is conceptually similar to the one Thomson used to determine the mass-to-charge ratio of the electron. First, electrons are removed from or added to atoms or molecules, thus producing charged particles called ions. When an electric field is applied, the ions are accelerated into a separate chamber where they are deflected from their initial trajectory by a magnetic field, like the electrons in Thomson's experiment. The extent of the deflection depends on the mass-to-charge ratio of the ion. By measuring the relative deflection of ions that have the same charge, scientists can determine their relative masses (Figure 1.25 "Determining Relative Atomic Masses Using a Mass Spectrometer"). Thus it is not possible to calculate absolute atomic masses accurately by simply adding together the masses of the electrons, the protons, and the neutrons, and *absolute* atomic masses cannot be measured, but *relative* masses can be measured very accurately. It is actually rather common in chemistry to encounter a quantity whose magnitude can be measured only relative to some other quantity, rather than absolutely. We will encounter many other examples later in this text. In such cases,

chemists usually define a standard by arbitrarily assigning a numerical value to one of the quantities, which allows them to calculate numerical values for the rest.

Figure 1.25 *Determining Relative Atomic Masses Using a Mass Spectrometer*



Chlorine consists of two isotopes, ^{35}Cl and ^{37}Cl , in approximately a 3:1 ratio. (a) When a sample of elemental chlorine is injected into the mass spectrometer, electrical energy is used to dissociate the Cl_2 molecules into chlorine atoms and convert the chlorine atoms to Cl^+ ions. The ions are then accelerated into a magnetic field. The extent to which the ions are deflected by the magnetic field depends on their relative mass-to-charge ratios. Note that the lighter $^{35}\text{Cl}^+$ ions are deflected more than the heavier $^{37}\text{Cl}^+$ ions. By measuring the relative deflections of the ions, chemists can determine their mass-to-charge ratios and thus their masses. (b) Each peak in the mass spectrum corresponds to an ion with a particular mass-to-charge ratio. The abundance of the two isotopes can be determined from the heights of the peaks.

The arbitrary standard that has been established for describing atomic mass is the atomic mass unit (amu), defined as one-twelfth of the mass of one atom of ^{12}C . Because the masses of all other atoms are calculated relative to the ^{12}C standard, ^{12}C is the only atom listed in Table 1.5 "Properties of Selected Isotopes" whose exact atomic mass is equal to the mass number. Experiments have shown that $1 \text{ amu} = 1.66 \times 10^{-24} \text{ g}$.

Mass spectrometric experiments give a value of 0.167842 for the ratio of the mass of ^2H to the mass of ^{12}C , so the absolute mass of ^2H is

$$\text{Mass of H (to the 2nd power)} / \text{mass of C (to the 12th power)} \times \text{mass of C to the 12th power} = 0.167842 \times 12 \text{ amu} = 2.014104 \text{ amu}$$

The masses of the other elements are determined in a similar way.

The periodic table (see Chapter 32 "Appendix H: Periodic Table of Elements") lists the atomic masses of all the elements. If you compare these values with those given for some of the isotopes in Table 1.5 "Properties of Selected Isotopes", you can see that the atomic masses given in the periodic table never correspond exactly to those of any of

the isotopes. Because most elements exist as mixtures of several stable isotopes, the **atomic mass** of an element is defined as the weighted average of the masses of the isotopes. For example, naturally occurring carbon is largely a mixture of two isotopes: 98.89% ^{12}C (mass = 12 amu by definition) and 1.11% ^{13}C (mass = 13.003355 amu). The percent abundance of ^{14}C is so low that it can be ignored in this calculation. The *average* atomic mass of carbon is then calculated as

$$(0.9889 \times 12 \text{ amu}) + (0.0111 \times 13.003355 \text{ amu}) = 12.01 \text{ amu}$$

Carbon is predominantly ^{12}C , so its average atomic mass should be close to 12 amu, which is in agreement with our calculation.

The value of 12.01 is shown under the symbol for C in the periodic table (see Chapter 32 "Appendix H: Periodic Table of Elements"), although without the abbreviation *amu*, which is customarily omitted. Thus the tabulated *atomic mass* of carbon or any other element is the weighted average of the masses of the naturally occurring isotopes.

EXAMPLE 6

Naturally occurring bromine consists of the two isotopes listed in the following table:

Isotope	Exact Mass (amu)	Percent Abundance (%)
^{79}Br	78.9183	50.69
^{81}Br	80.9163	49.31

Calculate the atomic mass of bromine.

Given: exact mass and percent abundance

Asked for: atomic mass

Strategy:

A Convert the percent abundances to decimal form to obtain the mass fraction of each isotope.

B Multiply the exact mass of each isotope by its corresponding mass fraction (percent abundance $\div$ 100) to obtain its weighted mass.

C Add together the weighted masses to obtain the atomic mass of the element.

D Check to make sure that your answer makes sense.

Solution:

A The atomic mass is the weighted average of the masses of the isotopes. In general, we can write

$$\text{atomic mass of element} = [(\text{mass of isotope 1 in amu}) (\text{mass fraction of isotope 1})] + [(\text{mass of isotope 2}) (\text{mass fraction of isotope 2})] + \dots$$

Bromine has only two isotopes. Converting the percent abundances to mass fractions gives

$$B79r: 50.69/100 = 0.5069$$

$$B81r: 49.31/100 = 0.4931$$

B Multiplying the exact mass of each isotope by the corresponding mass fraction gives the isotope's weighted mass:

$$^{79}\text{Br}: 79.9183 \text{ amu} \times 0.5069 = 40.00^{81}\text{Br}: 80.9163 \text{ amu} \times 0.4931 = 39.90 \text{ amu}$$

C The sum of the weighted masses is the atomic mass of bromine is
 $40.00 \text{ amu} + 39.90 \text{ amu} = 79.90 \text{ amu}$

D This value is about halfway between the masses of the two isotopes, which is expected because the percent abundance of each is approximately 50%.

Exercise

Magnesium has the three isotopes listed in the following table:

Isotope	Exact Mass (amu)	Percent Abundance (%)
^{24}Mg	23.98504	78.70
^{25}Mg	24.98584	10.13
^{26}Mg	25.98259	11.17

Use these data to calculate the atomic mass of magnesium.

Answer: 24.31 amu

Summary

Each atom of an element contains the same number of protons, which is the **atomic number** (Z). Neutral atoms have the same number of electrons and protons. Atoms of an element that contain different numbers of neutrons are called **isotopes**. Each isotope of a given element has the same atomic number but a different **mass number** (A), which is the sum of the numbers of protons and neutrons. The relative masses of atoms are reported using the **atomic mass unit (amu)**, which is defined as one-twelfth of the mass of one atom of carbon-12, with 6 protons, 6 neutrons, and 6 electrons. The **atomic mass** of an element is the weighted average of the masses of the naturally occurring isotopes. When one or more electrons are added to or removed from an atom or molecule, a charged particle called an **ion** is produced, whose charge is indicated by a superscript after the symbol.

KEY TAKEAWAY

- The mass of an atom is a weighted average that is largely determined by the number of its protons and neutrons, whereas the number of protons and electrons determines its charge.

CONCEPTUAL PROBLEMS

- Complete the following table for the missing elements, symbols, and numbers of electrons.

Element	Symbol	Number of Electrons
molybdenum		
		19
titanium		
	B	
		53
	Sm	
helium		
		14

- Complete the following table for the missing elements, symbols, and numbers of electrons.

Element	Symbol	Number of Electrons
lanthanum		
	Go	
aluminum		
		80
sodium		
	One	
		9
	Be	

- Is the mass of an ion the same as the mass of its parent atom? Explain your answer.
- What isotopic standard is used for determining the mass of an atom?
- Give the symbol X_ZA for these elements, all of which exist as a single isotope.
 - beryllium
 - ruthenium

- c. phosphorus
 - d. aluminum
 - e. cesium
 - f. praseodymium
 - g. cobalt
 - h. yttrium
 - i. arsenic
2. Give the symbol XZA for these elements, all of which exist as a single isotope.
- a. fluorine
 - b. helium
 - c. terbium
 - d. iodine
 - e. gold
 - f. scandium
 - g. sodium
 - h. niobium
 - i. manganese
3. Identify each element, represented by X, that have the given symbols.
- a. X 26 55
 - b. X 33 74
 - c. X 12 24
 - d. X 53 127
 - e. X 18 40
 - f. X 63 152

NUMERICAL PROBLEMS

Please be sure you are familiar with the topics discussed in Essential Skills 1 (Section 1.9 "Essential Skills 1") before proceeding to the Numerical Problems.

1. The isotopes ^{131}I and ^{60}Co are commonly used in medicine. Determine the number of neutrons, protons, and electrons in a neutral atom of each.

2. Determine the number of protons, neutrons, and electrons in a neutral atom of each isotope:
 - a. ^{97}Tc
 - b. ^{113}In
 - c. ^{63}Ni
 - d. ^{55}Fe
3. Both technetium-97 and americium-240 are produced in nuclear reactors. Determine the number of protons, neutrons, and electrons in the neutral atoms of each.
4. The following isotopes are important in archaeological research. How many protons, neutrons, and electrons does a neutral atom of each contain?
 - a. ^{207}Pb
 - b. ^{16}O
 - c. ^{40}K
 - d. ^{137}Cs
 - e. ^{40}Ar
5. Copper, an excellent conductor of heat, has two isotopes: ^{63}Cu and ^{65}Cu . Use the following information to calculate the average atomic mass of copper:

Isotope	Percent Abundance (%)	Atomic Mass (amu)
^{63}Cu	69.09	62.9298
^{65}Cu	30.92	64.9278

6. Silicon consists of three isotopes with the following percent abundances:

Isotope	Percent Abundance (%)	Atomic Mass (amu)
^{28}Si	92.18	27.976926
^{29}Si	4.71	28.976495
^{30}Si	3.12	29.973770

7. Calculate the average atomic mass of silicon.
8. Complete the following table for neon. The average atomic mass of neon is 20.1797 amu.

Isotope	Percent Abundance (%)	Atomic Mass (amu)
^{20}Ne	90.92	19.99244
^{21}Ne	0.257	20.99395

Isotope	Percent Abundance (%)	Atomic Mass (amu)
^{22}Ne		

9. Are X2863 and X2962 isotopes of the same element? Explain your answer.

10. Complete the following table:

Isotope	Number of Protons	Number of Neutrons	Number of Electrons
^{238}X			95
^{238}U			
	75	112	

11. Complete the following table:

Isotope	Number of Protons	Number of Neutrons	Number of Electrons
^{57}Fe			
^{40}X		20	
^{36}S			

12. Using a mass spectrometer, a scientist determined the percent abundances of the isotopes of sulfur to be 95.27% for ^{32}S , 0.51% for ^{33}S , and 4.22% for ^{34}S . Use the atomic mass of sulfur from the periodic table (see Chapter 32 "Appendix H: Periodic Table of Elements") and the following atomic masses to determine whether these data are accurate, assuming that these are the only isotopes of sulfur: 31.972071 amu for ^{32}S , 32.971459 amu for ^{33}S , and 33.967867 amu for ^{34}S .
13. The percent abundances of two of the three isotopes of oxygen are 99.76% for ^{16}O , and 0.204% for ^{18}O . Use the atomic mass of oxygen given in the periodic table (see Chapter 32 "Appendix H: Periodic Table of Elements") and the following data to determine the mass of ^{17}O : 15.994915 amu for ^{16}O and 17.999160 amu for ^{18}O .
14. Which element has the higher proportion by mass in NaI?
15. Which element has the higher proportion by mass in KBr?

[1] We will explain the rationale for the peculiar format of the periodic table in Chapter 7 "The Periodic Table and Periodic Trends".

1.7 Introduction to the Periodic Table

LEARNING OBJECTIVE

- To become familiar with the organization of the periodic table.

The elements are arranged in a **periodic table** (Figure 1.24 "The Periodic Table Showing the Elements in Order of Increasing "; also see Chapter 32 "Appendix H: Periodic Table of Elements"), which is probably the single most important learning aid in chemistry. It summarizes huge amounts of information about the elements in a way that permits you to predict many of their properties and chemical reactions. The elements are arranged in seven horizontal rows, in order of increasing atomic number from left to right and top to bottom. The rows are called periods, and they are numbered from 1 to 7. The elements are stacked in such a way that elements with similar chemical properties form vertical columns, called groups, numbered from 1 to 18 (older periodic tables use a system based on roman numerals). Groups 1, 2, and 13–18 are the main group elements, listed as *A* in older tables. Groups 3–12 are in the middle of the periodic table and are the transition elements, listed as *B* in older tables. The two rows of 14 elements at the bottom of the periodic table are the *lanthanides* and the *actinides*, whose positions in the periodic table are indicated in group 3. A more comprehensive description of the periodic table is found in Chapter 7 "The Periodic Table and Periodic Trends".

Metals, Nonmetals, and Semimetals

The heavy orange zigzag line running diagonally from the upper left to the lower right through groups 13–16 in Figure 1.24 "The Periodic Table Showing the Elements in Order of Increasing " divides the elements into metals (in blue, below and to the left of the line) and nonmetals (in bronze, above and to the right of the line). As you might expect, elements colored in gold that lie along the diagonal line exhibit properties intermediate between metals and nonmetals; they are called semimetals.

The distinction between metals and nonmetals is one of the most fundamental in chemistry. Metals—such as copper or gold—are good conductors of electricity and heat; they can be pulled into wires because they are ductile; they can be hammered or pressed into thin sheets or foils because they are malleable; and most have a shiny appearance, so they are lustrous. The vast majority of the known elements are metals. Of the metals, only mercury is a liquid at room temperature and pressure; all the rest are solids.

Nonmetals, in contrast, are generally poor conductors of heat and electricity and are not lustrous.

Nonmetals can be gases (such as chlorine), liquids (such as bromine), or solids (such as iodine) at room temperature and pressure. Most solid nonmetals are *brittle*, so they break into small pieces when hit with a hammer or pulled into a wire. As expected, semimetals exhibit properties intermediate between metals and nonmetals.

EXAMPLE 7

Based on its position in the periodic table, do you expect selenium to be a metal, a nonmetal, or a semimetal?

Given: element

Asked for: classification

Strategy:

Find selenium in the periodic table shown in Figure 1.24 "The Periodic Table Showing the Elements in Order of Increasing " and then classify the element according to its location.

Solution:

The atomic number of selenium is 34, which places it in period 4 and group 16. In Figure 1.24 "The Periodic Table Showing the Elements in Order of Increasing ", selenium lies above and to the right of the diagonal line marking the boundary between metals and nonmetals, so it should be a nonmetal. Note, however, that because selenium is close to the metal-nonmetal dividing line, it would not be surprising if selenium were similar to a semimetal in some of its properties.

Exercise

Based on its location in the periodic table, do you expect indium to be a nonmetal, a metal, or a semimetal?

Answer: metal

Descriptive Names

As we noted, the periodic table is arranged so that elements with similar chemical behaviors are in the same group. Chemists often make general statements about the properties of the elements in a group using descriptive names with historical origins. For example, the elements of group 1 are known as the alkali metals, group 2 are the alkaline earth metals, group 17 are the halogens, and group 18 are the noble gases.

The Alkali Metals

The alkali metals are lithium, sodium, potassium, rubidium, cesium, and francium. Hydrogen is unique in that it is generally placed in group 1, but it is not a metal.

The compounds of the alkali metals are common in nature and daily life. One example is table salt (sodium chloride); lithium compounds are used in greases, in batteries, and as drugs to treat patients who

exhibit manic-depressive, or bipolar, behavior. Although lithium, rubidium, and cesium are relatively rare in nature, and francium is so unstable and highly radioactive that it exists in only trace amounts, sodium and potassium are the seventh and eighth most abundant elements in Earth's crust, respectively.

The Alkaline Earth Metals

The alkaline earth metals are beryllium, magnesium, calcium, strontium, barium, and radium. Beryllium, strontium, and barium are rather rare, and radium is unstable and highly radioactive. In contrast, calcium and magnesium are the fifth and sixth most abundant elements on Earth, respectively; they are found in huge deposits of limestone and other minerals.

The Halogens

The halogens are fluorine, chlorine, bromine, iodine, and astatine. The name *halogenis* derived from the Greek for "salt forming," which reflects that all the halogens react readily with metals to form compounds, such as sodium chloride and calcium chloride (used in some areas as road salt).

Compounds that contain the fluoride ion are added to toothpaste and the water supply to prevent dental cavities. Fluorine is also found in Teflon coatings on kitchen utensils. Although chlorofluorocarbon propellants and refrigerants are believed to lead to the depletion of Earth's ozone layer and contain both fluorine and chlorine, the latter is responsible for the adverse effect on the ozone layer. Bromine and iodine are less abundant than chlorine, and astatine is so radioactive that it exists in only negligible amounts in nature.

The Noble Gases

The noble gases are helium, neon, argon, krypton, xenon, and radon. Because the noble gases are composed of only single atoms, they are monatomic. At room temperature and pressure, they are unreactive gases. Because of their lack of reactivity, for many years they were called inert gases or rare gases. However, the first chemical compounds containing the noble gases were prepared in 1962.

Although the noble gases are relatively minor constituents of the atmosphere, natural gas contains substantial amounts of helium. Because of its low reactivity, argon is often used as an unreactive (*inert*) atmosphere for welding and in light bulbs. The red light emitted by neon in a gas discharge tube is used in neon lights.

Note the Pattern

The noble gases are unreactive at room temperature and pressure.

Summary

The periodic table is an arrangement of the elements in order of increasing atomic number. Elements that exhibit similar chemistry appear in vertical columns called **groups** (numbered 1–18 from left to right); the seven horizontal rows are called **periods**. Some of the groups have widely used common names, including the **alkali metals** (group 1) and the **alkaline earth metals** (group 2) on the far left, and the **halogens** (group 17) and the **noble gases** (group 18) on the far right. The elements can be broadly divided into **metals**, **nonmetals**, and **semimetals**. Semimetals exhibit properties intermediate between those of metals and nonmetals. Metals are located on the left of the periodic table, and nonmetals are located on the upper right. They are separated by a diagonal band of semimetals. Metals are **lustrous**, good conductors of electricity, and readily shaped (they are **ductile** and **malleable**), whereas solid nonmetals are generally brittle and poor electrical conductors. Other important groupings of elements in the periodic table are the **main group elements**, the **transition metals**, the lanthanides, and the actinides.

KEY TAKEAWAY

- The periodic table is used as a predictive tool.

CONCEPTUAL PROBLEMS

1. Classify each element in Conceptual Problem 1 (Section 1.6 "Isotopes and Atomic Masses") as a metal, a nonmetal, or a semimetal. If a metal, state whether it is an alkali metal, an alkaline earth metal, or a transition metal.
2. Classify each element in Conceptual Problem 2 (Section 1.6 "Isotopes and Atomic Masses") as a metal, a nonmetal, or a semimetal. If a metal, state whether it is an alkali metal, an alkaline earth metal, or a transition metal.
3. Classify each element as a metal, a semimetal, or a nonmetal. If a metal, state whether it is an alkali metal, an alkaline earth metal, or a transition metal.
 - a. iron
 - b. tantalum
 - c. sulfur
 - d. silicon
 - e. chlorine

- f. nickel
 - g. potassium
 - h. radon
 - i. zirconium
4. Which of these sets of elements are all in the same period?
- a. potassium, vanadium, and ruthenium
 - b. lithium, carbon, and chlorine
 - c. sodium, magnesium, and sulfur
 - d. chromium, nickel, and krypton
5. Which of these sets of elements are all in the same period?
- a. barium, tungsten, and argon
 - b. yttrium, zirconium, and selenium
 - c. potassium, calcium, and zinc
 - d. scandium, bromine, and manganese
6. Which of these sets of elements are all in the same group?
- a. sodium, rubidium, and barium
 - b. nitrogen, phosphorus, and bismuth
 - c. copper, silver, and gold
 - d. magnesium, strontium, and samarium
7. Which of these sets of elements are all in the same group?
- a. iron, ruthenium, and osmium
 - b. nickel, palladium, and lead
 - c. iodine, fluorine, and oxygen
 - d. boron, aluminum, and gallium
8. Indicate whether each element is a transition metal, a halogen, or a noble gas.
- a. manganese
 - b. iridium
 - c. fluorine
 - d. xenon

- e. lithium
- f. carbon
- g. zinc
- h. sodium
- i. tantalum
- j. hafnium
- k. antimony
- l. cadmium

9. Which of the elements indicated in color in the periodic table shown below is most likely to exist as a monoatomic gas? As a diatomic gas? Which is most likely to be a semimetal? A reactive metal?

The periodic table is represented by a grid of squares. The following squares are colored to represent specific elements:

- Green:** Located at the bottom left, representing Lithium (Li).
- Purple:** Located in the second row, second column, representing Carbon (C).
- Blue:** Located in the fourth row, tenth column, representing Zinc (Zn).
- Orange:** Located in the fourth row, fifteenth column, representing Antimony (Sb).
- Yellow:** Located in the fifth row, sixteenth column, representing Cadmium (Cd).
- Red:** Located in the fifth row, seventeenth column, representing Bismuth (Bi).

10. Based on their locations in the periodic table, would you expect these elements to be malleable? Why or why not?

- a. phosphorus
- b. chromium
- c. rubidium
- d. copper
- e. aluminum
- f. bismuth
- g. neodymium

10. Based on their locations in the periodic table, would you expect these elements to be lustrous? Why or why not?
- a. sulfur
 - b. vanadium
 - c. nickel
 - d. arsenic
 - e. strontium
 - f. cerium
 - g. sodium

ANSWER

Symbol	Type
Fe	metal: transition metal
Ta	metal: transition metal
S	nonmetal
Si	semimetal
Cl	nonmetal (halogen)
Ni	metal: transition metal
K	metal: alkali metal
Rn	nonmetal (noble gas)
Zr	metal: transition metal

1.8 Essential Elements for Life

LEARNING OBJECTIVE

1. To understand the importance of elements to nutrition.

Of the approximately 115 elements known, only the 19 highlighted in purple in Figure 1.26 "The Essential Elements in the Periodic Table" are absolutely required in the human diet. These elements—called essential elements—are restricted to the first four rows of the periodic table (see Chapter 32 "Appendix H: Periodic Table of Elements"), with only two or three exceptions (molybdenum, iodine, and possibly tin in the fifth row). Some other elements are

essential for specific organisms. For example, boron is required for the growth of certain plants, bromine is widely distributed in marine organisms, and tungsten is necessary for some microorganisms.

Essential for humans Suggested to be essential for humans Nonessential for humans																	
1	2											13	14	15	16	17	18
1 H												5 B	6 C	7 N	8 O	9 F	10 Ne
3 Li	4 Be											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
11 Na	12 Mg	3	4	5	6	7	8	9	10	11	12	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	113 Nh	114 Fl	115 Mc			
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Uub	113 Uut	114 Uuq	115 Uup			

Figure 1.26 *The Essential Elements in the Periodic Table*

Elements that are known to be essential for human life are shown in purple; elements that are suggested to be essential are shown in green. Elements not known to be essential are shown in gray.

What makes an element “essential”? By definition, an essential element is one that is required for life and whose absence results in death. Because of the experimental difficulties involved in producing deficiencies severe enough to cause death, especially for elements that are required in very low concentrations in the diet, a somewhat broader definition is generally used. An element is considered to be essential if a deficiency consistently causes abnormal development or functioning and if dietary supplementation of that element—and *only that element*—prevents this adverse effect. Scientists determine whether an element is essential by raising rats, chicks, and other animals on a synthetic diet that has been carefully analyzed and supplemented with acceptable levels of all elements *except* the element of interest (E). Ultraclean environments, in which plastic cages are used and dust from the air is carefully

removed, minimize inadvertent contamination. If the animals grow normally on a diet that is as low as possible in E, then *either* E is not an essential element *or* the diet is not yet below the minimum required concentration. If the animals do not grow normally on a low-E diet, then their diets are supplemented with E until a level is reached at which the animals grow normally. This level is the *minimum required intake* of element E.

Classification of the Essential Elements

The approximate elemental composition of a healthy 70.0 kg (154 lb) adult human is listed in Table 1.6 "Approximate Elemental Composition of a Typical 70 kg Human". Note that most living matter consists primarily of the so-called *bulk elements*: oxygen, carbon, hydrogen, nitrogen, and sulfur—the building blocks of the compounds that constitute our organs and muscles. These five elements also constitute the bulk of our diet; tens of grams per day are required for humans. Six other elements—sodium, magnesium, potassium, calcium, chlorine, and phosphorus—are often referred to as *macrominerals* because they provide essential ions in body fluids and form the major structural components of the body. In addition, phosphorus is a key constituent of both DNA and RNA: the genetic building blocks of living organisms. The six macrominerals are present in the body in somewhat smaller amounts than the bulk elements, so correspondingly lower levels are required in the diet. The remaining essential elements—called *trace elements*—are present in very small amounts, ranging from a few grams to a few milligrams in an adult human. Finally, measurable levels of some elements are found in humans but are *not* required for growth or good health. Examples are rubidium and strontium, whose chemistry is similar to that of the elements immediately above them in the periodic table (potassium and calcium, respectively, which are essential elements). Because the body's mechanisms for extracting potassium and calcium from foods are not 100% selective, small amounts of rubidium and strontium, which have no known biological function, are absorbed.

Table 1.6 Approximate Elemental Composition of a Typical 70 kg Human

Bulk Elements (kg)		Macrominerals (g)	
oxygen	44	calcium	1700
carbon	12.6	phosphorus	680
hydrogen	6.6	potassium	250
nitrogen	1.8	chlorine	115
sulfur	0.1	sodium	70

		magnesium	42
Trace Elements (mg)			
iron	5000	lead	35
silicon	3000	barium	21
zinc	1750	molybdenum	14
rubidium	360	boron	14
copper	280	arsenic	~3
strontium	280	cobalt	~3
bromine	140	chromium	~3
tin	140	nickel	~3
manganese	70	selenium	~2
iodine	70	lithium	~2
aluminum	35	vanadium	~2

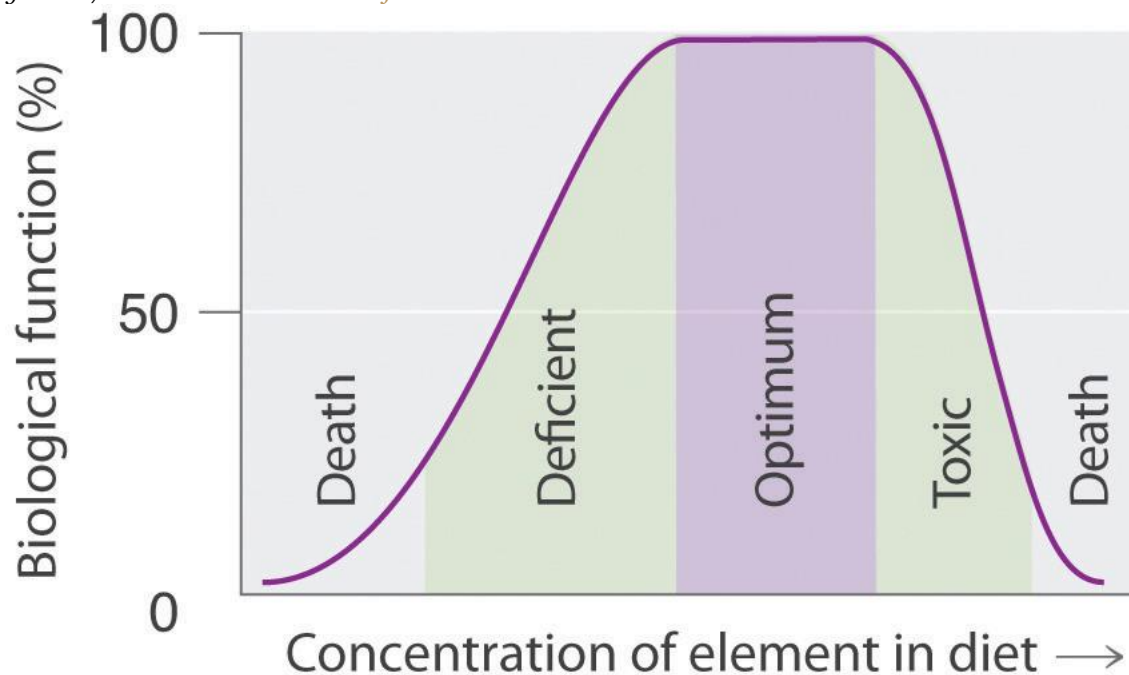
The Trace Elements

Because it is difficult to detect low levels of some essential elements, the trace elements were relatively slow to be recognized as essential. Iron was the first. In the 17th century, anemia was proved to be caused by an iron deficiency and often was cured by supplementing the diet with extracts of rusty nails. It was not until the 19th century, however, that trace amounts of iodine were found to eliminate goiter (an enlarged thyroid gland). This is why common table salt is “iodized”: a small amount of iodine is added. Copper was shown to be essential for humans in 1928, and manganese, zinc, and cobalt soon after that. Molybdenum was not known to be an essential element until 1953, and the need for chromium, selenium, vanadium, fluorine, and silicon was demonstrated only in the last 50 years. It seems likely that in the future other elements, possibly including tin, will be found to be essential at very low levels.

Many compounds of trace elements, such as arsenic, selenium, and chromium, are toxic and can even cause cancer, yet these elements are identified as essential elements in Figure 1.26 "The Essential Elements in the Periodic Table". In fact, there is some evidence that one bacterium has replaced phosphorus with arsenic, although the finding is controversial. This has opened up the possibility of a “shadow biosphere” on Earth in which life evolved from an as yet undetected common ancestor. How can elements toxic to life be essential? First, the toxicity of an element often depends on its chemical form—for example, only certain compounds of chromium are toxic, whereas others are used in mineral

supplements. Second, as shown in Figure 1.27 "Possible Concentrations of an Essential Element in the Diet", every element has three possible levels of dietary intake: *deficient*, *optimum*, and *toxic* in order of increasing concentration in the diet. Very low intake levels lead to symptoms of deficiency. Over some range of higher intake levels, an organism is able to maintain its tissue concentrations of the element at a level that optimizes biological functions. Finally, at some higher intake level, the normal regulatory mechanisms are overloaded, causing toxic symptoms to appear. Each element has its own characteristic curve. Both the width of the plateau and the specific concentration corresponding to the center of the plateau region differ by as much as several orders of magnitude for different elements. In the adult human, for example, the recommended daily dietary intake is 10–18 mg of iron, 2–3 mg of copper, and less than 0.1 mg of chromium and selenium.

Figure 1.27 Possible Concentrations of an Essential Element in the Diet



The deficient, optimum, and toxic concentrations are different for different elements.

Amplification

How can elements that are present in such minuscule amounts have such large effects on an organism's health? Our knowledge of the pathways by which each of the known trace elements affects health is far from complete, but certain general features are clear. The trace elements participate in an *amplification* mechanism; that is, they are essential components of larger biological molecules that are capable of interacting with or regulating the levels of relatively

large amounts of other molecules. For example, vitamin B₁₂ contains a single atom of cobalt, which is essential for its biological function. If the molecule whose level is controlled by the trace element can regulate the level of another molecule, and more and more molecules, then the potential exists for extreme amplification of small variations in the level of the trace element. One goal of modern chemical research is to elucidate in detail the roles of the essential elements. In subsequent chapters, we will introduce some results of this research to demonstrate the biological importance of many of the elements and their compounds.

Summary

About 19 of the approximately 115 known elements are essential for humans. An **essential element** is one whose absence results in abnormal biological function or development that is prevented by dietary supplementation with that element. Living organisms contain relatively large amounts of oxygen, carbon, hydrogen, nitrogen, and sulfur (these five elements are known as the bulk elements), along with sodium, magnesium, potassium, calcium, chlorine, and phosphorus (these six elements are known as macrominerals). The other essential elements are the trace elements, which are present in very small quantities. Dietary intakes of elements range from deficient to optimum to toxic with increasing quantities; the optimum levels differ greatly for the essential elements.

KEY TAKEAWAY

- The absence of some elements can result in abnormal biological function or development.

1.9 Essential Skills 1

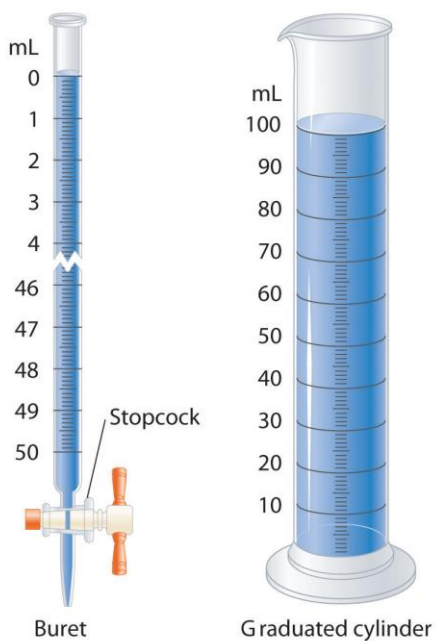
TOPICS

- Measurement
- Scientific Notation
- Significant Figures
- Accuracy and Precision

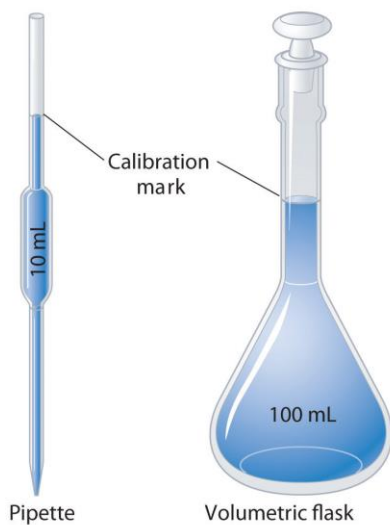
This section describes some of the fundamental mathematical skills you will need to complete the questions and problems in this text. For some of you, this discussion will serve as a review, whereas others may be encountering at least some of the ideas and techniques for the first time. We will introduce other mathematical skills in subsequent Essential Skills sections as the need arises. Be sure you are familiar with the topics discussed here before you start the Chapter 1 "Introduction to Chemistry" problems.

Measurement

Instruments of Measurement



Graduated glassware is used to deliver variable volumes of liquid.



Volumetric glassware is used to deliver (pipette) or contain (volumetric flask) a single volume accurately when filled to the calibration mark.



A **balance** is used to measure mass.

A variety of instruments are available for making direct measurements of the macroscopic properties of a chemical substance. For example, we usually measure the volume of a liquid sample with pipettes, burets, graduated cylinders, and volumetric flasks, whereas we usually measure the *mass* of a solid or liquid substance with a balance. Measurements on an atomic or molecular scale, in contrast, require specialized instrumentation, such as the mass spectrometer described in Section 1.6 "Isotopes and Atomic Masses".

SI Units

All reported measurements must include an appropriate unit of measurement because to say that a substance has “a mass of 10,” for example, does not tell whether the mass was measured in grams, pounds, tons, or some other unit. To establish worldwide standards for the consistent measurement of important physical and chemical properties, an international body called the General Conference on Weights and Measures devised the *Système internationale d’unités* (or SI). The International System of Units is based on metric units and requires that measurements be expressed in decimal form. Table 1.7 "SI Base Units" lists the seven base units of the SI system; all other SI units of measurement are derived from them.

By attaching prefixes to the base unit, the magnitude of the unit is indicated; each prefix indicates that the base unit is multiplied by a specified power of 10. The prefixes, their symbols, and their numerical significance are given in Table 1.8 "Prefixes Used with SI Units". To study chemistry, you need to know the information presented in Table 1.7 "SI Base Units" and Table 1.8 "Prefixes Used with SI Units".

Table 1.7 SI Base Units

Base Quantity	Unit Name	Abbreviation

Base Quantity	Unit Name	Abbreviation
mass	kilogram	kg
length	meter	m
time	second	s
temperature	kelvin	K
electric current	ampere	A
amount of substance	mole	mol
luminous intensity	candela	cd

Table 1.8 Prefixes Used with SI Units

Prefix	Symbol	Value	Power of 10	Meaning
tera	T	1,000,000,000,000	10^{12}	trillion
giga	G	1,000,000,000	10^9	billion
mega	M	1,000,000	10^6	million
kilo	k	1000	10^3	thousand
hecto	h	100	10^2	hundred
deca	da	10	10^1	ten
—	—	1	10^0	one
deci	d	0.1	10^{-1}	tenth
centi	c	0.01	10^{-2}	hundredth
milli	m	0.001	10^{-3}	thousandth
micro	μ	0.000001	10^{-6}	millionth
nano	n	0.000000001	10^{-9}	billionth
pico	p	0.000000000001	10^{-12}	trillionth
femto	f	0.000000000000001	10^{-15}	quadrillionth

Units of Mass, Volume, and Length

The units of measurement you will encounter most frequently in chemistry are those for mass, volume, and length. The basic SI unit for mass is the kilogram (kg), but in the laboratory, mass is usually expressed in either grams (g) or milligrams (mg): $1000\text{ g} = 1\text{ kg}$, $1000\text{ mg} = 1\text{ g}$, and $1,000,000\text{ mg} = 1\text{ kg}$. Units for volume are derived from the cube of the SI unit for length, which is the meter (m). Thus the basic SI unit for volume is cubic meters ($\text{length} \times \text{width} \times \text{height} = \text{m}^3$). In chemistry, however, volumes

are usually reported in cubic centimeters (cm^3) and cubic decimeters (dm^3) or milliliters (mL) and liters (L), although the liter is not an SI unit of measurement. The relationships between these units are as follows:

$$1 \text{ L} = 1000 \text{ mL} = 1 \text{ dm}^3 \quad 1 \text{ mL} = 1 \text{ cm}^3 \quad 1000 \text{ cm}^3 = 1 \text{ L}$$

Scientific Notation

Chemists often work with numbers that are exceedingly large or small. For example, entering the mass in grams of a hydrogen atom into a calculator requires a display with at least 24 decimal places. A system called scientific notation avoids much of the tedium and awkwardness of manipulating numbers with large or small magnitudes. In scientific notation, these numbers are expressed in the form $N \times 10^n$

where N is greater than or equal to 1 and less than 10 ($1 \leq N < 10$), and n is a positive or negative integer ($10^0 = 1$). The number 10 is called the *base* because it is this number that is raised to the power n . Although a base number may have values other than 10, the base number in scientific notation is *always* 10.

A simple way to convert numbers to scientific notation is to move the decimal point as many places to the left or right as needed to give a number from 1 to 10 (N). The magnitude of n is then determined as follows:

- If the decimal point is moved to the *left* n places, n is positive.
- If the decimal point is moved to the *right* n places, n is negative.

Another way to remember this is to recognize that as the number N decreases in magnitude, the exponent increases and vice versa. The application of this rule is illustrated in Skill Builder ES1.

SKILL BUILDER ES1

Convert each number to scientific notation.

- 637.8
- 0.0479
- 7.86
- 12,378
- 0.00032
- 61.06700

g. 2002.080

h. 0.01020

Solution

a. To convert 637.8 to a number from 1 to 10, we move the decimal point two places to the *left*:

6 3 7 . 8

Because the decimal point was moved two places to the left, $n = 2$. In scientific notation, $637.8 = 6.378 \times 10^2$.

b. To convert 0.0479 to a number from 1 to 10, we move the decimal point two places to the *right*:

0. 0 4 7 9

Because the decimal point was moved two places to the right, $n = -2$. In scientific notation, $0.0479 = 4.79 \times 10^{-2}$.

c. 7.86×10^0 : this is usually expressed simply as 7.86. (Recall that $10^0 = 1$.)

d. 1.2378×10^4 ; because the decimal point was moved four places to the left, $n = 4$.

e. 3.2×10^{-4} ; because the decimal point was moved four places to the right, $n = -4$.

f. 6.106700×10^1 : this is usually expressed as 6.1067×10 .

g. 2.002080×10^3

h. 1.020×10^{-2}

Addition and Subtraction

Before numbers expressed in scientific notation can be added or subtracted, they must be converted to a form in which all the exponents have the same value. The appropriate operation is then carried out on the values of N . Skill Builder ES2 illustrates how to do this.

SKILL BUILDER ES2

Carry out the appropriate operation on each number and then express the answer in scientific notation.

a. $(1.36 \times 10^2) + (4.73 \times 10^3)$

b. $(6.923 \times 10^{-3}) - (8.756 \times 10^{-4})$

Solution

a. Both exponents must have the same value, so these numbers are converted to either $(1.36 \times 10^2) + (47.3 \times 10^2)$ or $(0.136 \times 10^3) + (4.73 \times 10^3)$. Choosing either alternative gives the same answer, reported to two decimal places:

$$(1.36 \times 10^2) + (47.3 \times 10^2) = (1.36 + 47.3) \times 10^2 = 48.66 \times 10^2 = 4.87 \times 10^3$$

$$(0.136 \times 10^3) + (4.73 \times 10^3) = (0.136 + 4.73) \times 10^3 = 4.87 \times 10^3$$

In converting 48.66×10^2 to scientific notation, n has become more positive by 1 because the value of N has decreased.

b. Converting the exponents to the same value gives either $(6.923 \times 10^{-3}) - (0.8756 \times 10^{-3})$ or $(69.23 \times 10^{-4}) - (8.756 \times 10^{-4})$. Completing the calculations gives the same answer, expressed to three decimal places:

$$(6.923 \times 10^{-3}) - (0.8756 \times 10^{-3}) = (6.923 - 0.8756) \times 10^{-3} = 6.047 \times 10^{-3}$$

$$(69.23 \times 10^{-4}) - (8.756 \times 10^{-4}) = (69.23 - 8.756) \times 10^{-4} = 60.474 \times 10^{-4} = 6.047 \times 10^{-3}$$

Multiplication and Division

When multiplying numbers expressed in scientific notation, we multiply the values of N and add together the values of n . Conversely, when dividing, we divide N in the dividend (the number being divided) by N in the divisor (the number by which we are dividing) and then subtract n in the divisor from n in the dividend. In contrast to addition and subtraction, the exponents do *not* have to be the same in multiplication and division. Examples of problems involving multiplication and division are shown in Skill Builder ES3.

SKILL BUILDER ES3

Perform the appropriate operation on each expression and express your answer in scientific notation.

- a. $(6.022 \times 10^{23})(6.42 \times 10^{-2})$
- b. $1.67 \times 10^{-24} - 9.12 \times 10^{-28}$
- c. $(6.63 \times 10^{-34})(6.0 \times 10^{-8}) - 8.52 \times 10^{-2}$

Solution

a. In multiplication, we add the exponents:

$$(6.022 \times 10^{23})(6.42 \times 10^{-2}) = (6.022)(6.42) \times 10^{[23 + (-2)]} = 38.7 \times 10^{21} = 3.87 \times 10^{22}$$

b. In division, we subtract the exponents:

$$1.67 \times 10^{-24} / 9.12 \times 10^{-28} = 1.67 / 9.12 \times 10^{[-24 - (-28)]} = 0.183 \times 10^4 = 1.83 \times 10^3$$

c. This problem has both multiplication *and* division:

$$(6.63 \times 10^{-34})(6.0 \times 10) / (8.52 \times 10^{-2}) = 39.78 / 8.52 \times 10^{[-34 + 1 - (-2)]} = 4.7 \times 10^{-31}$$

Significant Figures

No measurement is free from error. Error is introduced by (1) the limitations of instruments and measuring devices (such as the size of the divisions on a graduated cylinder) and (2) the imperfection of human senses. Although errors in calculations can be enormous, they do *not* contribute to uncertainty in measurements. Chemists describe the estimated degree of error in a measurement as the uncertainty of the measurement, and they are careful to report all measured values using only significant figures, numbers that describe the value without exaggerating the degree to which it is known to be accurate. Chemists report as significant all numbers known with absolute certainty, plus one more digit that is understood to contain some uncertainty. The uncertainty in the final digit is usually assumed to be ± 1 , unless otherwise stated.

The following rules have been developed for counting the number of significant figures in a measurement or calculation:

1. Any nonzero digit is significant.
2. Any zeros between nonzero digits are significant. The number 2005, for example, has four significant figures.
3. Any zeros used as a placeholder preceding the first nonzero digit are not significant. So 0.05 has one significant figure because the zeros are used to indicate the placement of the digit 5. In contrast, 0.050 has two significant figures because the last two digits correspond to the number 50; the last zero is not a placeholder. As an additional example, 5.0 has two significant figures because the zero is used not to place the 5 but to indicate 5.0.
4. When a number does not contain a decimal point, zeros added after a nonzero number may or may not be significant. An example is the number 100, which may be interpreted as having one, two, or three

significant figures. (Note: treat all trailing zeros in exercises and problems in this text as significant unless you are specifically told otherwise.)

5. Integers obtained either by counting objects or from definitions are exact numbers, which are considered to have infinitely many significant figures. If we have counted four objects, for example, then the number 4 has an infinite number of significant figures (i.e., it represents 4.000...). Similarly, 1 foot (ft) is defined to contain 12 inches (in), so the number 12 in the following equation has infinitely many significant figures:

$$1 \text{ ft} = 12 \text{ in}$$

An effective method for determining the number of significant figures is to convert the measured or calculated value to scientific notation because any zero used as a placeholder is eliminated in the conversion. When 0.0800 is expressed in scientific notation as 8.00×10^{-2} , it is more readily apparent that the number has three significant figures rather than five; in scientific notation, the number preceding the exponential (i.e., N) determines the number of significant figures. Skill Builder ES4 provides practice with these rules.

SKILL BUILDER ES4

Give the number of significant figures in each. Identify the rule for each.

- a. 5.87
- b. 0.031
- c. 52.90
- d. 00.2001
- e. 500
- f. 6 atoms

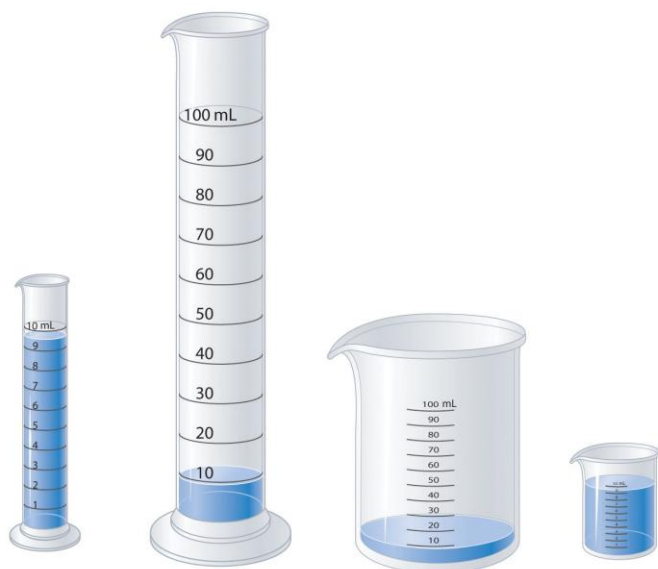
Solution

- a. three (rule 1)
- b. two (rule 3); in scientific notation, this number is represented as 3.1×10^{-2} , showing that it has two significant figures.
- c. four (rule 3)
- d. four (rule 2); this number is 2.001×10^{-1} in scientific notation, showing that it has four significant figures.
- e. one, two, or three (rule 4)

f. infinite (rule 5)

SKILL BUILDER ES5

Which measuring apparatus would you use to deliver 9.7 mL of water as accurately as possible? To how many significant figures can you measure that volume of water with the apparatus you selected?



Solution

Use the 10 mL graduated cylinder, which will be accurate to two significant figures.

Mathematical operations are carried out using all the digits given and then rounding the final result to the correct number of significant figures to obtain a reasonable answer. This method avoids compounding inaccuracies by successively rounding intermediate calculations. After you complete a calculation, you may have to round the last significant figure up or down depending on the value of the digit that follows it. If the digit is 5 or greater, then the number is rounded up. For example, when rounded to three significant figures, 5.215 is 5.22, whereas 5.213 is 5.21. Similarly, to three significant figures, 5.005 kg becomes 5.01 kg, whereas 5.004 kg becomes 5.00 kg. The procedures for dealing with significant figures are different for addition and subtraction versus multiplication and division.

When we add or subtract measured values, the value with the fewest significant figures to the right of the decimal point determines the number of significant figures to the right of the decimal point in the answer.

Drawing a vertical line to the right of the column corresponding to the smallest number of significant figures is a simple method of determining the proper number of significant figures for the answer:

$$3240.7 + 21.2 \quad 36 \quad 3261.9 \quad 36$$

The line indicates that the digits 3 and 6 are not significant in the answer. These digits are not significant because the values for the corresponding places in the other measurement are unknown (3240.7??).

Consequently, the answer is expressed as 3261.9, with five significant figures. Again, numbers greater than or equal to 5 are rounded up. If our second number in the calculation had been 21.256, then we would have rounded 3261.956 to 3262.0 to complete our calculation.

When we multiply or divide measured values, the answer is limited to the smallest number of significant figures in the calculation; thus, $42.9 \times 8.323 = 357.057 = 357$. Although the second number in the calculation has four significant figures, we are justified in reporting the answer to only three significant figures because the first number in the calculation has only three significant figures. An exception to this rule occurs when multiplying a number by an integer, as in 12.793×12 . In this case, the number of significant figures in the answer is determined by the number 12.793, because we are in essence adding 12.793 to itself 12 times. The correct answer is therefore 155.516, an increase of one significant figure, not 155.52.

When you use a calculator, it is important to remember that the number shown in the calculator display often shows more digits than can be reported as significant in your answer. When a measurement reported as 5.0 kg is divided by 3.0 L, for example, the display may show 1.666666667 as the answer. We are justified in reporting the answer to only two significant figures, giving 1.7 kg/L as the answer, with the last digit understood to have some uncertainty.

In calculations involving several steps, slightly different answers can be obtained depending on how rounding is handled, specifically whether rounding is performed on intermediate results or postponed until the last step. Rounding to the correct number of significant figures should *always* be performed at the end of a series of calculations because rounding of intermediate results can sometimes cause the final answer to be significantly in error.

In practice, chemists generally work with a calculator and carry all digits forward through subsequent calculations. When working on paper, however, we often want to minimize the number of digits we have to write out. Because successive rounding can compound inaccuracies, intermediate roundings need to be handled correctly. When working on paper, always round an intermediate result so as to retain at least one more digit than can be justified and carry this number into the next step in the calculation. The final answer is then rounded to the correct number of significant figures at the very end.

In the worked examples in this text, we will often show the results of intermediate steps in a calculation. In doing so, we will show the results to only the correct number of significant figures allowed for that step, in effect treating each step as a separate calculation. This procedure is intended to reinforce the rules for determining the number of significant figures, but in some cases it may give a final answer that differs in the last digit from that obtained using a calculator, where all digits are carried through to the last step.

Skill Builder ES6 provides practice with calculations using significant figures.

SKILL BUILDER ES6

Complete the calculations and report your answers using the correct number of significant figures.

- a. $87.25 \text{ mL} + 3.0201 \text{ mL}$
- a. $26.843 \text{ g} + 12.23 \text{ g}$
- b. 6×12.011
- c. $2(1.008) \text{ g} + 15.99 \text{ g}$
- d. $137.3 + 2(35.45)$
- e. $118.72 \text{ g} - 35.5 \text{ g}$
- f. $47.23 \text{ g} - 207.2592 \text{ g}$
- g. $77.6046467 - 4.8$
- h. $24.8620 - 3.26(0.98)$
- i. $(15.9994 \times 9) + 2.0158$

Solution

- a. 90.27 mL
- b. 39.07 g
- c. 72.066 (See rule 5 under "Significant Figures.")
- d. $2(1.008) \text{ g} + 15.99 \text{ g} = 2.016 \text{ g} + 15.99 \text{ g} = 18.01 \text{ g}$
- e. $137.3 + 2(35.45) = 137.3 + 70.90 = 208.2$
- f. $59.35 \text{ g} - 35.5 \text{ g} = 23.9 \text{ g}$
- g. $47.23 \text{ g} - 35.0 \text{ g} = 12.2 \text{ g}$
- h. $12.00 - 4.8 = 7.2$
- i. $12 - 3.2 = 9$
- j. $143.9946 + 2.0158 = 146.0104$

Accuracy and Precision

Measurements may be accurate, meaning that the measured value is the same as the true value; they may be precise, meaning that multiple measurements give nearly identical values (i.e., *reproducible results*); they may be both accurate and precise; or they may be neither accurate nor precise. The goal of scientists is to obtain measured values that are both accurate and precise.

Suppose, for example, that the mass of a sample of gold was measured on one balance and found to be 1.896 g. On a different balance, the same sample was found to have a mass of 1.125 g. Which was correct? Careful and repeated measurements, including measurements on a calibrated third balance, showed the sample to have a mass of 1.895 g. The masses obtained from the three balances are in the following table:

Balance 1	Balance 2	Balance 3
1.896 g	1.125 g	1.893 g
1.895 g	1.158 g	1.895 g
1.894 g	1.067 g	1.895 g

Whereas the measurements obtained from balances 1 and 3 are reproducible (precise) and are close to the accepted value (accurate), those obtained from balance 2 are neither. Even if the measurements obtained from balance 2 had been precise (if, for example, they had been 1.125, 1.124, and 1.125), they still would not have been accurate. We can assess the precision of a set of measurements by calculating the *average deviation* of the measurements as follows:

1. Calculate the average value of all the measurements:
$$\text{average} = \frac{\text{sum of measurements}}{\text{number of measurements}}$$
2. Calculate the *deviation* of each measurement, which is the absolute value of the difference between each measurement and the average value:
$$\text{deviation} = |\text{measurement} - \text{average}|$$

where $| |$ means absolute value (i.e., convert any negative number to a positive number).
3. Add all the deviations and divide by the number of measurements to obtain the average deviation:
$$\text{average} = \frac{\text{sum of deviations}}{\text{number of measurements}}$$

Then we can express the precision as a percentage by dividing the average deviation by the average value of the measurements and multiplying the result by 100. In the case of balance 2, the average value is $1.125 \text{ g} + 1.158 \text{ g} + 1.067 \text{ g} \div 3 = 1.117 \text{ g}$

The deviations are $1.125\text{ g} - 1.117\text{ g} = 0.008\text{ g}$, $1.158\text{ g} - 1.117\text{ g} = 0.041\text{ g}$, and $|1.067\text{ g} - 1.117\text{ g}| = 0.050\text{ g}$.

So the average deviation is

$$0.008\text{ g} + 0.041\text{ g} + 0.050\text{ g} = 0.099\text{ g}$$

The precision of this set of measurements is therefore

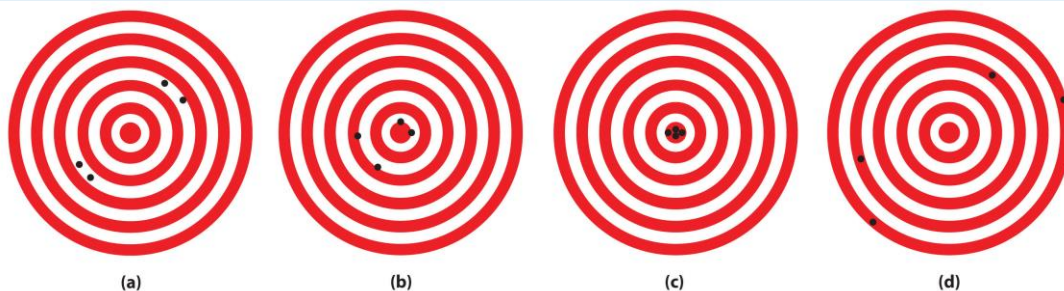
$$0.099\text{ g} \div 3 \times 100 = 3.3\%$$

When a series of measurements is precise but not accurate, the error is usually systematic. Systematic errors can be caused by faulty instrumentation or faulty technique. The difference between accuracy and precision is demonstrated in Skill Builder ES7.

SKILL BUILDER ES7

The following archery targets show marks that represent the results of four sets of measurements. Which target shows

- a. a precise but inaccurate set of measurements?
- a. an accurate but imprecise set of measurements?
- b. a set of measurements that is both precise and accurate?
- c. a set of measurements that is neither precise nor accurate?



Solution

- a. (c)
- a. (a)
- b. (b)
- c. (d)

SKILL BUILDER ES8

a. A 1-carat diamond has a mass of 200.0 mg. When a jeweler repeatedly weighed a 2-carat diamond, he obtained measurements of 450.0 mg, 459.0 mg, and 463.0 mg. Were the jeweler's measurements accurate? Were they precise?

- a. A single copper penny was tested three times to determine its composition. The first analysis gave a composition of 93.2% zinc and 2.8% copper, the second gave 92.9% zinc and 3.1% copper, and the third gave 93.5% zinc and 2.5% copper. The actual composition of the penny was 97.6% zinc and 2.4% copper. Were the results accurate? Were they precise?

Solution

- a. The expected mass of a 2-carat diamond is $2 \times 200.0 \text{ mg} = 400.0 \text{ mg}$. The average of the three measurements is 457.3 mg, about 13% greater than the true mass. These measurements are not particularly accurate.

The deviations of the measurements are 7.3 mg, 1.7 mg, and 5.7 mg, respectively, which give an average deviation of 4.9 mg and a precision of

$$4.9 \text{ mg} / 457.3 \text{ mg} \times 100 = 1.1\%$$

These measurements are rather precise.

- a. The average values of the measurements are 93.2% zinc and 2.8% copper versus the true values of 97.6% zinc and 2.4% copper. Thus these measurements are not very accurate, with errors of -4.5% and +17% for zinc and copper, respectively. (The sum of the measured zinc and copper contents is only 96.0% rather than 100%, which tells us that *either* there is a significant error in one or both measurements *or* some other element is present.)

The deviations of the measurements are 0.0%, 0.3%, and 0.3% for both zinc and copper, which give an average deviation of 0.2% for both metals. We might therefore conclude that the measurements are equally precise, but that is not the case. Recall that precision is the average deviation divided by the average value times 100. Because the average value of the zinc measurements is much greater than the average value of the copper measurements (93.2% versus 2.8%), the copper measurements are much less precise.

$$\text{precision (Zn)} = 0.2\% / 93.2\% \times 100 = 0.2\% \quad \text{precision (Cu)} = 0.2\% / 2.8\% \times 100 = 7\%$$

1.10 End-of-Chapter Material

APPLICATION PROBLEMS

Please be sure you are familiar with the topics discussed in Essential Skills 1 (Section 1.9 "Essential Skills 1") before proceeding to the Application Problems. Problems marked with a ♦ involve multiple concepts.

1. In 1953, James Watson and Francis Crick spent three days analyzing data to develop a model that was consistent with the known facts about the structure of DNA, the chemical substance that is the basis for life. They were awarded the Nobel Prize in Physiology or Medicine for their work. Based on this information, would you classify their proposed model for the structure of DNA as an experiment, a law, a hypothesis, or a theory? Explain your reasoning.
2. In each scenario, state the observation and the hypothesis.
 - a. A recently discovered Neanderthal throat bone has been found to be similar in dimensions and appearance to that of modern humans; therefore, some scientists believe that Neanderthals could talk.
 - b. Because DNA profiles from samples of human tissue are widely used in criminal trials, DNA sequences from plant residue on clothing can be used to place a person at the scene of a crime.
3. Small quantities of gold from far underground are carried to the surface by groundwater, where the gold can be taken up by certain plants and stored in their leaves. By identifying the kinds of plants that grow around existing gold deposits, one should be able to use this information to discover potential new gold deposits.
 - a. State the observation.
 - b. State the hypothesis.
 - c. Devise an experiment to test the hypothesis.
4. Large amounts of nitrogen are used by the electronics industry to provide a gas blanket over a component during production. This ensures that undesired reactions with oxygen will not occur. Classify each statement as an extensive property or an intensive property of nitrogen.
 - a. Nitrogen is a colorless gas.
 - b. A volume of 22.4 L of nitrogen gas weighs 28 g at 0°C.
 - c. Liquid nitrogen boils at 77.4 K.
 - d. Nitrogen gas has a density of 1.25 g/L at 0°C.
5. Oxygen is the third most abundant element in the universe and makes up about two-thirds of the human body. Classify each statement as an extensive property or an intensive property of oxygen.

- Liquid oxygen boils at 90.2 K.
 - Liquid oxygen is pale blue.
 - A volume of 22.4 L of oxygen gas weighs 32 g at 0°C.
 - Oxygen has a density of 1.43 g/L at 0°C.
- One of the first high-temperature superconductors was found to contain elements in the ratio 1Y:2Ba:3Cu:6.8O. A material that contains elements in the ratio 1Y:2Ba:3Cu:6O, however, was not a high-temperature superconductor. Do these materials obey the law of multiple proportions? Is the ratio of elements in each compound consistent with Dalton's law of indivisible atoms?
 - ♦ There has been increased evidence that human activities are causing changes in Earth's atmospheric chemistry. Recent research efforts have focused on atmospheric ozone (O₃) concentrations. The amount of ozone in the atmosphere is influenced by concentrations of gases that contain only nitrogen and oxygen, among others. The following table gives the masses of nitrogen that combine with 1.00 g of oxygen to form three of these compounds.

Compound	Mass of Nitrogen (g)
A	0.875
B	0.438
C	0.350

- Determine the ratios of the masses of nitrogen that combine with 1.00 g of oxygen in these compounds. Are these data consistent with the law of multiple proportions?
 - Predict the mass of nitrogen that would combine with 1.00 g of oxygen to form another possible compound in the series.
- Indium has an average atomic mass of 114.818 amu. One of its two isotopes has an atomic mass of 114.903 amu with a percent abundance of 95.70. What is the mass of the other isotope?
 - Earth's core is largely composed of iron, an element that is also a major component of black sands on beaches. Iron has four stable isotopes. Use the data to calculate the average atomic mass of iron.

Isotope	Percent Abundance (%)	Atomic Mass (amu)
⁵⁴ Fe	5.82	53.9396
⁵⁶ Fe	91.66	55.9349
⁵⁷ Fe	2.19	56.9354

Isotope	Percent Abundance (%)	Atomic Mass (amu)
^{58}Fe	0.33	57.9333

10. ♦ Because ores are deposited during different geologic periods, lead ores from different mining regions of the world can contain different ratios of isotopes. Archaeologists use these differences to determine the origin of lead artifacts. For example, the following table lists the percent abundances of three lead isotopes from one artifact recovered from Rio Tinto in Spain.

Isotope	Percent Abundance (%)	Atomic mass (amu)
^{204}Pb		203.973028
^{206}Pb	24.41	205.974449
^{207}Pb	20.32	206.97580
^{208}Pb	50.28	207.976636

- If the only other lead isotope in the artifact is ^{204}Pb , what is its percent abundance?
 - What is the average atomic mass of lead if the only other isotope in the artifact is ^{204}Pb ?
 - An artifact from Laurion, Greece, was found to have a ^{207}Pb : ^{206}Pb ratio of 0.8307. From the data given, can you determine whether the lead in the artifact from Rio Tinto came from the same source as the lead in the artifact from Laurion, Greece?
11. The macrominerals sodium, magnesium, potassium, calcium, chlorine, and phosphorus are widely distributed in biological substances, although their distributions are far from uniform. Classify these elements by both their periods and their groups and then state whether each is a metal, a nonmetal, or a semimetal. If a metal, is the element a transition metal?
12. The composition of fingernails is sensitive to exposure to certain elements, including sodium, magnesium, aluminum, chlorine, potassium, calcium, selenium, vanadium, chromium, manganese, iron, cobalt, copper, zinc, scandium, arsenic, and antimony. Classify these elements by both their periods and their groups and then determine whether each is a metal, a nonmetal, or a semimetal. Of the metals, which are transition metals? Based on your classifications, predict other elements that could prove to be detectable in fingernails.
13. Mercury levels in hair have been used to identify individuals who have been exposed to toxic levels of mercury. Is mercury an essential element? a trace element?

14. Trace elements are usually present at levels of less than 50 mg/kg of body weight. Classify the essential trace elements by their groups and periods in the periodic table. Based on your classifications, would you predict that arsenic, cadmium, and lead are potential essential trace elements?

Chapter 2

Molecules, Ions, and Chemical Formulas

Chapter 1 "Introduction to Chemistry" introduced some of the fundamental concepts of chemistry, with particular attention to the basic properties of atoms and elements. These entities are the building blocks of all substances we encounter, yet most common substances do not consist of only pure elements or individual atoms. Instead, nearly all substances are chemical compounds or mixtures of chemical compounds. Although there are only about 115 elements (of which about 86 occur naturally), millions of chemical compounds are known, with a tremendous range of physical and chemical properties. Consequently, the emphasis of modern chemistry (and this text) is on understanding the relationship between the structures and properties of chemical compounds.

Petroleum refining. Using chemicals, catalysts, heat, and pressure, a petroleum refinery will separate, combine, and rearrange the structure and bonding patterns of the basic carbon-hydrogen molecules found in crude oil. The final products include gasoline, paraffin, diesel fuel, lubricants, and bitumen.

In this chapter, you will learn how to describe the composition of chemical compounds. We introduce you to *chemical nomenclature*—the language of chemistry—that will enable you to recognize and name the most common kinds of compounds. An understanding of chemical nomenclature not only is essential for your study of chemistry but also has other benefits—for example, it helps you understand the labels on products found in the supermarket and the pharmacy. You will also be better equipped to understand many of the important environmental and medical issues that face society. By the end of this chapter, you will be able to describe what happens chemically when a doctor prepares a cast to stabilize a broken bone, and you will know the composition of common substances such as laundry bleach, the active ingredient in baking powder, and the foul-smelling compound responsible for the odor of spoiled fish. Finally, you will be able to explain the chemical differences among different grades of gasoline.

2.1 Chemical Compounds

LEARNING OBJECTIVE

1. To understand the differences between covalent and ionic bonding.

The atoms in all substances that contain more than one atom are held together by electrostatic interactions—interactions between electrically charged particles such as protons and electrons. Electrostatic attraction between oppositely charged species (positive and negative) results in a force that causes them to move toward each other, like the attraction between opposite poles of two magnets. In contrast, electrostatic repulsion between two species with the same charge (either both positive or both negative) results in a force that causes them to repel each other, as do the same poles of two magnets. Atoms form chemical compounds when the attractive electrostatic interactions between them are stronger than the repulsive interactions. Collectively, we refer to the attractive interactions between atoms as chemical bonds.

Chemical bonds are generally divided into two fundamentally different kinds: ionic and covalent. In reality, however, the bonds in most substances are neither purely ionic nor purely covalent, but they are closer to one of these extremes. Although purely ionic and purely covalent bonds represent extreme cases that are seldom encountered in anything but very simple substances, a brief discussion of these two extremes helps us understand why substances that have different kinds of chemical bonds have very different properties. Ionic compounds consist of positively and negatively charged ions held together by strong electrostatic forces, whereas covalent compounds generally consist of molecules, which are groups of atoms in which one or more pairs of electrons are shared between bonded atoms. In a covalent bond, the atoms are held together by the electrostatic attraction between the positively charged nuclei of the bonded atoms and the negatively charged electrons they share. We begin our discussion of structures and formulas by describing covalent compounds. The energetic factors involved in bond formation are described in more quantitative detail in Chapter 8 "Ionic versus Covalent Bonding".

Note the Pattern

Ionic compounds consist of ions of opposite charges held together by strong electrostatic forces, whereas pairs of electrons are shared between bonded atoms in covalent compounds.

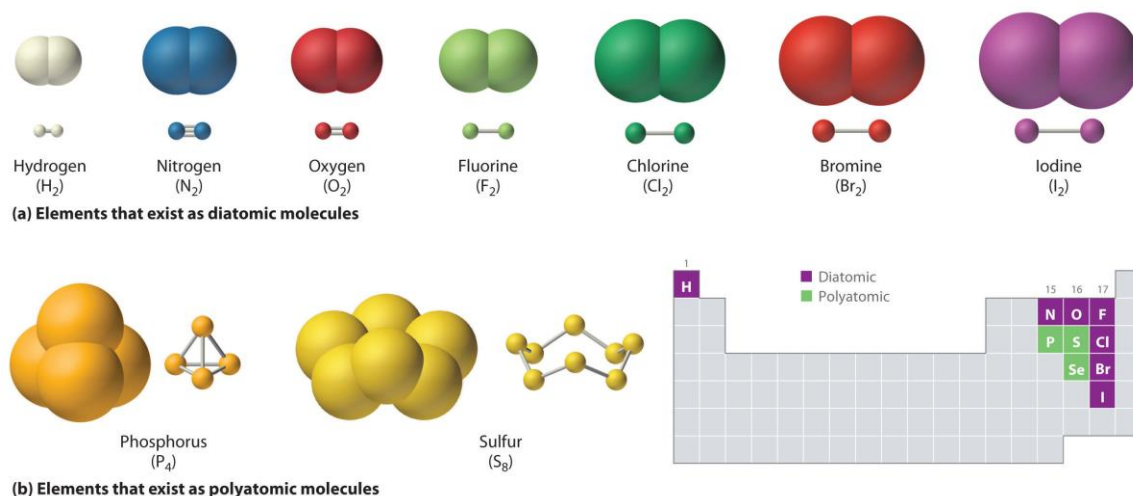
Covalent Molecules and Compounds

Just as an atom is the simplest unit that has the fundamental chemical properties of an element, a molecule is the simplest unit that has the fundamental chemical properties of a covalent compound. Some pure elements exist as covalent molecules. Hydrogen, nitrogen, oxygen, and the halogens occur naturally

as the *diatomic* (“two atoms”) *molecules* H_2 , N_2 , O_2 , F_2 , Cl_2 , Br_2 , and I_2 (part (a) in Figure 2.1 “Elements That Exist as Covalent Molecules”). Similarly, a few pure elements are polyatomic (“many atoms”) *molecules*, such as elemental phosphorus and sulfur, which occur as P_4 and S_8 (part (b) in Figure 2.1 “Elements That Exist as Covalent Molecules”).

Each covalent compound is represented by a molecular formula, which gives the atomic symbol for each component element, in a prescribed order, accompanied by a subscript indicating the number of atoms of that element in the molecule. The subscript is written only if the number of atoms is greater than 1. For example, water, with two hydrogen atoms and one oxygen atom per molecule, is written as H_2O . Similarly, carbon dioxide, which contains one carbon atom and two oxygen atoms in each molecule, is written as CO_2 .

Figure 2.1 *Elements That Exist as Covalent Molecules*



(a) Several elements naturally exist as diatomic molecules, in which two atoms (E) are joined by one or more covalent bonds to form a molecule with the general formula E_2 . (b) A few elements naturally exist as polyatomic molecules, which contain more than two atoms. For example, phosphorus exists as P_4 tetrahedra—regular polyhedra with four triangular sides—with a phosphorus atom at each vertex. Elemental sulfur consists of a puckered ring of eight sulfur atoms connected by single bonds. Selenium is not shown due to the complexity of its structure.

Covalent compounds that contain predominantly carbon and hydrogen are called organic compounds. The convention for representing the formulas of organic compounds is to write carbon first, followed by hydrogen and then any other elements in alphabetical order (e.g., CH_4O is methyl alcohol, a fuel).

Compounds that consist primarily of elements other than carbon and hydrogen are called inorganic compounds; they include both covalent and ionic compounds. In inorganic compounds, the component elements are listed beginning with the one farthest to the left in the periodic table (see Chapter 32 "Appendix H: Periodic Table of Elements"), such as we see in CO_2 or SF_6 . Those in the same group are listed beginning with the lower element and working up, as in ClF . By convention, however, when an inorganic compound contains both hydrogen and an element from groups 13–15, the hydrogen is usually listed last in the formula. Examples are ammonia (NH_3) and silane (SiH_4). Compounds such as water, whose compositions were established long before this convention was adopted, are always written with hydrogen first: Water is always written as H_2O , not OH_2 . The conventions for inorganic acids, such as hydrochloric acid (HCl) and sulfuric acid (H_2SO_4), are described in Section 2.5 "Acids and Bases".

Note the Pattern

For organic compounds: write C first, then H, and then the other elements in alphabetical order. For molecular inorganic compounds: start with the element at far left in the periodic table; list elements in same group beginning with the lower element and working up.

EXAMPLE 1

Write the molecular formula of each compound.

- The phosphorus-sulfur compound that is responsible for the ignition of so-called strike anywhere matches has 4 phosphorus atoms and 3 sulfur atoms per molecule.
- Ethyl alcohol, the alcohol of alcoholic beverages, has 1 oxygen atom, 2 carbon atoms, and 6 hydrogen atoms per molecule.
- Freon-11, once widely used in automobile air conditioners and implicated in damage to the ozone layer, has 1 carbon atom, 3 chlorine atoms, and 1 fluorine atom per molecule.

Given: identity of elements present and number of atoms of each

Asked for: molecular formula

Strategy:

A Identify the symbol for each element in the molecule. Then identify the substance as either an organic compound or an inorganic compound.

B If the substance is an organic compound, arrange the elements in order beginning with carbon and hydrogen and then list the other elements alphabetically. If it is an inorganic compound, list the elements beginning with the one farthest left in the periodic table. List elements in the same group starting with the lower element and working up.

C From the information given, add a subscript for each kind of atom to write the molecular formula.

Solution:

A The molecule has 4 phosphorus atoms and 3 sulfur atoms. Because the compound does not contain mostly carbon and hydrogen, it is inorganic. **B** Phosphorus is in group 15, and sulfur is in group 16. Because phosphorus is to the left of sulfur, it is written first. **C** Writing the number of each kind of atom as a right-hand subscript gives P_4S_3 as the molecular formula.

a. **A** Ethyl alcohol contains predominantly carbon and hydrogen, so it is an organic compound. **B** The formula for an organic compound is written with the number of carbon atoms first, the number of hydrogen atoms next, and the other atoms in alphabetical order: CHO. **C** Adding subscripts gives the molecular formula C_2H_6O .

A Freon-11 contains carbon, chlorine, and fluorine. It can be viewed as either an inorganic compound or an organic compound (in which fluorine has replaced hydrogen). The formula for Freon-11 can therefore be written using either of the two conventions.

B According to the convention for inorganic compounds, carbon is written first because it is farther left in the periodic table. Fluorine and chlorine are in the same group, so they are listed beginning with the lower element and working up: CClF. Adding subscripts gives the molecular formula CCl_3F .

C We obtain the same formula for Freon-11 using the convention for organic compounds. The number of carbon atoms is written first, followed by the number of hydrogen atoms (zero) and then the other elements in alphabetical order, also giving CCl_3F .

Exercise

Write the molecular formula for each compound.

a. Nitrous oxide, also called “laughing gas,” has 2 nitrogen atoms and 1 oxygen atom per molecule. Nitrous oxide is used as a mild anesthetic for minor surgery and as the propellant in cans of whipped cream.

a. Sucrose, also known as cane sugar, has 12 carbon atoms, 11 oxygen atoms, and 22 hydrogen atoms.

b. Sulfur hexafluoride, a gas used to pressurize “unpressurized” tennis balls and as a coolant in nuclear reactors, has 6 fluorine atoms and 1 sulfur atom per molecule.

Answer:

a. N_2O

a. $\text{C}_{12}\text{H}_{22}\text{O}_{11}$

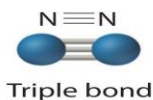
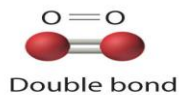
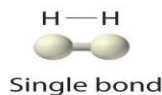
b. SF_6

Representations of Molecular Structures

Molecular formulas give only the elemental composition of molecules. In contrast, structural formulas show which atoms are bonded to one another and, in some cases, the approximate arrangement of the atoms in space. Knowing the structural formula of a compound enables chemists to create a three-dimensional model, which provides information about how that compound will behave physically and chemically.

The structural formula for H_2 can be drawn as $\text{H}-\text{H}$ and that for I_2 as $\text{I}-\text{I}$, where the line indicates a single pair of shared electrons, a single bond. Two pairs of electrons are shared in a double bond, which is indicated by two lines—for example, O_2 is $\text{O}=\text{O}$. Three electron pairs are shared in a triple bond, which is indicated by three lines—for example, N_2 is $\text{N}\equiv\text{N}$ (see Figure 2.2 “Molecules That Contain Single, Double, and Triple Bonds”). Carbon is unique in the extent to which it forms single, double, and triple bonds to itself and other elements. The number of bonds formed by an atom in its covalent compounds is *not* arbitrary. As you will learn in Chapter 8 “Ionic versus Covalent Bonding”, hydrogen, oxygen, nitrogen, and carbon have a very strong tendency to form substances in which they have one, two, three, and four bonds to other atoms, respectively (Table 2.1 “The Number of Bonds That Selected Atoms Commonly Form to Other Atoms”).

Figure 2.2 Molecules That Contain Single, Double, and Triple Bonds

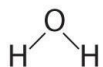


Hydrogen (H_2) has a single bond between atoms. Oxygen (O_2) has a double bond between atoms, indicated by two lines ($=$). Nitrogen (N_2) has a triple bond between atoms, indicated by three lines ($\equiv$). Each bond represents an electron pair.

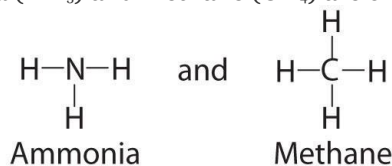
Table 2.1 The Number of Bonds That Selected Atoms Commonly Form to Other Atoms

Atom	Number of Bonds
H (group 1)	1
O (group 16)	2
N (group 15)	3
C (group 14)	4

The structural formula for water can be drawn as follows:

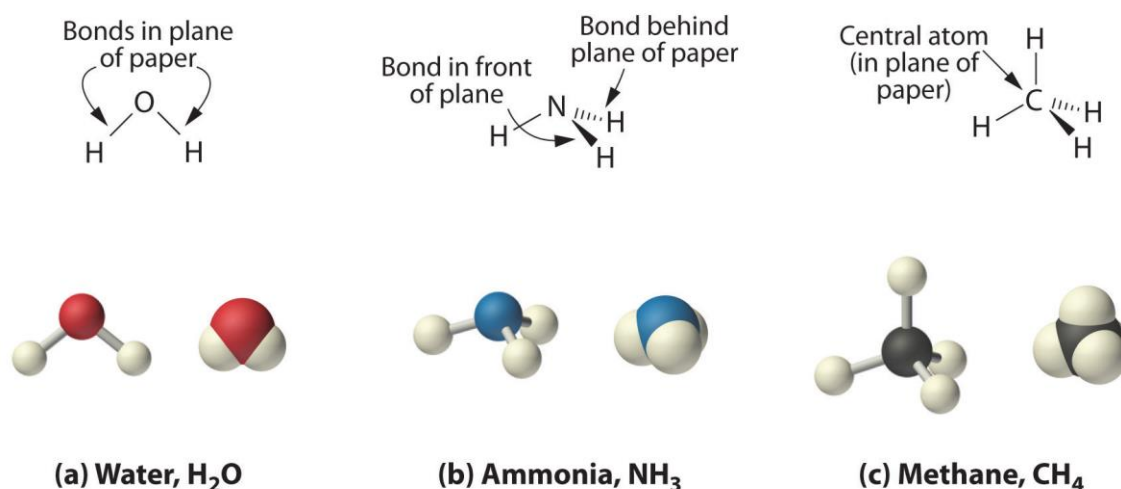


Because the latter approximates the experimentally determined shape of the water molecule, it is more informative. Similarly, ammonia (NH_3) and methane (CH_4) are often written as planar molecules:



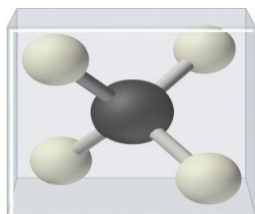
As shown in Figure 2.3 "The Three-Dimensional Structures of Water, Ammonia, and Methane", however, the actual three-dimensional structure of NH_3 looks like a pyramid with a triangular base of three hydrogen atoms. The structure of CH_4 , with four hydrogen atoms arranged around a central carbon atom as shown in Figure 2.3 "The Three-Dimensional Structures of Water, Ammonia, and Methane", is *tetrahedral*. That is, the hydrogen atoms are positioned at every other vertex of a cube. Many compounds—carbon compounds, in particular—have four bonded atoms arranged around a central atom to form a tetrahedron.

Figure 2.3 *The Three-Dimensional Structures of Water, Ammonia, and Methane*



(a) Water is a V-shaped molecule, in which all three atoms lie in a plane. (b) In contrast, ammonia has a pyramidal structure, in which the three hydrogen atoms form the base of the pyramid and the nitrogen atom is at the vertex.

(c) The four hydrogen atoms of methane form a tetrahedron; the carbon atom lies in the center.



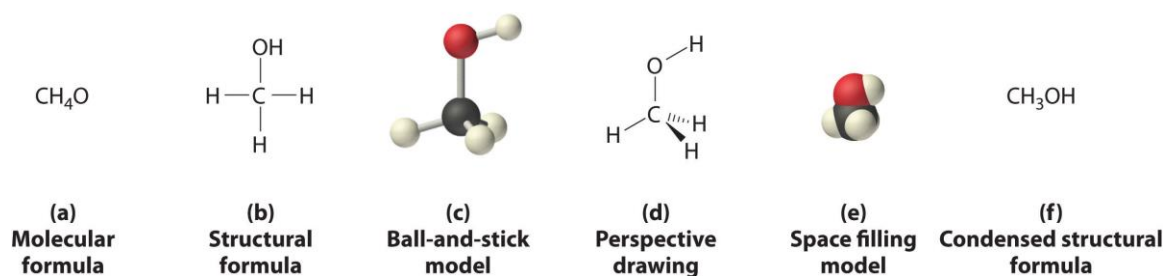
Tetrahedral structure
of methane, CH_4

CH₄. Methane has a three-dimensional, tetrahedral structure.

Figure 2.1 "Elements That Exist as Covalent Molecules", Figure 2.2 "Molecules That Contain Single, Double, and Triple Bonds", and Figure 2.3 "The Three-Dimensional Structures of Water, Ammonia, and Methane" illustrate different ways to represent the structures of molecules. It should be clear that there is no single "best" way to draw the structure of a molecule; the method you use depends on which aspect of the structure you want to emphasize and how much time and effort you want to spend. Figure 2.4 "Different Ways of Representing the Structure of a Molecule" shows some of the different ways to portray the structure of a slightly more complex molecule: methanol. These representations differ greatly in their information content. For example, the molecular formula for methanol (part (a) in Figure 2.4 "Different Ways of Representing the Structure of a Molecule") gives only the number of each kind of atom; writing methanol as CH_4O tells nothing about its structure. In contrast, the structural formula (part (b) in Figure 2.4 "Different Ways of Representing the Structure of a Molecule")

indicates how the atoms are connected, but it makes methanol look as if it is planar (which it is not). Both the ball-and-stick model (part (c) in Figure 2.4 "Different Ways of Representing the Structure of a Molecule") and the perspective drawing (part (d) in Figure 2.4 "Different Ways of Representing the Structure of a Molecule") show the three-dimensional structure of the molecule. The latter (also called a *wedge-and-dash* representation) is the easiest way to sketch the structure of a molecule in three dimensions. It shows which atoms are above and below the plane of the paper by using wedges and dashes, respectively; the central atom is always assumed to be in the plane of the paper. The space-filling model (part (e) in Figure 2.4 "Different Ways of Representing the Structure of a Molecule") illustrates the approximate relative sizes of the atoms in the molecule, but it does not show the bonds between the atoms. Also, in a space-filling model, atoms at the "front" of the molecule may obscure atoms at the "back."

Figure 2.4 *Different Ways of Representing the Structure of a Molecule*



(a) The molecular formula for methanol gives only the number of each kind of atom present. (b) The structural formula shows which atoms are connected. (c) The ball-and-stick model shows the atoms as spheres and the bonds as sticks. (d) A perspective drawing (also called a *wedge-and-dash* representation) attempts to show the three-dimensional structure of the molecule. (e) The space-filling model shows the atoms in the molecule but not the bonds. (f) The condensed structural formula is by far the easiest and most common way to represent a molecule. Although a structural formula, a ball-and-stick model, a perspective drawing, and a space-filling model provide a significant amount of information about the structure of a molecule, each requires time and effort. Consequently, chemists often use a *condensed structural formula* (part (f) in Figure 2.4 "Different Ways of Representing the Structure of a Molecule"), which omits the lines representing bonds between atoms and simply lists the atoms bonded to a given atom next to it. Multiple groups attached to the same atom are shown in parentheses, followed by a subscript that indicates the number of such groups. For example, the condensed structural formula for methanol is CH_3OH , which tells us that the molecule contains a CH_3 unit that looks like a fragment of methane (CH_4). Methanol can therefore be viewed either as a methane molecule in which one hydrogen atom has been replaced by an $-\text{OH}$

group or as a water molecule in which one hydrogen atom has been replaced by a -CH_3 fragment. Because of their ease of use and information content, we use condensed structural formulas for molecules throughout this text. Ball-and-stick models are used when needed to illustrate the three-dimensional structure of molecules, and space-filling models are used only when it is necessary to visualize the relative sizes of atoms or molecules to understand an important point.

EXAMPLE 2

Write the molecular formula for each compound. The condensed structural formula is given.

- Sulfur monochloride (also called disulfur dichloride) is a vile-smelling, corrosive yellow liquid used in the production of synthetic rubber. Its condensed structural formula is ClSSCl .
- Ethylene glycol is the major ingredient in antifreeze. Its condensed structural formula is $\text{HOCH}_2\text{CH}_2\text{OH}$.
- Trimethylamine is one of the substances responsible for the smell of spoiled fish. Its condensed structural formula is $(\text{CH}_3)_3\text{N}$.

Given: condensed structural formula

Asked for: molecular formula

Strategy:

A Identify every element in the condensed structural formula and then determine whether the compound is organic or inorganic.

B As appropriate, use either organic or inorganic convention to list the elements. Then add appropriate subscripts to indicate the number of atoms of each element present in the molecular formula.

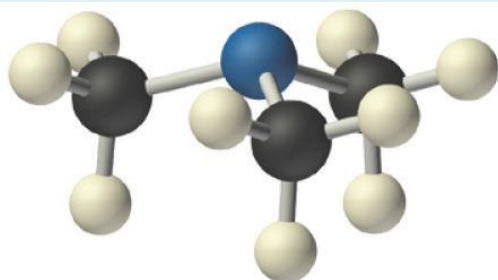
Solution:

The molecular formula lists the elements in the molecule and the number of atoms of each.

- A** Each molecule of sulfur monochloride has two sulfur atoms and two chlorine atoms. Because it does not contain mostly carbon and hydrogen, it is an inorganic compound. **B** Sulfur lies to the left of chlorine in the periodic table, so it is written first in the formula. Adding subscripts gives the molecular formula S_2Cl_2 .
- A** Counting the atoms in ethylene glycol, we get six hydrogen atoms, two carbon atoms, and two oxygen atoms per molecule. The compound consists mostly of carbon and

hydrogen atoms, so it is organic. **B** As with all organic compounds, C and H are written first in the molecular formula. Adding appropriate subscripts gives the molecular formula $\text{C}_2\text{H}_6\text{O}_2$.

- c. **A** The condensed structural formula shows that trimethylamine contains three CH_3 units, so we have one nitrogen atom, three carbon atoms, and nine hydrogen atoms per molecule. Because trimethylamine contains mostly carbon and hydrogen, it is an organic compound. **B** According to the convention for organic compounds, C and H are written first, giving the molecular formula $\text{C}_3\text{H}_9\text{N}$.

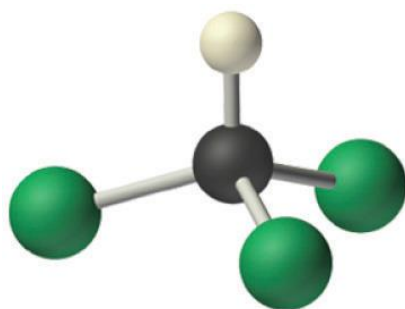


Trimethylamine

Exercise

Write the molecular formula for each molecule.

- Chloroform, which was one of the first anesthetics and was used in many cough syrups until recently, contains one carbon atom, one hydrogen atom, and three chlorine atoms. Its condensed structural formula is CHCl_3 .
- Hydrazine is used as a propellant in the attitude jets of the space shuttle. Its condensed structural formula is H_2NNH_2 .
- Putrescine is a pungent-smelling compound first isolated from extracts of rotting meat. Its condensed structural formula is $\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$. This is often written as $\text{H}_2\text{N}(\text{CH}_2)_4\text{NH}_2$ to indicate that there are four CH_2 fragments linked together.



Chloroform

Answer:

a. CHCl_3

a. N_2H_4

b. $\text{C}_4\text{H}_{12}\text{N}_2$

Ionic Compounds

The substances described in the preceding discussion are composed of molecules that are electrically neutral; that is, the number of positively charged protons in the nucleus is equal to the number of negatively charged electrons. In contrast, *ions* are atoms or assemblies of atoms that have a net electrical charge. Ions that contain fewer electrons than protons have a net positive charge and are called cations. Conversely, ions that contain more electrons than protons have a net negative charge and are called anions. *Ionic compounds* contain both cations and anions in a ratio that results in no net electrical charge.

Note the Pattern

Ionic compounds contain both cations and anions in a ratio that results in zero electrical charge.

In covalent compounds, electrons are shared between bonded atoms and are simultaneously attracted to more than one nucleus. In contrast, ionic compounds contain cations and anions rather than discrete neutral molecules. Ionic compounds are held together by the attractive electrostatic interactions between cations and anions. In an ionic compound, the cations and anions are arranged in space to form an extended three-dimensional array that maximizes the number of attractive electrostatic interactions and minimizes the number of repulsive electrostatic interactions (Figure 2.5 "Covalent and Ionic Bonding"). As shown in Equation 2.1, the electrostatic energy of the interaction between two charged particles is proportional to the product of the charges on the particles and inversely proportional to the distance between them:

Equation 2.1

$$\text{electrostatic energy} \propto \frac{Q_1 Q_2}{r}$$

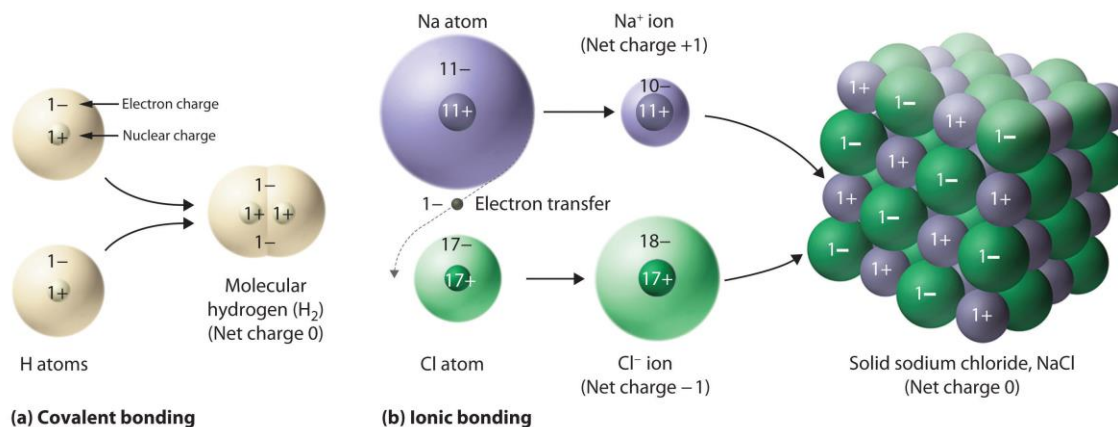
where Q_1 and Q_2 are the electrical charges on particles 1 and 2, and r is the distance between them.

When Q_1 and Q_2 are both positive, corresponding to the charges on cations, the cations repel each other and the electrostatic energy is positive. When Q_1 and Q_2 are both negative, corresponding to the charges on anions, the anions repel each other and the electrostatic energy is again positive. The electrostatic energy is negative only when the charges have opposite signs; that is, positively charged species are attracted to negatively charged species and vice versa. As shown in Figure 2.6 "The Effect of Charge and Distance on the Strength of Electrostatic Interactions", the strength of the interaction is proportional to the *magnitude* of the charges and decreases as the *distance* between the particles increases. We will return to these energetic factors in Chapter 8 "Ionic versus Covalent Bonding", where they are described in greater quantitative detail.

Note the Pattern

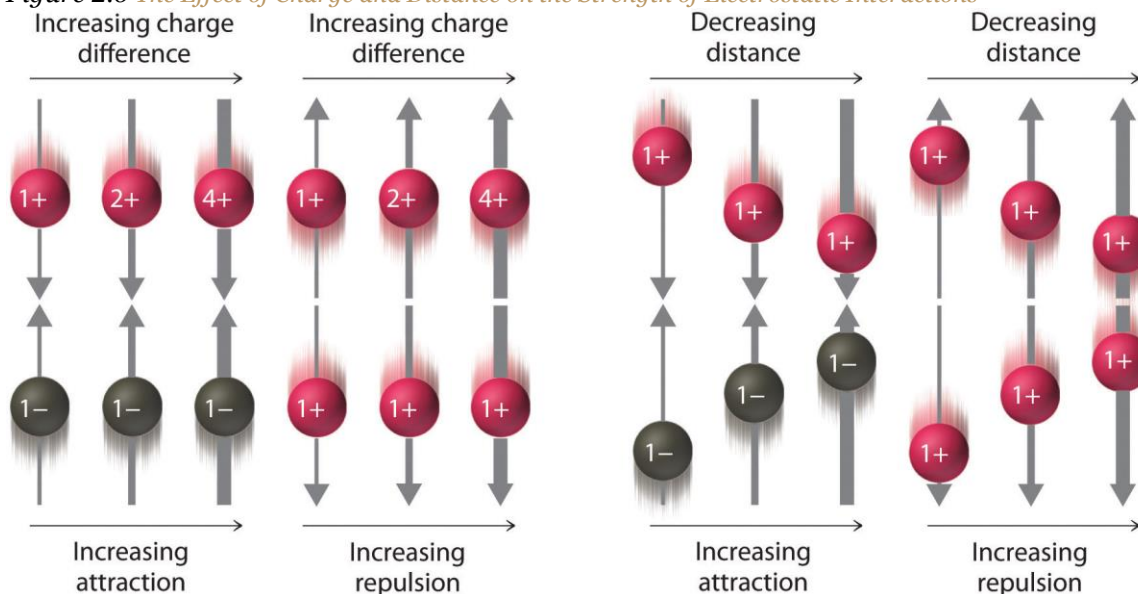
If the electrostatic energy is positive, the particles repel each other; if the electrostatic energy is negative, the particles are attracted to each other.

Figure 2.5 *Covalent and Ionic Bonding*



(a) In molecular hydrogen (H₂), two hydrogen atoms share two electrons to form a covalent bond. (b) The ionic compound NaCl forms when electrons from sodium atoms are transferred to chlorine atoms. The resulting Na⁺ and Cl⁻ ions form a three-dimensional solid that is held together by attractive electrostatic interactions.

Figure 2.6 *The Effect of Charge and Distance on the Strength of Electrostatic Interactions*



As the charge on ions increases or the distance between ions decreases, so does the strength of the attractive ($-...+$) or repulsive ($-...-$ or $+...+$) interactions. The strength of these interactions is represented by the thickness of the arrows.

One example of an ionic compound is sodium chloride (NaCl ; Figure 2.7 "Sodium Chloride: an Ionic Solid"), formed from sodium and chlorine. In forming chemical compounds, many elements have a tendency to gain or lose enough electrons to attain the same number of electrons as the noble gas closest to them in the periodic table. When sodium and chlorine come into contact, each sodium atom gives up an electron to become a Na^+ ion, with 11 protons in its nucleus but only 10 electrons (like neon), and each chlorine atom gains an electron to become a Cl^- ion, with 17 protons in its nucleus and 18 electrons (like argon), as shown in part (b) in Figure 2.5 "Covalent and Ionic Bonding". Solid sodium chloride contains equal numbers of cations (Na^+) and anions (Cl^-), thus maintaining electrical neutrality. Each Na^+ ion is surrounded by 6 Cl^- ions, and each Cl^- ion is surrounded by 6 Na^+ ions. Because of the large number of attractive Na^+Cl^- interactions, the total attractive electrostatic energy in NaCl is great.

Consistent with a tendency to have the same number of electrons as the nearest noble gas, when forming ions, elements in groups 1, 2, and 3 tend to *lose* one, two, and three electrons, respectively, to form cations, such as Na^+ and Mg^{2+} . They then have the same number of electrons as the nearest noble gas: neon. Similarly, K^+ , Ca^{2+} , and Sc^{3+} have 18 electrons each, like the nearest noble gas: argon. In addition, the elements in group 13 *lose* three electrons to form cations, such as Al^{3+} , again attaining the same number of electrons as the noble gas closest to them in the periodic table. Because the lanthanides and actinides

formally belong to group 3, the most common ion formed by these elements is M^{3+} , where M represents the metal. Conversely, elements in groups 17, 16, and 15 often react to *gain* one, two, and three electrons, respectively, to form ions such as Cl^- , S^{2-} , and P^{3-} . Ions such as these, which contain only a single atom, are called monatomic ions. You can predict the charges of most monatomic ions derived from the main group elements by simply looking at the periodic table and counting how many columns an element lies from the extreme left or right. For example, you can predict that barium (in group 2) will form Ba^{2+} to have the same number of electrons as its nearest noble gas, xenon, that oxygen (in group 16) will form O^{2-} to have the same number of electrons as neon, and cesium (in group 1) will form Cs^+ to also have the same number of electrons as xenon. Note that this method does not usually work for most of the transition metals, as you will learn in Section 2.3 "Naming Ionic Compounds". Some common monatomic ions are in Table 2.2 "Some Common Monatomic Ions and Their Names".

Note the Pattern

Elements in groups 1, 2, and 3 tend to form $1+$, $2+$, and $3+$ ions, respectively; elements in groups 15, 16, and 17 tend to form $3-$, $2-$, and $1-$ ions, respectively.

Table 2.2 Some Common Monatomic Ions and Their Names

Group 1	Group 2	Group 3	Group 13	Group 15	Group 16	Group 17
Li^+ lithium	Be^{2+} beryllium			N^{3-} nitride (azide)	O^{2-} oxide	F^- fluoride
Na^+ sodium	Mg^{2+} magnesium		Al^{3+} aluminum	P^{3-} phosphide	S^{2-} sulfide	Cl^- chloride
K^+ potassium	Ca^{2+} calcium	Sc^{3+} scandium	Ga^{3+} gallium	As^{3-} arsenide	Se^{2-} selenide	Br^- bromide
Rb^+ rubidium	Sr^{2+} strontium	Y^{3+} yttrium	In^{3+} indium		Te^{2-} telluride	I^- iodide
Cs^+ cesium	Ba^{2+} barium	La^{3+} lanthanum				

EXAMPLE 3

Predict the charge on the most common monatomic ion formed by each element.

- a. aluminum, used in the quantum logic clock, the world's most precise clock
- b. selenium, used to make ruby-colored glass
- c. yttrium, used to make high-performance spark plugs

Given: element

Asked for: ionic charge

Strategy:

A Identify the group in the periodic table to which the element belongs. Based on its location in the periodic table, decide whether the element is a metal, which tends to lose electrons; a nonmetal, which tends to gain electrons; or a semimetal, which can do either.

B After locating the noble gas that is closest to the element, determine the number of electrons the element must gain or lose to have the same number of electrons as the nearest noble gas.

Solution:

A Aluminum is a metal in group 13; consequently, it will tend to lose electrons.

B The nearest noble gas to aluminum is neon. Aluminum will lose three electrons to form the Al^{3+} ion, which has the same number of electrons as neon.

A Selenium is a nonmetal in group 16, so it will tend to gain electrons.

B The nearest noble gas is krypton, so we predict that selenium will gain two electrons to form the Se^{2-} ion, which has the same number of electrons as krypton.

- a. **A** Yttrium is in group 3, and elements in this group are metals that tend to lose electrons. **B** The nearest noble gas to yttrium is krypton, so yttrium is predicted to lose three electrons to form Y^{3+} , which has the same number of electrons as krypton.

Exercise

Predict the charge on the most common monatomic ion formed by each element.

- a. calcium, used to prevent osteoporosis
- b. iodine, required for the synthesis of thyroid hormones
- c. zirconium, widely used in nuclear reactors

Answer:

- a. Ca^{2+}
- b. I^-
- c. Zr^{4+}

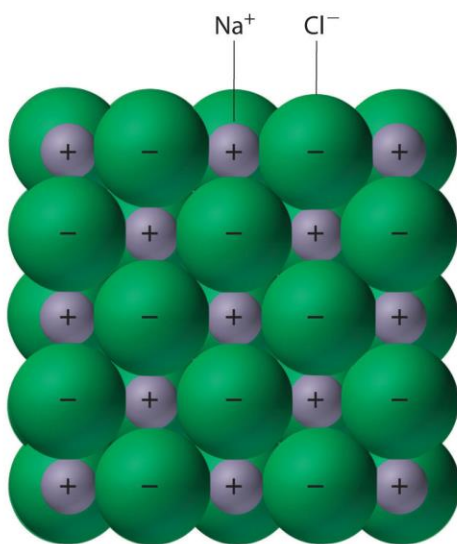
Physical Properties of Ionic and Covalent Compounds

In general, ionic and covalent compounds have different physical properties. Ionic compounds usually form hard crystalline solids that melt at rather high temperatures and are *very* resistant to evaporation. These properties stem from the characteristic internal structure of an ionic solid, illustrated schematically in part (a) in Figure 2.8 "Interactions in Ionic and Covalent Solids", which shows the three-dimensional array of alternating positive and negative ions held together by strong electrostatic attractions. In contrast, as shown in part (b) in Figure 2.8 "Interactions in Ionic and Covalent Solids", most covalent compounds consist of discrete molecules held together by comparatively weak *intermolecular* forces (the forces between molecules), even though the atoms within each molecule are held together by strong *intramolecular* covalent bonds (the forces within the molecule). Covalent substances can be gases, liquids, or solids at room temperature and pressure, depending on the strength of the intermolecular interactions. Covalent molecular solids tend to form soft crystals that melt at rather low temperatures and evaporate relatively easily.^[1] The covalent bonds that hold the atoms together in the molecules are unaffected when covalent substances melt or evaporate, so a liquid or vapor of discrete, independent molecules is formed. For example, at room temperature, methane, the major constituent of natural gas, is a gas that is composed of discrete CH_4 molecules. A comparison of the different physical properties of ionic compounds and covalent molecular substances is given in Table 2.3 "The Physical Properties of Typical Ionic Compounds and Covalent Molecular Substances".

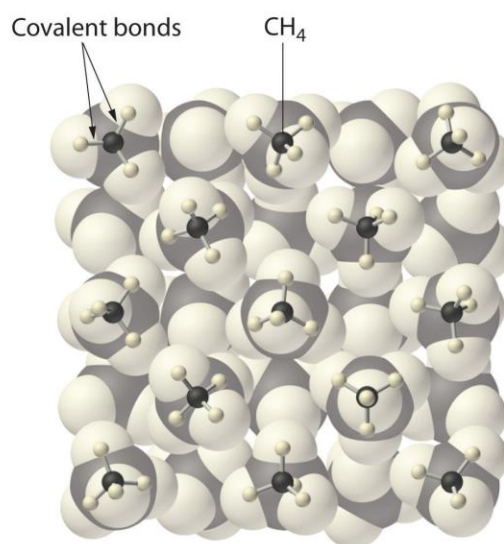
Table 2.3 The Physical Properties of Typical Ionic Compounds and Covalent Molecular Substances

Ionic Compounds	Covalent Molecular Substances
hard solids	gases, liquids, or soft solids
high melting points	low melting points
nonvolatile	volatile

Figure 2.8 *Interactions in Ionic and Covalent Solids*



(a) Ionic solid: strong electrostatic interactions



(b) Molecular solid: weak intermolecular forces

(a) The positively and negatively charged ions in an ionic solid such as sodium chloride (NaCl) are held together by strong electrostatic interactions. (b) In this representation of the packing of methane (CH_4) molecules in solid methane, a prototypical molecular solid, the methane molecules are held together in the solid only by relatively weak intermolecular forces, even though the atoms within each methane molecule are held together by strong covalent bonds.

Summary

The atoms in chemical compounds are held together by attractive electrostatic interactions known as **chemical bonds**. **Ionic compounds** contain positively and negatively charged ions in a ratio that results in an overall charge of zero. The ions are held together in a regular spatial arrangement by electrostatic forces. Most **covalent compounds** consist of **molecules**, groups of atoms in which one or more pairs of electrons are shared by at least two atoms to form a covalent bond. The atoms in molecules are held together by the **electrostatic attraction** between the positively charged nuclei of the bonded atoms and the negatively charged electrons shared by the nuclei. The **molecular formula** of a covalent compound gives the types and numbers of atoms present. Compounds that contain predominantly carbon and hydrogen are called **organic compounds**, whereas compounds that consist primarily of elements other than carbon and hydrogen are **inorganic compounds**. *Diatomic molecules* contain two atoms, and *polyatomic molecules* contain more than two. A **structural formula** indicates the composition and approximate structure and shape of a molecule. **Single bonds**, **double bonds**, and **triple bonds** are covalent bonds in which one, two, and three pairs of electrons, respectively, are shared between two

bonded atoms. Atoms or groups of atoms that possess a net electrical charge are called *ions*; they can have either a positive charge (**cations**) or a negative charge (**anions**). Ions can consist of one atom (**monatomic ions**) or several (*polyatomic ions*). The charges on monatomic ions of most main group elements can be predicted from the location of the element in the periodic table. Ionic compounds usually form hard crystalline solids with high melting points. Covalent molecular compounds, in contrast, consist of discrete molecules held together by weak intermolecular forces and can be gases, liquids, or solids at room temperature and pressure.

KEY TAKEAWAY

- There are two fundamentally different kinds of chemical bonds (covalent and ionic) that cause substances to have very different properties.

CONCEPTUAL PROBLEMS

1. Ionic and covalent compounds are held together by electrostatic attractions between oppositely charged particles. Describe the differences in the nature of the attractions in ionic and covalent compounds. Which class of compounds contains pairs of electrons shared between bonded atoms?
2. Which contains fewer electrons than the neutral atom—the corresponding cation or the anion?
3. What is the difference between an organic compound and an inorganic compound?
4. What is the advantage of writing a structural formula as a condensed formula?
5. The majority of elements that exist as diatomic molecules are found in one group of the periodic table. Identify the group.
6. Discuss the differences between covalent and ionic compounds with regard to
 - a. the forces that hold the atoms together.
 - b. melting points.
 - c. physical states at room temperature and pressure.
7. Why do covalent compounds generally tend to have lower melting points than ionic compounds?

ANSWER

7. Covalent compounds generally melt at lower temperatures than ionic compounds because the intermolecular interactions that hold the molecules together in a molecular solid are weaker than the electrostatic attractions that hold oppositely charged ions together in an ionic solid.

NUMERICAL PROBLEMS

1. The structural formula for chloroform (CHCl_3) was shown in Example 2. Based on this information, draw the structural formula of dichloromethane (CH_2Cl_2).
2. What is the total number of electrons present in each ion?
 - a. F^-
 - b. Rb^+
 - c. Ce^{3+}
 - d. Zr^{4+}
 - e. Zn^{2+}
 - f. Kr^{2+}
 - g. B^{3+}
3. What is the total number of electrons present in each ion?
 - a. Ca^{2+}
 - b. Se^{2-}
 - c. In^{3+}
 - d. Sr^{2+}
 - e. As^{3+}
 - f. N^{3-}
 - g. Tl^+
4. Predict how many electrons are in each ion.
 - a. an oxygen ion with a -2 charge
 - b. a beryllium ion with a $+2$ charge
 - c. a silver ion with a $+1$ charge
 - d. a selenium ion with a $+4$ charge
 - e. an iron ion with a $+2$ charge
 - f. a chlorine ion with a -1 charge
5. Predict how many electrons are in each ion.
 - a. a copper ion with a $+2$ charge
 - b. a molybdenum ion with a $+4$ charge
 - c. an iodine ion with a -1 charge

- d. a gallium ion with a +3 charge
 - e. an ytterbium ion with a +3 charge
 - f. a scandium ion with a +3 charge
6. Predict the charge on the most common monatomic ion formed by each element.
- a. chlorine
 - b. phosphorus
 - c. scandium
 - d. magnesium
 - e. arsenic
 - f. oxygen
7. Predict the charge on the most common monatomic ion formed by each element.
- a. sodium
 - b. selenium
 - c. barium
 - d. rubidium
 - e. nitrogen
 - f. aluminum
8. For each representation of a monatomic ion, identify the parent atom, write the formula of the ion using an appropriate superscript, and indicate the period and group of the periodic table in which the element is found.
- a. X_{49}^{2+}
 - b. X_{11}^{-}
 - c. X_{816}^{2-}
9. For each representation of a monatomic ion, identify the parent atom, write the formula of the ion using an appropriate superscript, and indicate the period and group of the periodic table in which the element is found.
- a. X_{37}^{+}
 - b. X_{919}^{-}
 - c. X_{1327}^{3+}

ANSWERS

5.

- a. 27
- b. 38
- c. 54
- d. 28
- e. 67
- f. 18

9.

- a. Li, Li^+ , 2nd period, group 1
- b. F, F^- , 2nd period, group 17
- c. Al, Al^{3+} , 3rd period, group 13

[1] Some covalent substances, however, are not molecular but consist of infinite three-dimensional arrays of covalently bonded atoms and include some of the hardest materials known, such as diamond. This topic will be addressed in Chapter 12 "Solids".

2.2 Chemical Formulas

LEARNING OBJECTIVE

1. To describe the composition of a chemical compound.

When chemists synthesize a new compound, they may not yet know its molecular or structural formula. In such cases, they usually begin by determining its empirical formula, the *relative* numbers of atoms of the elements in a compound, reduced to the smallest whole numbers. Because the empirical formula is based on experimental measurements of the numbers of atoms in a sample of the compound, it shows only the ratios of the numbers of the elements present. The difference between *empirical* and *molecular* formulas can be illustrated with butane, a covalent compound used as the fuel in disposable lighters. The molecular formula for butane is C_4H_{10} . The ratio of carbon atoms to hydrogen atoms in butane is 4:10, which can be reduced to 2:5. The empirical formula for butane is therefore C_2H_5 . The formula unit is the *absolute* grouping of atoms or ions represented by the empirical formula of a compound, either ionic or covalent. Butane, for example, has the empirical formula C_2H_5 , but it contains two C_2H_5 formula units, giving a molecular formula of C_4H_{10} .

Because ionic compounds do not contain discrete molecules, empirical formulas are used to indicate their compositions. All compounds, whether ionic or covalent, must be electrically neutral. Consequently, the positive and negative charges in a formula unit must exactly cancel each other. If the cation and the anion have charges of equal

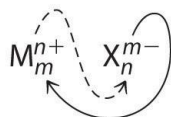
magnitude, such as Na^+ and Cl^- , then the compound must have a 1:1 ratio of cations to anions, and the empirical formula must be NaCl . If the charges are not the same magnitude, then a cation:anion ratio other than 1:1 is needed to produce a neutral compound. In the case of Mg^{2+} and Cl^- , for example, two Cl^- ions are needed to balance the two positive charges on each Mg^{2+} ion, giving an empirical formula of MgCl_2 . Similarly, the formula for the ionic compound that contains Na^+ and O^{2-} ions is Na_2O .

Note the Pattern

Ionic compounds do not contain discrete molecules, so empirical formulas are used to indicate their compositions.

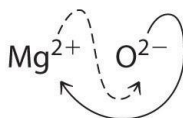
Binary Ionic Compounds

An ionic compound that contains only two elements, one present as a cation and one as an anion, is called a binary ionic compound. One example is MgCl_2 , a coagulant used in the preparation of tofu from soybeans. For binary ionic compounds, the subscripts in the empirical formula can also be obtained by crossing charges: use the absolute value of the charge on one ion as the subscript for the other ion. This method is shown schematically as follows:



Crossing charges. One method for obtaining subscripts in the empirical formula is by crossing charges.

When crossing charges, you will sometimes find it necessary to reduce the subscripts to their simplest ratio to write the empirical formula. Consider, for example, the compound formed by Mg^{2+} and O^{2-} . Using the absolute values of the charges on the ions as subscripts gives the formula Mg_2O_2 :



This simplifies to its correct empirical formula MgO . The empirical formula has one Mg^{2+} ion and one O^{2-} ion.

EXAMPLE 4

Write the empirical formula for the simplest binary ionic compound formed from each ion or element pair.

- Ga^{3+} and As^{3-}
- Eu^{3+} and O^{2-}
- calcium and chlorine

Given: ions or elements

Asked for: empirical formula for binary ionic compound

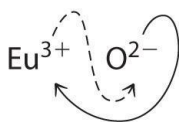
Strategy:

A If not given, determine the ionic charges based on the location of the elements in the periodic table.

B Use the absolute value of the charge on each ion as the subscript for the other ion. Reduce the subscripts to the lowest numbers to write the empirical formula. Check to make sure the empirical formula is electrically neutral.

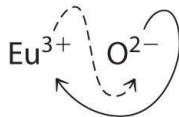
Solution:

- a. **B** Using the absolute values of the charges on the ions as the subscripts gives Ga_3As_3 :



a. Reducing the subscripts to the smallest whole numbers gives the empirical formula GaAs , which is electrically neutral [$+3 + (-3) = 0$]. Alternatively, we could recognize that Ga^{3+} and As^{3-} have charges of equal magnitude but opposite signs. One Ga^{3+} ion balances the charge on one As^{3-} ion, and a 1:1 compound will have no net charge. Because we write subscripts only if the number is greater than 1, the empirical formula is GaAs . GaAs is gallium arsenide, which is widely used in the electronics industry in transistors and other devices.

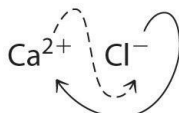
- b. **B** Because Eu^{3+} has a charge of +3 and O^{2-} has a charge of -2 , a 1:1 compound would have a net charge of +1. We must therefore find multiples of the charges that cancel. We cross charges, using the absolute value of the charge on one ion as the subscript for the other ion:



- a. The subscript for Eu^{3+} is 2 (from O^{2-}), and the subscript for O^{2-} is 3 (from Eu^{3+}), giving Eu_2O_3 ; the subscripts cannot be reduced further. The empirical formula contains a positive charge of $2(+3) = +6$ and a negative charge of $3(-2) = -6$, for a net charge of 0. The compound Eu_2O_3 is neutral. Europium oxide is responsible for the red color in television and computer screens.

b. **A** Because the charges on the ions are not given, we must first determine the charges expected for the most common ions derived from calcium and chlorine. Calcium lies in group 2, so it should lose two electrons to form Ca^{2+} . Chlorine lies in group 17, so it should gain one electron to form Cl^- .

B Two Cl^- ions are needed to balance the charge on one Ca^{2+} ion, which leads to the empirical formula CaCl_2 . We could also cross charges, using the absolute value of the charge on Ca^{2+} as the subscript for Cl and the absolute value of the charge on Cl^- as the subscript for Ca:



a. The subscripts in CaCl_2 cannot be reduced further. The empirical formula is electrically neutral [$+2 + 2(-1) = 0$]. This compound is calcium chloride, one of the substances used as “salt” to melt ice on roads and sidewalks in winter.

Exercise

Write the empirical formula for the simplest binary ionic compound formed from each ion or element pair.

- a. Li^+ and N^{3-}
- b. Al^{3+} and O^{2-}
- c. lithium and oxygen

Answer:

- a. Li_3N
- b. Al_2O_3
- c. Li_2O

Polyatomic Ions

Polyatomic ions are groups of atoms that bear a net electrical charge, although the atoms in a polyatomic ion are held together by the same covalent bonds that hold atoms together in molecules. Just as there are many more kinds of molecules than simple elements, there are many more kinds of polyatomic ions than monatomic ions. Two examples of polyatomic cations are the ammonium (NH_4^+) and the methylammonium (CH_3NH_3^+) ions. Polyatomic anions are much more numerous than polyatomic cations; some common examples are in Table 2.4 "Common Polyatomic Ions and Their Names".

Table 2.4 Common Polyatomic Ions and Their Names

Formula	Name of Ion
NH_4^+	ammonium
CH_3NH_3^+	methyammonium
OH^-	hydroxide
O_2^{2-}	peroxide
CN^-	cyanide
SCN^-	thiocyanate
NO_2^-	nitrite
NO_3^-	nitrate
CO_3^{2-}	carbonate
HCO_3^-	hydrogen carbonate, or bicarbonate
SO_3^{2-}	sulfite
SO_4^{2-}	sulfate
HSO_4^-	hydrogen sulfate, or bisulfate
PO_4^{3-}	phosphate
HPO_4^{2-}	hydrogen phosphate
H_2PO_4^-	dihydrogen phosphate
ClO^-	hypochlorite
ClO_2^-	chlorite
ClO_3^-	chlorate
ClO_4^-	perchlorate
MnO_4^-	permanganate
CrO_4^{2-}	chromate
$\text{Cr}_2\text{O}_7^{2-}$	dichromate
$\text{C}_2\text{O}_4^{2-}$	oxalate
HCO_2^-	formate
CH_3CO_2^-	acetate
$\text{C}_6\text{H}_5\text{CO}_2^-$	benzoate

The method we used to predict the empirical formulas for ionic compounds that contain monatomic ions can also be used for compounds that contain polyatomic ions. The overall charge on the cations must balance the overall charge on the anions in the formula unit. Thus K^+ and NO_3^- ions combine in a 1:1 ratio

to form KNO_3 (potassium nitrate or saltpeter), a major ingredient in black gunpowder. Similarly, Ca^{2+} and SO_4^{2-} form CaSO_4 (calcium sulfate), which combines with varying amounts of water to form gypsum and plaster of Paris. The polyatomic ions NH_4^+ and NO_3^- form NH_4NO_3 (ammonium nitrate), which is a widely used fertilizer and, in the wrong hands, an explosive. One example of a compound in which the ions have charges of different magnitudes is calcium phosphate, which is composed of Ca^{2+} and PO_4^{3-} ions; it is a major component of bones. The compound is electrically neutral because the ions combine in a ratio of three Ca^{2+} ions [$3(+2) = +6$] for every two ions [$2(-3) = -6$], giving an empirical formula of $\text{Ca}_3(\text{PO}_4)_2$; the parentheses around PO_4 in the empirical formula indicate that it is a polyatomic ion. Writing the formula for calcium phosphate as $\text{Ca}_3\text{P}_2\text{O}_8$ gives the correct number of each atom in the formula unit, but it obscures the fact that the compound contains readily identifiable PO_4^{3-} ions.

EXAMPLE 5

Write the empirical formula for the compound formed from each ion pair.

- Na^+ and HPO_4^{2-}
- potassium cation and cyanide anion
- calcium cation and hypochlorite anion

Given: ions

Asked for: empirical formula for ionic compound

Strategy:

A If it is not given, determine the charge on a monatomic ion from its location in the periodic table.

Use Table 2.4 "Common Polyatomic Ions and Their Names" to find the charge on a polyatomic ion.

B Use the absolute value of the charge on each ion as the subscript for the other ion. Reduce the subscripts to the smallest whole numbers when writing the empirical formula.

Solution:

- B** Because HPO_4^{2-} has a charge of -2 and Na^+ has a charge of $+1$, the empirical formula requires two Na^+ ions to balance the charge of the polyatomic ion, giving Na_2HPO_4 . The subscripts are reduced to the lowest numbers, so the empirical formula is Na_2HPO_4 . This compound is sodium hydrogen phosphate, which is used to provide texture in processed cheese, puddings, and instant breakfasts.

- b. **A** The potassium cation is K^+ , and the cyanide anion is CN^- . **B** Because the magnitude of the charge on each ion is the same, the empirical formula is KCN. Potassium cyanide is highly toxic, and at one time it was used as rat poison. This use has been discontinued, however, because too many people were being poisoned accidentally.
- c. **A** The calcium cation is Ca^{2+} , and the hypochlorite anion is ClO^- . **B** Two ClO^- ions are needed to balance the charge on one Ca^{2+} ion, giving $Ca(ClO)_2$. The subscripts cannot be reduced further, so the empirical formula is $Ca(ClO)_2$. This is calcium hypochlorite, the "chlorine" used to purify water in swimming pools.

Exercise

Write the empirical formula for the compound formed from each ion pair.

- a. Ca^{2+} and $H_2PO_4^-$
- b. sodium cation and bicarbonate anion
- c. ammonium cation and sulfate anion

Answer:

- a. $Ca(H_2PO_4)_2$: calcium dihydrogen phosphate is one of the ingredients in baking powder.
- b. $NaHCO_3$: sodium bicarbonate is found in antacids and baking powder; in pure form, it is sold as baking soda.
- c. $(NH_4)_2SO_4$: ammonium sulfate is a common source of nitrogen in fertilizers.

Hydrates

Many ionic compounds occur as hydrates, compounds that contain specific ratios of loosely bound water molecules, called waters of hydration. Waters of hydration can often be removed simply by heating. For example, calcium dihydrogen phosphate can form a solid that contains one molecule of water per $Ca(H_2PO_4)_2$ unit and is used as a leavening agent in the food industry to cause baked goods to rise. The empirical formula for the solid is $Ca(H_2PO_4)_2 \cdot H_2O$. In contrast, copper sulfate usually forms a blue solid that contains *five* waters of hydration per formula unit, with the empirical formula $CuSO_4 \cdot 5H_2O$. When heated, all five water molecules are lost, giving a white solid with the empirical formula $CuSO_4$ (Figure 2.9 "Loss of Water from a Hydrate with Heating").

Compounds that differ only in the numbers of waters of hydration can have very different properties. For example, $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ is plaster of Paris, which was often used to make sturdy casts for broken arms or legs, whereas $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is the less dense, flakier gypsum, a mineral used in drywall panels for home construction. When a cast would set, a mixture of plaster of Paris and water crystallized to give solid $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Similar processes are used in the setting of cement and concrete.

Summary

An **empirical formula** gives the *relative* numbers of atoms of the elements in a compound, reduced to the lowest whole numbers. The **formula unit** is the *absolute* grouping represented by the empirical formula of a compound, either ionic or covalent. Empirical formulas are particularly useful for describing the composition of ionic compounds, which do not contain readily identifiable molecules. Some ionic compounds occur as **hydrates**, which contain specific ratios of loosely bound water molecules called **waters of hydration**.

KEY TAKEAWAY

- The composition of a compound is represented by an empirical or molecular formula, each consisting of at least one formula unit.

CONCEPTUAL PROBLEMS

1. What are the differences and similarities between a polyatomic ion and a molecule?
2. Classify each compound as ionic or covalent.
 - a. $\text{Zn}_3(\text{PO}_4)_2$
 - b. $\text{C}_6\text{H}_5\text{CO}_2\text{H}$
 - c. $\text{K}_2\text{Cr}_2\text{O}_7$
 - d. $\text{CH}_3\text{CH}_2\text{SH}$
 - e. NH_4Br
 - f. CCl_2F_2
3. Classify each compound as ionic or covalent. Which are organic compounds and which are inorganic compounds?
 - a. $\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$
 - b. CaCl_2
 - c. $\text{Y}(\text{NO}_3)_3$

- d. H_2S
- e. $\text{NaC}_2\text{H}_3\text{O}_2$
4. Generally, one cannot determine the molecular formula directly from an empirical formula. What other information is needed?
5. Give two pieces of information that we obtain from a structural formula that we cannot obtain from an empirical formula.
6. The formulas of alcohols are often written as ROH rather than as empirical formulas. For example, methanol is generally written as CH_3OH rather than CH_4O . Explain why the ROH notation is preferred.
7. The compound dimethyl sulfide has the empirical formula $\text{C}_2\text{H}_6\text{S}$ and the structural formula CH_3SCH_3 . What information do we obtain from the structural formula that we do not get from the empirical formula? Write the condensed structural formula for the compound.
8. What is the correct formula for magnesium hydroxide— MgOH_2 or $\text{Mg}(\text{OH})_2$? Why?
9. Magnesium cyanide is written as $\text{Mg}(\text{CN})_2$, not MgCN_2 . Why?
10. Does a given hydrate always contain the same number of waters of hydration?

ANSWER

7. The structural formula gives us the connectivity of the atoms in the molecule or ion, as well as a schematic representation of their arrangement in space. Empirical formulas tell us only the ratios of the atoms present. The condensed structural formula of dimethylsulfide is $(\text{CH}_3)_2\text{S}$.

NUMERICAL PROBLEMS

1. Write the formula for each compound.
 - a. magnesium sulfate, which has 1 magnesium atom, 4 oxygen atoms, and 1 sulfur atom
 - b. ethylene glycol (antifreeze), which has 6 hydrogen atoms, 2 carbon atoms, and 2 oxygen atoms
 - c. acetic acid, which has 2 oxygen atoms, 2 carbon atoms, and 4 hydrogen atoms
 - d. potassium chlorate, which has 1 chlorine atom, 1 potassium atom, and 3 oxygen atoms
 - e. sodium hypochlorite pentahydrate, which has 1 chlorine atom, 1 sodium atom, 6 oxygen atoms, and 10 hydrogen atoms
2. Write the formula for each compound.
 - a. cadmium acetate, which has 1 cadmium atom, 4 oxygen atoms, 4 carbon atoms, and 6 hydrogen atoms

- b. barium cyanide, which has 1 barium atom, 2 carbon atoms, and 2 nitrogen atoms
 - c. iron(III) phosphate dihydrate, which has 1 iron atom, 1 phosphorus atom, 6 oxygen atoms, and 4 hydrogen atoms
 - d. manganese(II) nitrate hexahydrate, which has 1 manganese atom, 12 hydrogen atoms, 12 oxygen atoms, and 2 nitrogen atoms
 - e. silver phosphate, which has 1 phosphorus atom, 3 silver atoms, and 4 oxygen atoms
3. Complete the following table by filling in the formula for the ionic compound formed by each cation-anion pair.

Ion	K^+	Fe^{3+}	NH_4^+	Ba^{2+}
Cl^-	KCl			
SO_4^{2-}				
PO_4^{3-}				
NO_3^-				
OH^-				

4. Write the empirical formula for the binary compound formed by the most common monatomic ions formed by each pair of elements.
- a. zinc and sulfur
 - b. barium and iodine
 - c. magnesium and chlorine
 - d. silicon and oxygen
 - e. sodium and sulfur
5. Write the empirical formula for the binary compound formed by the most common monatomic ions formed by each pair of elements.
- a. lithium and nitrogen
 - b. cesium and chlorine
 - c. germanium and oxygen
 - d. rubidium and sulfur
 - e. arsenic and sodium
6. Write the empirical formula for each compound.
- a. $Na_2S_2O_4$

- b. B_2H_6
 - c. $C_6H_{12}O_6$
 - d. P_4O_{10}
 - e. $KMnO_4$
7. Write the empirical formula for each compound.
- a. Al_2Cl_6
 - b. $K_2Cr_2O_7$
 - c. C_2H_4
 - d. $(NH_2)_2CNH$
 - e. CH_3COOH

ANSWERS

- 1.
- a. $MgSO_4$
 - b. $C_2H_6O_2$
 - c. $C_2H_4O_2$
 - d. $KClO_3$
 - e. $NaOCl \cdot 5H_2O$

3.

Ion	K^+	Fe^{3+}	NH_4^+	Ba^{2+}
Cl^-	KCl	$FeCl_3$	NH_4Cl	$BaCl_2$
SO_4^{2-}	K_2SO_4	$Fe_2(SO_4)_3$	$(NH_4)_2SO_4$	$BaSO_4$
PO_4^{3-}	K_3PO_4	$FePO_4$	$(NH_4)_3PO_4$	$Ba_3(PO_4)_2$
NO_3^-	KNO_3	$Fe(NO_3)_3$	NH_4NO_3	$Ba(NO_3)_2$
OH^-	KOH	$Fe(OH)_3$	NH_4OH	$Ba(OH)_2$

- 2.
- a. Li_3N
 - b. $CsCl$
 - c. GeO_2
 - d. Rb_2S
 - e. Na_3As

5.

- f. AlCl_3
- g. $\text{K}_2\text{Cr}_2\text{O}_7$
- h. CH_2
- i. CH_5N_3
- j. CH_2O

2.3 Naming Ionic Compounds

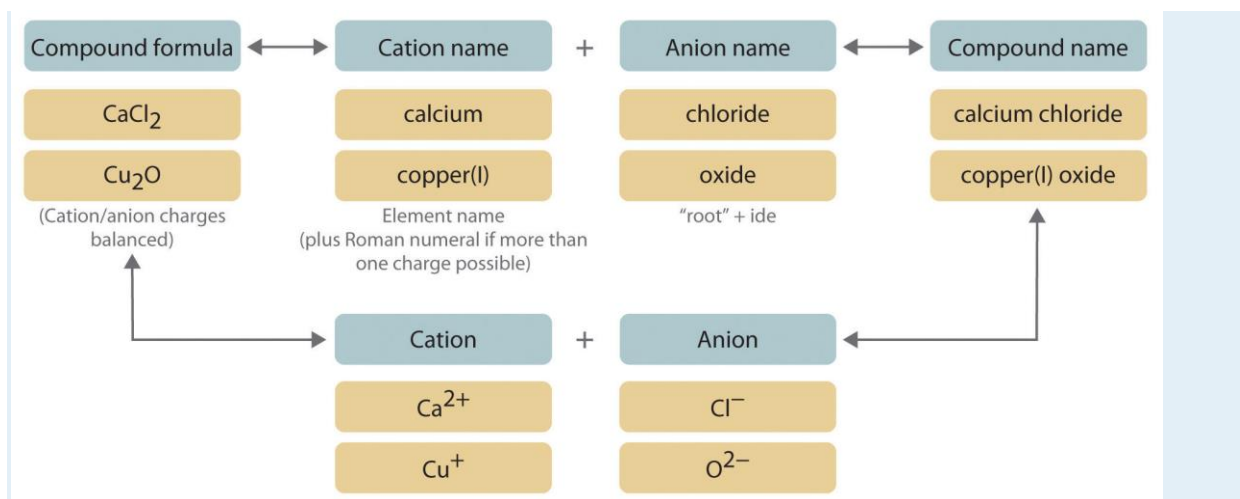
LEARNING OBJECTIVE

1. To name ionic compounds.

The empirical and molecular formulas discussed in the preceding section are precise and highly informative, but they have some disadvantages. First, they are inconvenient for routine verbal communication. For example, saying “C-A-three-P-O-four-two” for $\text{Ca}_3(\text{PO}_4)_2$ is much more difficult than saying “calcium phosphate.” In addition, you will see in Section 2.4 “Naming Covalent Compounds” that many compounds have the same empirical and molecular formulas but different arrangements of atoms, which result in very different chemical and physical properties. In such cases, it is necessary for the compounds to have different names that distinguish among the possible arrangements. Many compounds, particularly those that have been known for a relatively long time, have more than one name: a *common* name (sometimes more than one) and a *systematic* name, which is the name assigned by adhering to specific rules. Like the names of most elements, the common names of chemical compounds generally have historical origins, although they often appear to be unrelated to the compounds of interest. For example, the systematic name for KNO_3 is potassium nitrate, but its common name is saltpeter.

In this text, we use a systematic nomenclature to assign meaningful names to the millions of known substances. Unfortunately, some chemicals that are widely used in commerce and industry are still known almost exclusively by their common names; in such cases, you must be familiar with the common name as well as the systematic one. The objective of this and the next two sections is to teach you to write the formula for a simple inorganic compound from its name—and vice versa—and introduce you to some of the more frequently encountered common names. We begin with *binary ionic compounds*, which contain only two elements. The procedure for naming such compounds is outlined in Figure 2.10 “Naming an Ionic Compound” and uses the following steps:

Figure 2.10 Naming an Ionic Compound



1. Place the ions in their proper order: cation and then anion.

2. Name the cation.

a. **Metals that form only one cation.** As noted in Section 2.1 "Chemical Compounds", these metals are usually in groups 1–3, 12, and 13. The name of the cation of a metal that forms only one cation is the same as the name of the metal (with the word *ion* added if the cation is by itself). For example, Na⁺ is the sodium ion, Ca²⁺ is the calcium ion, and Al³⁺ is the aluminum ion.

b. **Metals that form more than one cation.** As shown in Figure 2.11 "Metals That Form More Than One Cation and Their Locations in the Periodic Table", many metals can form more than one cation. This behavior is observed for most transition metals, many actinides, and the heaviest elements of groups 13–15. In such cases, the positive charge on the metal is indicated by a roman numeral in parentheses immediately following the name of the metal. Thus Cu⁺ is copper(I) (read as "copper one"), Fe²⁺ is iron(II), Fe³⁺ is iron(III), Sn²⁺ is tin(II), and Sn⁴⁺ is tin(IV).

An older system of nomenclature for such cations is still widely used, however. The name of the cation with the *higher* charge is formed from the root of the element's Latin name with the suffix *-ic* attached, and the name of the cation with the *lower* charge has the same root with the suffix *-ous*. The names of Fe³⁺, Fe²⁺, Sn⁴⁺, and Sn²⁺ are therefore ferric, ferrous, stannic, and stannous, respectively. Even though this text uses the systematic names with roman numerals, you should be able to recognize these common names because they are still often used. For example, on the label of your dentist's fluoride rinse, the compound chemists call tin(II) fluoride is usually listed as stannous fluoride.

Some examples of metals that form more than one cation are in Table 2.5 "Common Cations of Metals That Form More Than One Ion" along with the names of the ions. Note that the simple Hg^+ cation does not occur in chemical compounds. Instead, all compounds of mercury(I) contain a *dimeric* cation, Hg_2^{2+} , in which the two Hg atoms are bonded together.

Table 2.5 Common Cations of Metals That Form More Than One Ion

Cation	Systematic Name	Common Name	Cation	Systematic Name	Common Name
Cr^{2+}	chromium(II)	chromous	Cu^{2+}	copper(II)	cupric
Cr^{3+}	chromium(III)	chromic	Cu^+	copper(I)	cuprous
Mn^{2+}	manganese(II)	manganous*	Hg_2^{2+}	mercury(II)	mercuric
Mn^{3+}	manganese(III)	manganic*	Hg_2^{2+}	mercury(I)	mercurous†
Fe^{2+}	iron(II)	ferrous	Sn^{4+}	tin(IV)	stannic
Fe^{3+}	iron(III)	ferric	Sn^{2+}	tin(II)	stannous
Co^{2+}	cobalt(II)	cobaltous*	Pb^{4+}	lead(IV)	plumbic*
Co^{3+}	cobalt(III)	cobaltic*	Pb^{2+}	lead(II)	plumbous*
* Not widely used.					
†The isolated mercury(I) ion exists only as the gaseous ion.					

c. **Polyatomic cations.** The names of the common polyatomic cations that are relatively important in ionic compounds (such as, the ammonium ion) are in Table 2.4 "Common Polyatomic Ions and Their Names".

3. Name the anion.

. **Monatomic anions.** Monatomic anions are named by adding the suffix *-ide* to the root of the name of the parent element; thus, Cl^- is chloride, O^{2-} is oxide, P^{3-} is phosphide, N^{3-} is nitride (also called azide), and C^{4-} is carbide. Because the charges on these ions can be predicted from their position in the periodic table, it is *not* necessary to specify the charge in the name. Examples of monatomic anions are in Table 2.2 "Some Common Monatomic Ions and Their Names".

a. **Polyatomic anions.** Polyatomic anions typically have common names that you must learn; some examples are in Table 2.4 "Common Polyatomic Ions and Their Names". Polyatomic anions that contain a single metal or nonmetal atom plus one or more oxygen atoms are called *oxoanions* (or *oxyanions*). In cases where only two oxoanions are known for an element, the name of the oxoanion with

more oxygen atoms ends in *-ate*, and the name of the oxoanion with fewer oxygen atoms ends in *-ite*. For example, NO_3^- is nitrate and NO_2^- is nitrite.

The halogens and some of the transition metals form more extensive series of oxoanions with as many as four members. In the names of these oxoanions, the prefix *per-* is used to identify the oxoanion with the most oxygen (so that ClO_4^- is perchlorate and ClO_3^- is chlorate), and the prefix *hypo-* is used to identify the anion with the fewest oxygen (ClO_2^- is chlorite and ClO^- is hypochlorite). The relationship between the names of oxoanions and the number of oxygen atoms present is diagrammed in Figure 2.12 "The Relationship between the Names of Oxoanions and the Number of Oxygen Atoms Present".

Differentiating the oxoanions in such a series is no trivial matter. For example, the hypochlorite ion is the active ingredient in laundry bleach and swimming pool disinfectant, but compounds that contain the perchlorate ion can explode if they come into contact with organic substances.

4. Write the name of the compound as the name of the cation followed by the name of the anion.

It is *not* necessary to indicate the number of cations or anions present per formula unit in the name of an ionic compound because this information is implied by the charges on the ions. You must consider the charge of the ions when writing the formula for an ionic compound from its name, however. Because the charge on the chloride ion is -1 and the charge on the calcium ion is $+2$, for example, consistent with their positions in the periodic table, simple arithmetic tells you that calcium chloride must contain twice as many chloride ions as calcium ions to maintain electrical neutrality. Thus the formula is CaCl_2 . Similarly, calcium phosphate must be $\text{Ca}_3(\text{PO}_4)_2$ because the cation and the anion have charges of $+2$ and -3 , respectively. The best way to learn how to name ionic compounds is to work through a few examples, referring to Figure 2.10 "Naming an Ionic Compound", Table 2.2 "Some Common Monatomic Ions and Their Names", Table 2.4 "Common Polyatomic Ions and Their Names", and Table 2.5 "Common Cations of Metals That Form More Than One Ion" as needed.

Figure 2.11 Metals That Form More Than One Cation and Their Locations in the Periodic Table

Main group elements												Main group elements											
1	2													13	14	15	16	17	18				
1	H	2													5	6	7	8	9	10			
2	Li	Be													13	14	15	16	17	18			
3	Na	Mg	Transition elements												Al	Si	P	S	Cl	Ar			
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr					
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe					
6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn					
7	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup								
Lanthanides			58	59	60	61	62	63	64	65	66	67	68	69	70	71							
6			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu							
Actinides			90	91	92	93	94	95	96	97	98	99	100	101	102	103							
7			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr							

With only a few exceptions, these metals are usually transition metals or actinides.

Figure 2.12 The Relationship between the Names of Oxoanions and the Number of Oxygen Atoms Present

	Rule	Example
most ↑ Number of oxygens in oxoanion	per + "root" + ate	perchlorate ClO_4^-
more	"root" + ate	chlorate ClO_3^-
less	"root" + ite	chlorite ClO_2^-
least ↓	hypo + "root" + ite	hypochlorite ClO^-

Note the Pattern

Cations are always named before anions.

Most transition metals, many actinides, and the heaviest elements of groups 13–15 can form more than one cation.

EXAMPLE 6

Write the systematic name (and the common name if applicable) for each ionic compound.

- a. LiCl
- b. MgSO_4
- c. $(\text{NH}_4)_3\text{PO}_4$
- d. Cu_2O

Given: empirical formula

Asked for: name

Strategy:

A If only one charge is possible for the cation, give its name, consulting Table 2.2 "Some Common Monatomic Ions and Their Names" or Table 2.4 "Common Polyatomic Ions and Their Names" if necessary. If the cation can have more than one charge (Table 2.5 "Common Cations of Metals That Form More Than One Ion"), specify the charge using roman numerals.

B If the anion does not contain oxygen, name it according to step 3a, using Table 2.2 "Some Common Monatomic Ions and Their Names" and Table 2.4 "Common Polyatomic Ions and Their Names" if necessary. For polyatomic anions that contain oxygen, use Table 2.4 "Common Polyatomic Ions and Their Names" and the appropriate prefix and suffix listed in step 3b.

C Beginning with the cation, write the name of the compound.

Solution:

- a. **A B** Lithium is in group 1, so we know that it forms only the Li^+ cation, which is the lithium ion. Similarly, chlorine is in group 7, so it forms the Cl^- anion, which is the chloride ion. **C** Because we begin with the name of the cation, the name of this compound is lithium chloride, which is used medically as an antidepressant drug.
- b. **A B** The cation is the magnesium ion, and the anion, which contains oxygen, is sulfate. **C** Because we list the cation first, the name of this compound is magnesium sulfate. A hydrated form of magnesium sulfate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) is sold in drugstores as Epsom salts, a harsh but effective laxative.
- c. **A B** The cation is the ammonium ion (from Table 2.4 "Common Polyatomic Ions and Their Names"), and the anion is phosphate. **C** The compound is therefore ammonium phosphate, which is widely used as a fertilizer. It is not necessary to

specify that the formula unit contains three ammonium ions because three are required to balance the negative charge on phosphate.

- d. **A B** The cation is a transition metal that often forms more than one cation (Table 2.5 "Common Cations of Metals That Form More Than One Ion"). We must therefore specify the positive charge on the cation in the name: copper(I) or, according to the older system, cuprous. The anion is oxide. **C** The name of this compound is copper(I) oxide or, in the older system, cuprous oxide. Copper(I) oxide is used as a red glaze on ceramics and in antifouling paints to prevent organisms from growing on the bottoms of boats.

Exercise

Write the systematic name (and the common name if applicable) for each ionic compound.

- a. CuCl_2
- b. MgCO_3
- c. FePO_4

Answer:

- a. copper(II) chloride (or cupric chloride)
- b. magnesium carbonate
- c. iron(III) phosphate (or ferric phosphate)

EXAMPLE 7

Write the formula for each compound.

- a. calcium dihydrogen phosphate
- b. aluminum sulfate
- c. chromium(III) oxide

Given: systematic name

Asked for: formula

Strategy:

A Identify the cation and its charge using the location of the element in the periodic table and Table 2.2 "Some Common Monatomic Ions and Their Names", Table 2.3 "The Physical Properties of Typical Ionic

Compounds and Covalent Molecular Substances", Table 2.4 "Common Polyatomic Ions and Their Names", and Table 2.5 "Common Cations of Metals That Form More Than One Ion". If the cation is derived from a metal that can form cations with different charges, use the appropriate roman numeral or suffix to indicate its charge.

B Identify the anion using Table 2.2 "Some Common Monatomic Ions and Their Names" and Table 2.4 "Common Polyatomic Ions and Their Names". Beginning with the cation, write the compound's formula and then determine the number of cations and anions needed to achieve electrical neutrality.

Solution:

- a. **A** Calcium is in group 2, so it forms only the Ca^{2+} ion. **B** Dihydrogen phosphate is the H_2PO_4^- ion (Table 2.4 "Common Polyatomic Ions and Their Names"). Two H_2PO_4^- ions are needed to balance the positive charge on Ca^{2+} , to give $\text{Ca}(\text{H}_2\text{PO}_4)_2$. A hydrate of calcium dihydrogen phosphate, $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, is the active ingredient in baking powder.
- b. **A** Aluminum, near the top of group 13 in the periodic table, forms only one cation, Al^{3+} (Figure 2.11 "Metals That Form More Than One Cation and Their Locations in the Periodic Table"). **B** Sulfate is SO_4^{2-} (Table 2.4 "Common Polyatomic Ions and Their Names"). To balance the electrical charges, we need two Al^{3+} cations and three SO_4^{2-} anions, giving $\text{Al}_2(\text{SO}_4)_3$. Aluminum sulfate is used to tan leather and purify drinking water.
- c. **A** Because chromium is a transition metal, it can form cations with different charges. The roman numeral tells us that the positive charge in this case is +3, so the cation is Cr^{3+} . **B** Oxide is O^{2-} . Thus two cations (Cr^{3+}) and three anions (O^{2-}) are required to give an electrically neutral compound, Cr_2O_3 . This compound is a common green pigment that has many uses, including camouflage coatings.

Cr₂O₃. Chromium(III) oxide (Cr_2O_3) is a common pigment in dark green paints, such as camouflage paint.

Exercise

Write the formula for each compound.

- a. barium chloride
- b. sodium carbonate

c. iron(III) hydroxide

Answer:

a. BaCl_2

b. Na_2CO_3

c. $\text{Fe}(\text{OH})_3$

Summary

Ionic compounds are named according to systematic procedures, although common names are widely used. Systematic nomenclature enables us to write the structure of any compound from its name and vice versa. Ionic compounds are named by writing the cation first, followed by the anion. If a metal can form cations with more than one charge, the charge is indicated by roman numerals in parentheses following the name of the metal. **Oxoanions** are polyatomic anions that contain a single metal or nonmetal atom and one or more oxygen atoms.

KEY TAKEAWAY

- There is a systematic method used to name ionic compounds.

CONCEPTUAL PROBLEMS

1. Name each cation.

a. K^+

b. Al^{3+}

c. NH_4^+

d. Mg^{2+}

e. Li^+

2. Name each anion.

a. Br^-

b. CO_3^{2-}

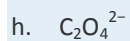
c. S^{2-}

d. NO_3^-

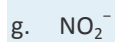
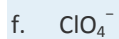
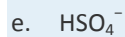
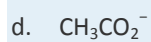
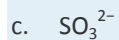
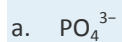
e. HCO_2^-

f. F^-

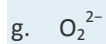
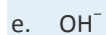
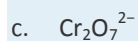
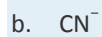
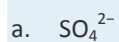
g. ClO^-



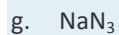
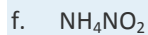
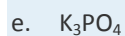
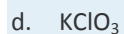
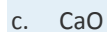
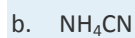
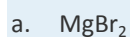
3. Name each anion.



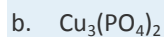
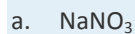
4. Name each anion.



5. Name each compound.



6. Name each compound.



- c. NaOH
 - d. Li_4C
 - e. CaF_2
 - f. NH_4Br
 - g. MgCO_3
7. Name each compound.
- a. RbBr
 - b. $\text{Mn}_2(\text{SO}_4)_3$
 - c. NaClO
 - d. $(\text{NH}_4)_2\text{SO}_4$
 - e. NaBr
 - f. KIO_3
 - g. Na_2CrO_4
8. Name each compound.
- a. NH_4ClO_4
 - b. SnCl_4
 - c. $\text{Fe}(\text{OH})_2$
 - d. Na_2O
 - e. MgCl_2
 - f. K_2SO_4
 - g. RaCl_2
9. Name each compound.
- a. KCN
 - b. LiOH
 - c. CaCl_2
 - d. NiSO_4
 - e. NH_4ClO_2
 - f. LiClO_4
 - g. $\text{La}(\text{CN})_3$

ANSWER

1.
 - a. rubidium bromide
 - b. manganese(III) sulfate
 - c. sodium hypochlorite
 - d. ammonium sulfate
 - e. sodium bromide
 - f. potassium iodate
 - g. sodium chromate

NUMERICAL PROBLEMS

1. For each ionic compound, name the cation and the anion and give the charge on each ion.
 - a. BeO
 - b. $\text{Pb}(\text{OH})_2$
 - c. BaS
 - d. $\text{Na}_2\text{Cr}_2\text{O}_7$
 - e. ZnSO_4
 - f. KClO
 - g. NaH_2PO_4
2. For each ionic compound, name the cation and the anion and give the charge on each ion.
 - a. $\text{Zn}(\text{NO}_3)_2$
 - b. CoS
 - c. BeCO_3
 - d. Na_2SO_4
 - e. $\text{K}_2\text{C}_2\text{O}_4$
 - f. NaCN
 - g. FeCl_2
3. Write the formula for each compound.
 - a. magnesium carbonate

- b. aluminum sulfate
 - c. potassium phosphate
 - d. lead(IV) oxide
 - e. silicon nitride
 - f. sodium hypochlorite
 - g. titanium(IV) chloride
 - h. disodium ammonium phosphate
4. Write the formula for each compound.
- a. lead(II) nitrate
 - b. ammonium phosphate
 - c. silver sulfide
 - d. barium sulfate
 - e. cesium iodide
 - f. sodium bicarbonate
 - g. potassium dichromate
 - h. sodium hypochlorite
5. Write the formula for each compound.
- a. zinc cyanide
 - b. silver chromate
 - c. lead(II) iodide
 - d. benzene
 - e. copper(II) perchlorate
6. Write the formula for each compound.
- a. calcium fluoride
 - b. sodium nitrate
 - c. iron(III) oxide
 - d. copper(II) acetate
 - e. sodium nitrite
7. Write the formula for each compound.

- a. sodium hydroxide
 - b. calcium cyanide
 - c. magnesium phosphate
 - d. sodium sulfate
 - e. nickel(II) bromide
 - f. calcium chlorite
 - g. titanium(IV) bromide
8. Write the formula for each compound.
- a. sodium chlorite
 - b. potassium nitrite
 - c. sodium nitride (also called sodium azide)
 - d. calcium phosphide
 - e. tin(II) chloride
 - f. calcium hydrogen phosphate
 - g. iron(II) chloride dihydrate
9. Write the formula for each compound.
- a. potassium carbonate
 - b. chromium(III) sulfite
 - c. cobalt(II) phosphate
 - d. magnesium hypochlorite
 - e. nickel(II) nitrate hexahydrate

2.4 Naming Covalent Compounds

LEARNING OBJECTIVE

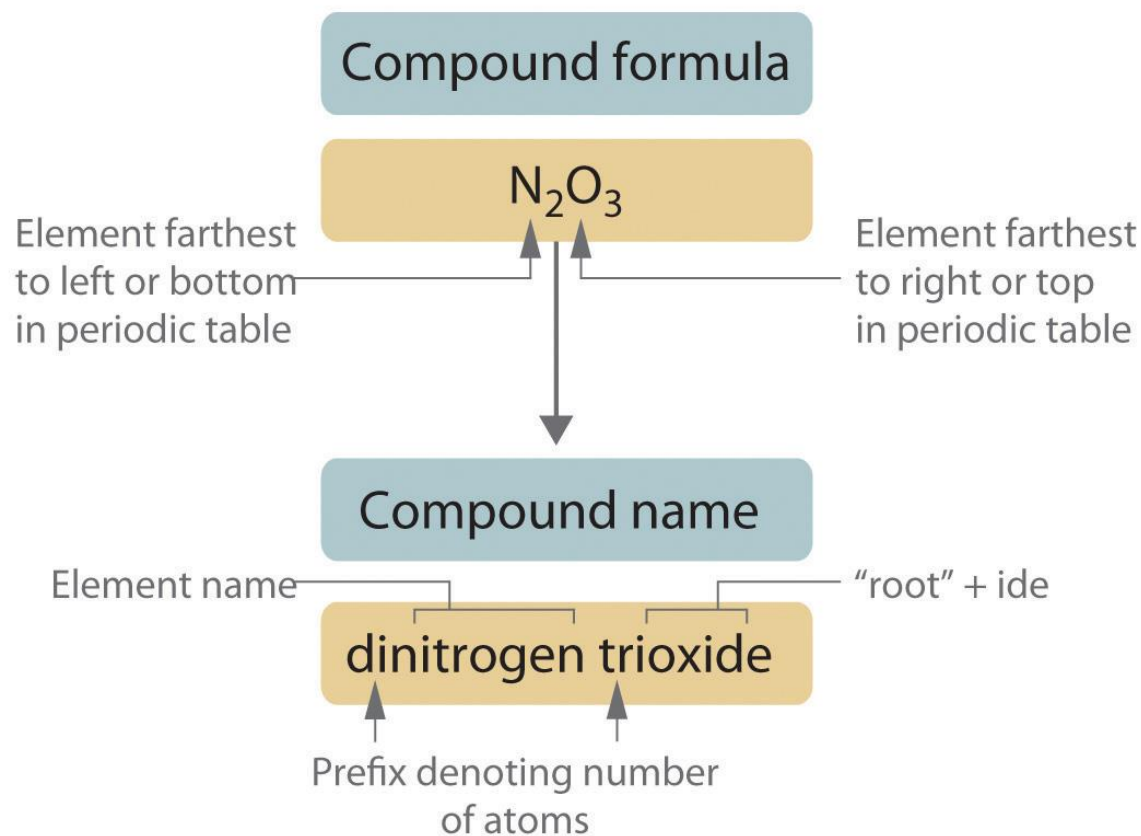
1. To name covalent compounds that contain up to three elements.

As with ionic compounds, the system that chemists have devised for naming covalent compounds enables us to write the molecular formula from the name and vice versa. In this and the following section, we describe the rules for naming simple covalent compounds. We begin with inorganic compounds and then turn to simple organic compounds that contain only carbon and hydrogen.

Binary Inorganic Compounds

Binary covalent compounds—that is, covalent compounds that contain only two elements—are named using a procedure similar to that used to name simple ionic compounds, but prefixes are added as needed to indicate the number of atoms of each kind. The procedure, diagrammed in Figure 2.13 "Naming a Covalent Inorganic Compound", uses the following steps:

Figure 2.13 *Naming a Covalent Inorganic Compound*



1. Place the elements in their proper order.
 - a. The element farthest to the left in the periodic table is usually named first. If both elements are in the same group, the element closer to the bottom of the column is named first.
 - b. The second element is named as if it were a monatomic anion in an ionic compound (even though it is not), with the suffix *-ide* attached to the root of the element name.
2. Identify the number of each type of atom present.

Prefixes derived from Greek stems are used to indicate the number of each type of atom in the formula unit (Table 2.6 "Prefixes for Indicating the Number of Atoms in Chemical Names"). The prefix *mono-* ("one") is used only when absolutely necessary to avoid confusion, just as we omit the subscript 1 when writing molecular formulas.

To demonstrate steps 1 and 2a, we name HCl as hydrogen chloride (because hydrogen is to the left of chlorine in the periodic table) and PCl₅ as phosphorus pentachloride. The order of the elements in the name of BrF₃, bromine trifluoride, is determined by the fact that bromine lies below fluorine in group 17.

Table 2.6 Prefixes for Indicating the Number of Atoms in Chemical Names

Prefix	Number
mono-	1
di-	2
tri-	3
tetra-	4
penta-	5
hexa-	6
hepta-	7
octa-	8
nona-	9
deca-	10
undeca-	11
dodeca-	12

- If a molecule contains more than one atom of both elements, then prefixes are used for both. Thus N₂O₃ is *dinitrogen trioxide*, as shown in Figure 2.13 "Naming a Covalent Inorganic Compound".
- In some names, the final *a* or *o* of the prefix is dropped to avoid awkward pronunciation. Thus OsO₄ is osmium tetroxide rather than osmium tetraoxide.
- Write the name of the compound.

Binary compounds of the elements with oxygen are generally named as "element oxide," with prefixes that indicate the number of atoms of each element per formula unit. For example, CO is carbon monoxide. The only exception is binary compounds of oxygen with fluorine, which are named as oxygen fluorides. (The reasons for this

convention will become clear in Chapter 7 "The Periodic Table and Periodic Trends" and Chapter 8 "Ionic versus Covalent Bonding".)

- a. Certain compounds are *always* called by the common names that were assigned long ago when names rather than formulas were used. For example, H_2O is water (not dihydrogen oxide); NH_3 is ammonia; PH_3 is phosphine; SiH_4 is silane; and B_2H_6 , a *dimer* of BH_3 , is diborane. For many compounds, the systematic name and the common name are both used frequently, so you must be familiar with them. For example, the systematic name for NO is nitrogen monoxide, but it is much more commonly called nitric oxide. Similarly, N_2O is usually called nitrous oxide rather than dinitrogen monoxide. Notice that the suffixes *-ic* and *-ous* are the same ones used for ionic compounds.

Note the Pattern

Start with the element at the far left in the periodic table and work to the right. If two or more elements are in the same group, start with the bottom element and work up.

EXAMPLE 8

Write the name of each binary covalent compound.

- a. SF_6
b. N_2O_4
c. ClO_2

Given: molecular formula

Asked for: name of compound

Strategy:

A List the elements in order according to their positions in the periodic table. Identify the number of each type of atom in the chemical formula and then use Table 2.6 "Prefixes for Indicating the Number of Atoms in Chemical Names" to determine the prefixes needed.

B If the compound contains oxygen, follow step 3a. If not, decide whether to use the common name or the systematic name.

Solution:

- a. **A** Because sulfur is to the left of fluorine in the periodic table, sulfur is named first. Because there is only one sulfur atom in the formula, no prefix is needed. **B** There are, however, six fluorine atoms, so we use the prefix for six: *hexa-* (Table 2.6 "Prefixes for Indicating the Number of Atoms in Chemical Names"). The compound is sulfur hexafluoride.
- b. **A** Because nitrogen is to the left of oxygen in the periodic table, nitrogen is named first. Because more than one atom of each element is present, prefixes are needed to indicate the number of atoms of each. According to Table 2.6 "Prefixes for Indicating the Number of Atoms in Chemical Names", the prefix for two is *di-*, and the prefix for four is *tetra-*. **B** The compound is dinitrogen tetroxide (omitting the *a* in *tetra-* according to step 2c) and is used as a component of some rocket fuels.
- c. **A** Although oxygen lies to the left of chlorine in the periodic table, it is not named first because ClO_2 is an oxide of an element other than fluorine (step 3a). Consequently, chlorine is named first, but a prefix is not necessary because each molecule has only one atom of chlorine. **B** Because there are two oxygen atoms, the compound is a dioxide. Thus the compound is chlorine dioxide. It is widely used as a substitute for chlorine in municipal water treatment plants because, unlike chlorine, it does not react with organic compounds in water to produce potentially toxic chlorinated compounds.

Exercise

Write the name of each binary covalent compound.

- a. IF_7
- b. N_2O_5
- c. OF_2

Answer:

- a. iodine heptafluoride
- b. dinitrogen pentoxide
- c. oxygen difluoride

EXAMPLE 9

Write the formula for each binary covalent compound.

- a. sulfur trioxide
- b. diiodine pentoxide

Given: name of compound

Asked for: formula

Strategy:

List the elements in the same order as in the formula, use Table 2.6 "Prefixes for Indicating the Number of Atoms in Chemical Names" to identify the number of each type of atom present, and then indicate this quantity as a subscript to the right of that element when writing the formula.

Solution:

- a. Sulfur has no prefix, which means that each molecule has only one sulfur atom. The prefix *tri-* indicates that there are three oxygen atoms. The formula is therefore SO_3 . Sulfur trioxide is produced industrially in huge amounts as an intermediate in the synthesis of sulfuric acid.
- b. The prefix *di-* tells you that each molecule has two iodine atoms, and the prefix *penta-* indicates that there are five oxygen atoms. The formula is thus I_2O_5 , a compound used to remove carbon monoxide from air in respirators.

Exercise

Write the formula for each binary covalent compound.

- a. silicon tetrachloride
- b. disulfur decafluoride

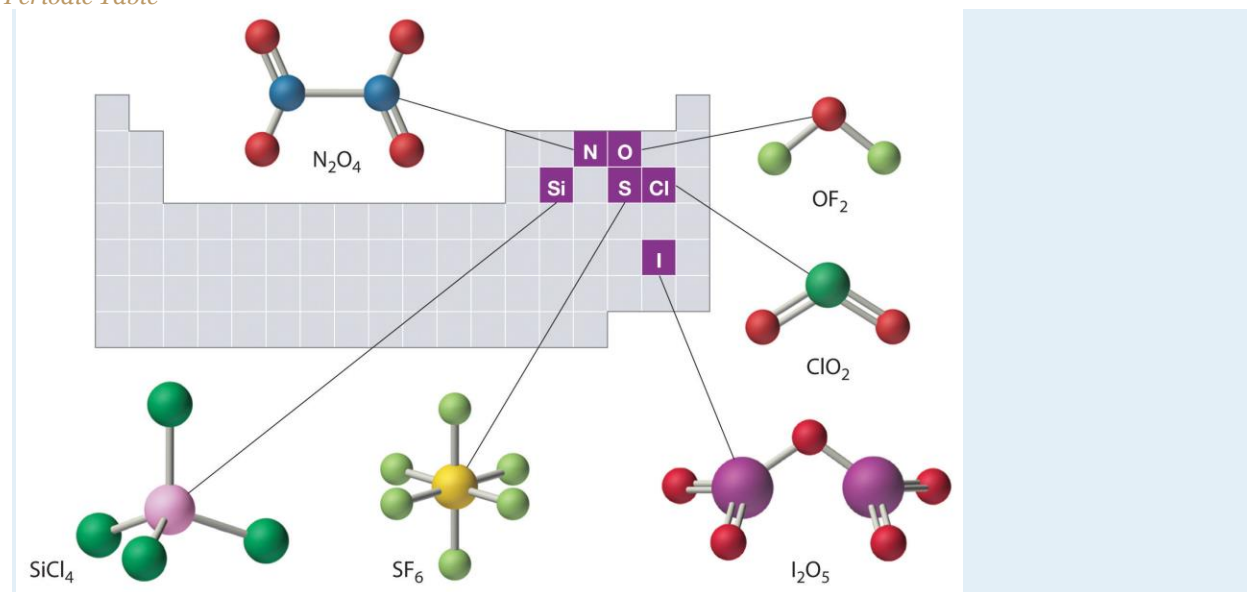
Answer:

- a. SiCl_4
- b. S_2F_{10}

The structures of some of the compounds in Example 8 and Example 9 are shown in Figure 2.14 "The Structures of Some Covalent Inorganic Compounds and the Locations of the "Central Atoms" in the Periodic Table", along with the location of the "central atom" of each compound in the periodic table. It may seem that the compositions and structures of such compounds are entirely random, but this is not true. After you have mastered the material

in Chapter 7 "The Periodic Table and Periodic Trends" and Chapter 8 "Ionic versus Covalent Bonding", you will be able to predict the compositions and structures of compounds of this type with a high degree of accuracy.

Figure 2.14 *The Structures of Some Covalent Inorganic Compounds and the Locations of the "Central Atoms" in the Periodic Table*



The compositions and structures of covalent inorganic compounds are not random. As you will learn in Chapter 7 "The Periodic Table and Periodic Trends" and Chapter 8 "Ionic versus Covalent Bonding", they can be predicted from the locations of the component atoms in the periodic table.

Hydrocarbons

Approximately one-third of the compounds produced industrially are organic compounds. All living organisms are composed of organic compounds, as is most of the food you consume, the medicines you take, the fibers in the clothes you wear, and the plastics in the materials you use. Section 2.1 "Chemical Compounds" introduced two organic compounds: methane (CH_4) and methanol (CH_3OH). These and other organic compounds appear frequently in discussions and examples throughout this text.

The detection of organic compounds is useful in many fields. In one recently developed application, scientists have devised a new method called "material degradomics" to make it possible to monitor the degradation of old books and historical documents. As paper ages, it produces a familiar "old book smell" from the release of organic compounds in gaseous form. The composition of the gas depends on the original type of paper used, a book's binding, and the applied media. By analyzing these organic gases and

isolating the individual components, preservationists are better able to determine the condition of an object and those books and documents most in need of immediate protection.

The simplest class of organic compounds is the hydrocarbons, which consist entirely of carbon and hydrogen. Petroleum and natural gas are complex, naturally occurring mixtures of many different hydrocarbons that furnish raw materials for the chemical industry. The four major classes of hydrocarbons are the alkanes, which contain only carbon–hydrogen and carbon–carbon single bonds; the alkenes, which contain at least one carbon–carbon double bond; the alkynes, which contain at least one carbon–carbon triple bond; and the aromatic hydrocarbons, which usually contain rings of six carbon atoms that can be drawn with alternating single and double bonds. Alkanes are also called *saturated* hydrocarbons, whereas hydrocarbons that contain multiple bonds (alkenes, alkynes, and aromatics) are *unsaturated*.

Alkanes

The simplest alkane is methane (CH_4), a colorless, odorless gas that is the major component of natural gas. In larger alkanes whose carbon atoms are joined in an unbranched chain (*straight-chain alkanes*), each carbon atom is bonded to at most two other carbon atoms. The structures of two simple alkanes are shown in Figure 2.15 "Straight-Chain Alkanes with Two and Three Carbon Atoms", and the names and condensed structural formulas for the first 10 straight-chain alkanes are in Table 2.7 "The First 10 Straight-Chain Alkanes". The names of all alkanes end in *-ane*, and their boiling points increase as the number of carbon atoms increases.

Figure 2.15 *Straight-Chain Alkanes with Two and Three Carbon Atoms*

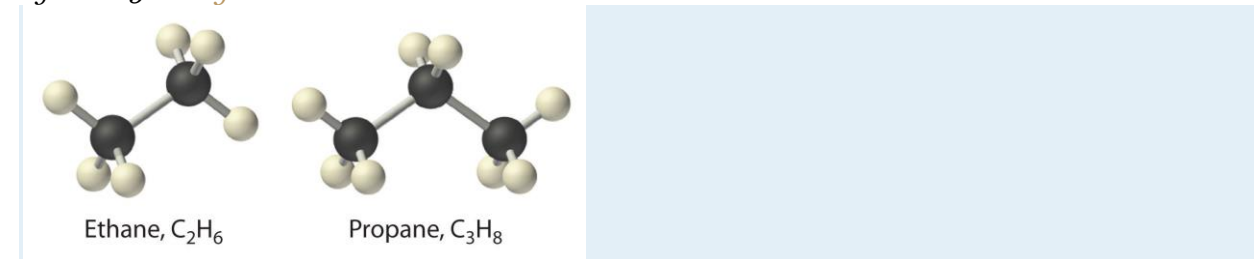
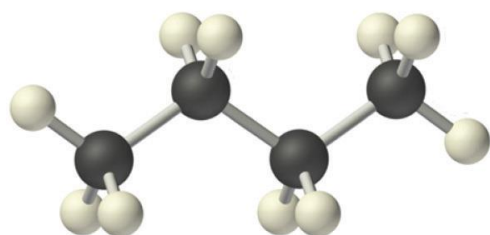


Table 2.7 The First 10 Straight-Chain Alkanes

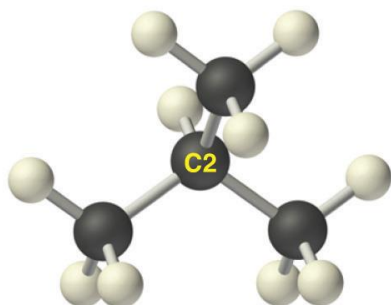
Name	Number of Carbon Atoms	Molecular Formula	Condensed Structural Formula	Boiling Point ($^{\circ}\text{C}$)	Uses
methane	1	CH_4	CH_4	–162	natural gas constituent
ethane	2	C_2H_6	CH_3CH_3	–89	natural gas

Name	Number of Carbon Atoms	Molecular Formula	Condensed Structural Formula	Boiling Point (°C)	Uses
					constituent
propane	3	C ₃ H ₈	CH ₃ CH ₂ CH ₃	-42	bottled gas
butane	4	C ₄ H ₁₀	CH ₃ CH ₂ CH ₂ CH ₃ or CH ₃ (CH ₂) ₂ CH ₃	0	lighters, bottled gas
pentane	5	C ₅ H ₁₂	CH ₃ (CH ₂) ₃ CH ₃	36	solvent, gasoline
hexane	6	C ₆ H ₁₄	CH ₃ (CH ₂) ₄ CH ₃	69	solvent, gasoline
heptane	7	C ₇ H ₁₆	CH ₃ (CH ₂) ₅ CH ₃	98	solvent, gasoline
octane	8	C ₈ H ₁₈	CH ₃ (CH ₂) ₆ CH ₃	126	gasoline
nonane	9	C ₉ H ₂₀	CH ₃ (CH ₂) ₇ CH ₃	151	gasoline
decane	10	C ₁₀ H ₂₂	CH ₃ (CH ₂) ₈ CH ₃	174	kerosene

Alkanes with four or more carbon atoms can have more than one arrangement of atoms. The carbon atoms can form a single unbranched chain, or the primary chain of carbon atoms can have one or more shorter chains that form branches. For example, butane (C₄H₁₀) has two possible structures. *Normal* butane (usually called *n*-butane) is CH₃CH₂CH₂CH₃, in which the carbon atoms form a single unbranched chain. In contrast, the condensed structural formula for *isobutane* is (CH₃)₂CHCH₃, in which the primary chain of three carbon atoms has a one-carbon chain branching at the central carbon. Three-dimensional representations of both structures are as follows:

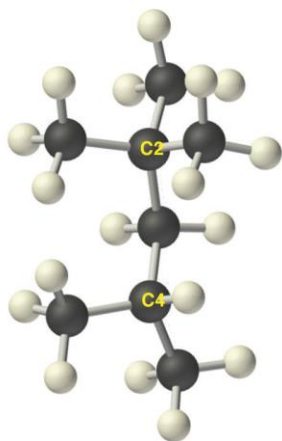


n-Butane, C₄H₁₀



Isobutane (2-methylpropane), C₄H₁₀

The systematic names for branched hydrocarbons use the lowest possible number to indicate the position of the branch along the longest straight carbon chain in the structure. Thus the systematic name for isobutane is 2-methylpropane, which indicates that a methyl group (a branch consisting of $-\text{CH}_3$) is attached to the second carbon of a propane molecule. Similarly, you will learn in Section 2.6 "Industrially Important Chemicals" that one of the major components of gasoline is commonly called isooctane; its structure is as follows:



Isooctane (2,2,4-trimethylpentane)

As you can see, the compound has a chain of five carbon atoms, so it is a derivative of pentane. There are two methyl group branches at one carbon atom and one methyl group at another. Using the lowest possible numbers for the branches gives 2,2,4-trimethylpentane for the systematic name of this compound.

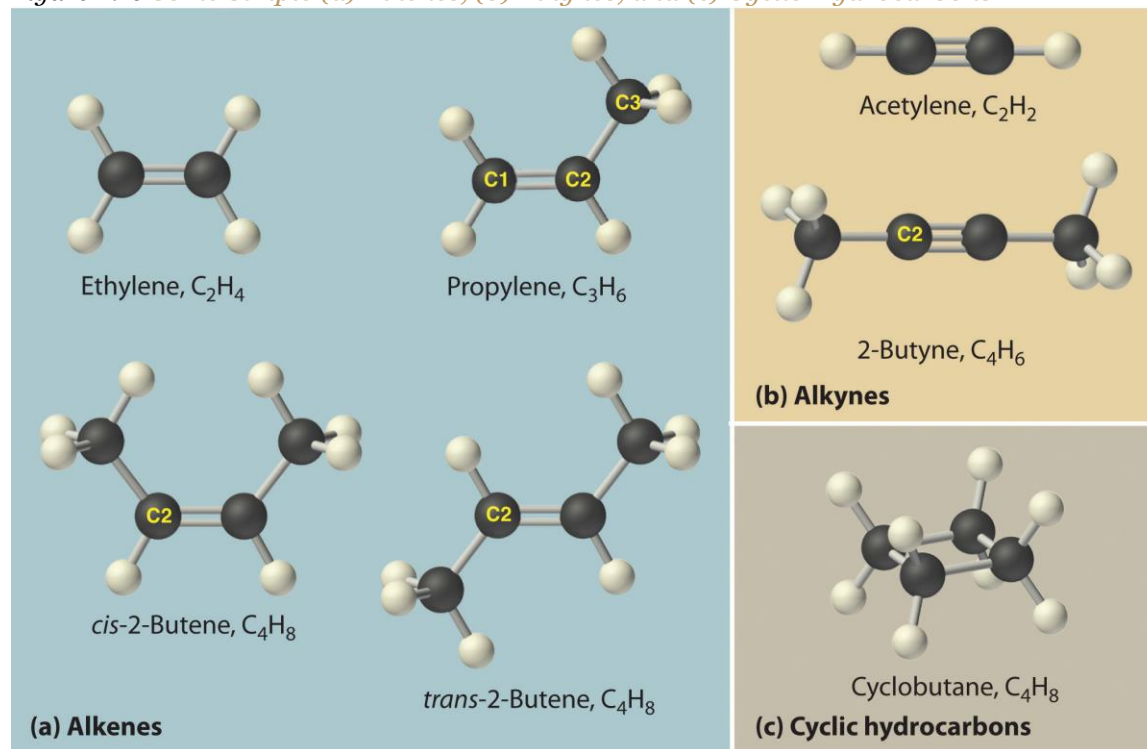
Alkenes

The simplest alkenes are *ethylene*, C_2H_4 or $\text{CH}_2=\text{CH}_2$, and *propylene*, C_3H_6 or $\text{CH}_3\text{CH}=\text{CH}_2$ (part (a) in Figure 2.16 "Some Simple (a) Alkenes, (b) Alkynes, and (c) Cyclic Hydrocarbons"). The names of alkenes that have more than three carbon atoms use the same stems as the names of the alkanes (Table 2.7 "The First 10 Straight-Chain Alkanes") but end in *-ene* instead of *-ane*.

Once again, more than one structure is possible for alkenes with four or more carbon atoms. For example, an alkene with four carbon atoms has three possible structures. One is $\text{CH}_2=\text{CHCH}_2\text{CH}_3$ (1-butene), which has the double bond between the first and second carbon atoms in the chain. The other two structures have the double bond between the second and third carbon atoms and are forms of $\text{CH}_3\text{CH}=\text{CHCH}_3$ (2-butene). All four carbon atoms in 2-butene lie in the same plane, so there are two possible structures (part (a) in Figure 2.16 "Some Simple (a) Alkenes, (b) Alkynes, and (c) Cyclic Hydrocarbons"). If the two methyl

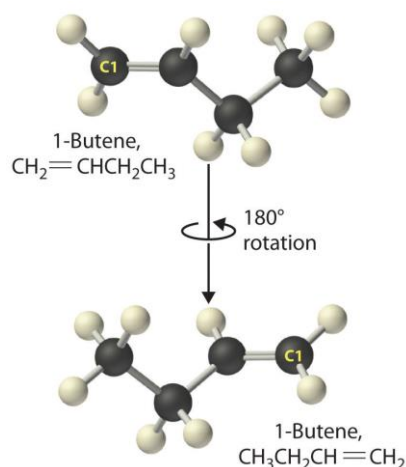
groups are on the same side of the double bond, the compound is *cis*-2-butene (from the Latin *cis*, meaning “on the same side”). If the two methyl groups are on opposite sides of the double bond, the compound is *trans*-2-butene (from the Latin *trans*, meaning “across”). These are distinctly different molecules: *cis*-2-butene melts at -138.9°C , whereas *trans*-2-butene melts at -105.5°C .

Figure 2.16 Some Simple (a) Alkenes, (b) Alkynes, and (c) Cyclic Hydrocarbons



The positions of the carbon atoms in the chain are indicated by C1 or C2.

Just as a number indicates the positions of branches in an alkane, the number in the name of an alkene specifies the position of the *first* carbon atom of the double bond. The name is based on the lowest possible number starting from *either end* of the carbon chain, so $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$ is called 1-butene, *not* 3-butene. Note that $\text{CH}_2=\text{CHCH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$ are different ways of writing the *same molecule* (1-butene) in two different orientations.



The name of a compound does not depend on its orientation. As illustrated for 1-butene, both condensed structural formulas and molecular models show different orientations of the same molecule. Don't let orientation fool you; you must be able to recognize the same structure no matter what its orientation.

Note the Pattern

The positions of groups or multiple bonds are always indicated by the lowest number possible.

Alkynes

The simplest alkyne is *acetylene*, C_2H_2 or $\text{HC}\equiv\text{CH}$ (part (b) in Figure 2.16 "Some Simple (a) Alkenes, (b) Alkynes, and (c) Cyclic Hydrocarbons"). Because a mixture of acetylene and oxygen burns with a flame that is hot enough ($>3000^\circ\text{C}$) to cut metals such as hardened steel, acetylene is widely used in cutting and welding torches. The names of other alkynes are similar to those of the corresponding alkanes but end in *-yne*. For example, $\text{HC}\equiv\text{CCH}_3$ is *propyne*, and $\text{CH}_3\text{C}\equiv\text{CCH}_3$ is *2-butyne* because the multiple bond begins on the second carbon atom.

Note the Pattern

The number of bonds between carbon atoms in a hydrocarbon is indicated in the suffix:

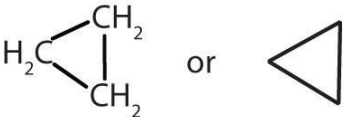
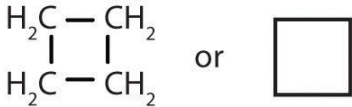
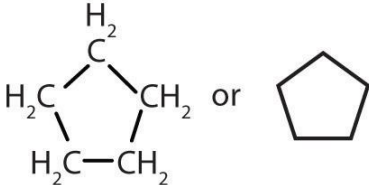
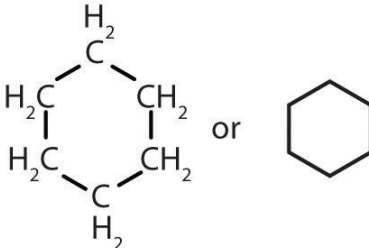
- *alkane*: only carbon–carbon single bonds
- *alkene*: at least one carbon–carbon double bond
- *alkyne*: at least one carbon–carbon triple bond

Cyclic Hydrocarbons

In a cyclic hydrocarbon, the ends of a hydrocarbon chain are connected to form a ring of covalently bonded carbon atoms. Cyclic hydrocarbons are named by attaching the prefix *cyclo-* to the name of the

alkane, the alkene, or the alkyne. The simplest cyclic alkanes are *cyclopropane* (C_3H_6) a flammable gas that is also a powerful anesthetic, and *cyclobutane* (C_4H_8) (part (c) in Figure 2.16 "Some Simple (a) Alkenes, (b) Alkynes, and (c) Cyclic Hydrocarbons"). The most common way to draw the structures of cyclic alkanes is to sketch a polygon with the same number of vertices as there are carbon atoms in the ring; each vertex represents a CH_2 unit. The structures of the cycloalkanes that contain three to six carbon atoms are shown schematically in Figure 2.17 "The Simple Cycloalkanes".

Figure 2.17 The Simple Cycloalkanes

Name	Molecular Formula	Structural Formula
cyclopropane	C_3H_6	
cyclobutane	C_4H_8	
cyclopentane	C_5H_{10}	
cyclohexane	C_6H_{12}	

Aromatic Hydrocarbons

Alkanes, alkenes, alkynes, and cyclic hydrocarbons are generally called **aliphatic hydrocarbons**. The name comes from the Greek *aleiphar*, meaning "oil," because the first examples were extracted from animal fats. In contrast, the first examples of **aromatic hydrocarbons**, also called *arenes*, were obtained by the distillation and degradation of highly scented (thus *aromatic*) resins from tropical trees.

The simplest aromatic hydrocarbon is *benzene* (C_6H_6), which was first obtained from a coal distillate. The word *aromatic* now refers to benzene and structurally similar compounds. As shown in part (a) in Figure 2.18 "Two Aromatic Hydrocarbons: (a) Benzene and (b) Toluene", it is possible to draw the structure of benzene in two different

but equivalent ways, depending on which carbon atoms are connected by double bonds or single bonds. *Toluene* is similar to benzene, except that one hydrogen atom is replaced by a -CH_3 group; it has the formula C_7H_8 (part (b) in Figure 2.18 "Two Aromatic Hydrocarbons: (a) Benzene and (b) Toluene"). As you will soon learn, the chemical behavior of aromatic compounds differs from the behavior of aliphatic compounds. Benzene and toluene are found in gasoline, and benzene is the starting material for preparing substances as diverse as aspirin and nylon.

Figure 2.18 *Two Aromatic Hydrocarbons: (a) Benzene and (b) Toluene*

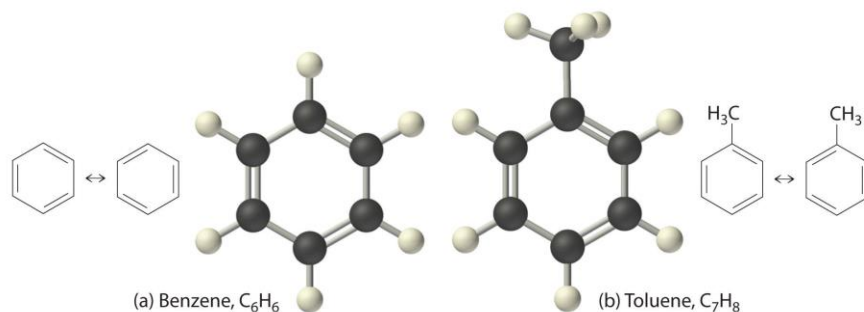
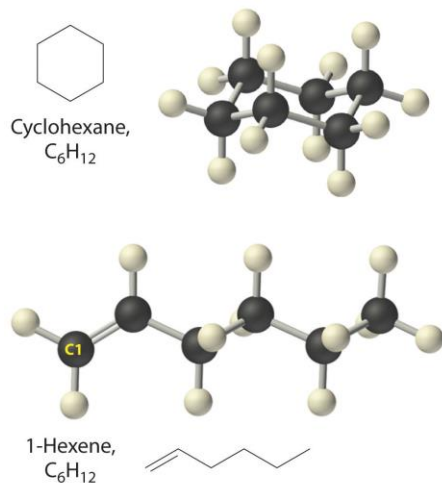


Figure 2.19 "Two Hydrocarbons with the Molecular Formula C_6H_{12} " illustrates two of the molecular structures possible for hydrocarbons that have six carbon atoms. As you can see, compounds with the same molecular formula can have very different structures.

Figure 2.19 *Two Hydrocarbons with the Molecular Formula C_6H_{12}*



EXAMPLE 10

Write the condensed structural formula for each hydrocarbon.

- n*-heptane
- 2-pentene

- c. 2-butyne
- d. cyclooctene

Given: name of hydrocarbon

Asked for: condensed structural formula

Strategy:

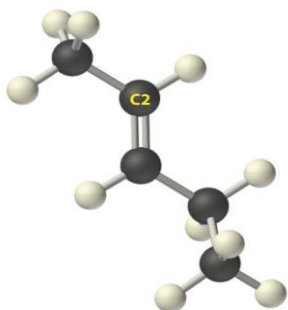
A Use the prefix to determine the number of carbon atoms in the molecule and whether it is cyclic. From the suffix, determine whether multiple bonds are present.

B Identify the position of any multiple bonds from the number(s) in the name and then write the condensed structural formula.

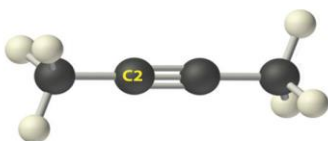
Solution:

a. **A** The prefix *hept-* tells us that this hydrocarbon has seven carbon atoms, and *n-* indicates that the carbon atoms form a straight chain. The suffix *-ane* tells that it is an alkane, with no carbon–carbon double or triple bonds. **B** The condensed structural formula is $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, which can also be written as $\text{CH}_3(\text{CH}_2)_5\text{CH}_3$.

b. **A** The prefix *pent-* tells us that this hydrocarbon has five carbon atoms, and the suffix *-ene* indicates that it is an alkene, with a carbon–carbon double bond. **B** The 2- tells us that the double bond begins on the second carbon of the five-carbon atom chain. The condensed structural formula of the compound is therefore $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_3$.

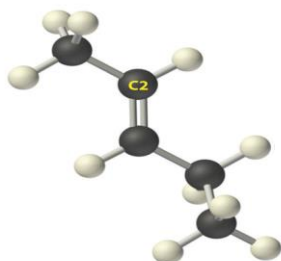


2-Pentene

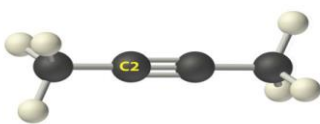


2-Butyne

C. **A** The prefix *but-* tells us that the compound has a chain of four carbon atoms, and the suffix *-yne* indicates that it has a carbon–carbon triple bond. **B** The 2- tells us that the triple bond begins on the second carbon of the four-carbon atom chain. So the condensed structural formula for the compound is $\text{CH}_3\text{C}\equiv\text{CCH}_3$.

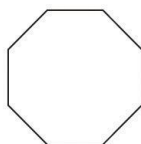


2-Pentene

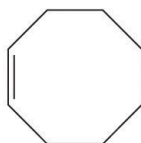


2-Butyne

d. **A** The prefix *cyclo-* tells us that this hydrocarbon has a ring structure, and *oct-* indicates that it contains eight carbon atoms, which we can draw as



The suffix *-ene* tells us that the compound contains a carbon–carbon double bond, but where in the ring do we place the double bond? **B** Because all eight carbon atoms are identical, it doesn't matter. We can draw the structure of cyclooctene as



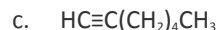
Exercise

Write the condensed structural formula for each hydrocarbon.

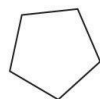
- n*-octane
- 2-hexene
- 1-heptyne
- cyclopentane

Answer:

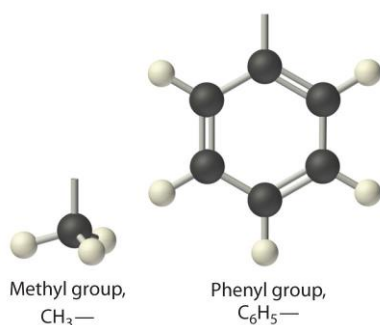
- $\text{CH}_3(\text{CH}_2)_6\text{CH}_3$
- $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_2\text{CH}_3$



d.



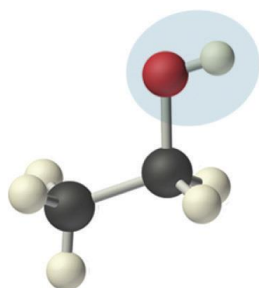
e. The general name for a group of atoms derived from an alkane is an *alkyl group*. The name of an alkyl group is derived from the name of the alkane by adding the suffix *-yl*. Thus the $-\text{CH}_3$ fragment is a *methyl* group, the $-\text{CH}_2\text{CH}_3$ fragment is an *ethyl* group, and so forth, where the dash represents a single bond to some other atom or group. Similarly, groups of atoms derived from aromatic hydrocarbons are *aryl groups*, which sometimes have unexpected names. For example, the $-\text{C}_6\text{H}_5$ fragment is derived from benzene, but it is called a *phenyl* group. In general formulas and structures, alkyl and aryl groups are often abbreviated as R.



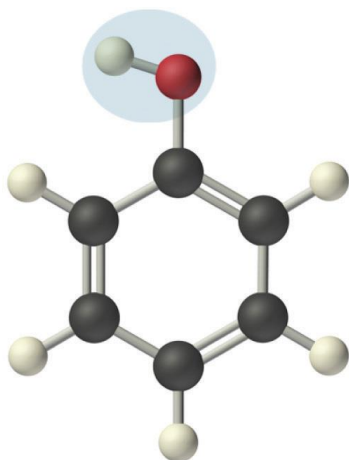
Structures of alkyl and aryl groups. The methyl group is an example of an alkyl group, and the phenyl group is an example of an aryl group.

Alcohols

Replacing one or more hydrogen atoms of a hydrocarbon with an $-\text{OH}$ group gives alcohol, represented as ROH . The simplest alcohol (CH_3OH) is called either *methanol* (its systematic name) or *methyl alcohol* (its common name) (see Figure 2.4 "Different Ways of Representing the Structure of a Molecule"). Methanol is the antifreeze in automobile windshield washer fluids, and it is also used as an efficient fuel for racing cars, most notably in the Indianapolis 500. Ethanol (or ethyl alcohol, $\text{CH}_3\text{CH}_2\text{OH}$) is familiar as the alcohol in fermented or distilled beverages, such as beer, wine, and whiskey; it is also used as a gasoline additive (Section 2.6 "Industrially Important Chemicals"). The simplest alcohol derived from an aromatic hydrocarbon is $\text{C}_6\text{H}_5\text{OH}$, *phenol* (shortened from *phenyl* alcohol), a potent disinfectant used in some sore throat medications and mouthwashes.



Ethanol, $\text{CH}_3\text{CH}_2\text{OH}$



Phenol, $\text{C}_6\text{H}_5\text{OH}$

Ethanol, which is easy to obtain from fermentation processes, has successfully been used as an alternative fuel for several decades. Although it is a “green” fuel when derived from plants, it is an imperfect substitute for fossil fuels because it is less efficient than gasoline. Moreover, because ethanol absorbs water from the atmosphere, it can corrode an engine’s seals. Thus other types of processes are being developed that use bacteria to create more complex alcohols, such as octanol, that are more energy efficient and that have a lower tendency to absorb water. As scientists attempt to reduce mankind’s dependence on fossil fuels, the development of these so-called *biofuels* is a particularly active area of research.

Summary

Covalent inorganic compounds are named by a procedure similar to that used for ionic compounds, using prefixes to indicate the numbers of atoms in the molecular formula. The simplest organic compounds are the **hydrocarbons**, which contain *only* carbon and hydrogen. **Alkanes** contain only carbon–hydrogen and carbon–carbon single bonds, **alkenes** contain at least one carbon–carbon double bond, and **alkynes** contain one or more carbon–carbon triple bonds. Hydrocarbons can also be **cyclic**, with the

ends of the chain connected to form a ring. Collectively, alkanes, alkenes, and alkynes are called **aliphatic hydrocarbons**. **Aromatic hydrocarbons**, or *arenes*, are another important class of hydrocarbons that contain rings of carbon atoms related to the structure of benzene (C_6H_6). A derivative of an alkane or an arene from which one hydrogen atom has been removed is called an *alkyl group* or an *aryl group*, respectively. **Alcohols** are another common class of organic compound, which contain an $-\text{OH}$ group covalently bonded to either an alkyl group or an aryl group (often abbreviated **R**).

KEY TAKEAWAY

- Covalent inorganic compounds are named using a procedure similar to that used for ionic compounds, whereas hydrocarbons use a system based on the number of bonds between carbon atoms.

CONCEPTUAL PROBLEMS

1. Benzene (C_6H_6) is an organic compound, and KCl is an ionic compound. The sum of the masses of the atoms in each empirical formula is approximately the same. How would you expect the two to compare with regard to each of the following? What species are present in benzene vapor?
 - a. melting point
 - b. type of bonding
 - c. rate of evaporation
 - d. structure
2. Can an inorganic compound be classified as a hydrocarbon? Why or why not?
3. Is the compound NaHCO_3 a hydrocarbon? Why or why not?
4. Name each compound.
 - a. NiO
 - b. TiO_2
 - c. N_2O
 - d. CS_2
 - e. SO_3
 - f. NF_3
 - g. SF_6
5. Name each compound.
 - a. HgCl_2

b. IF_5

c. N_2O_5

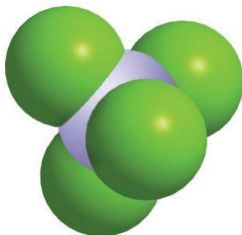
d. Cl_2O

e. HgS

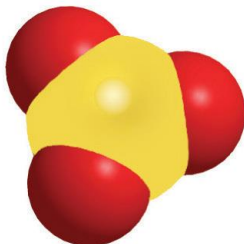
f. PCl_5

6. For each structural formula, write the condensed formula and the name of the compound.

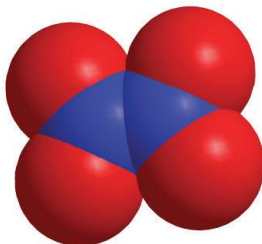
a.



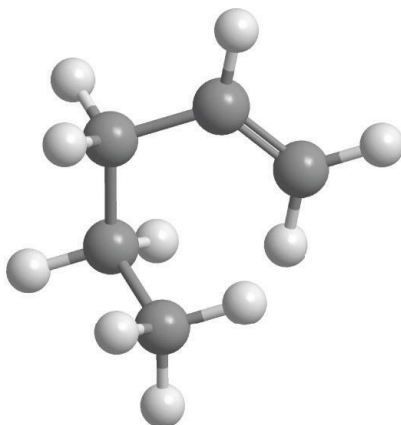
b.



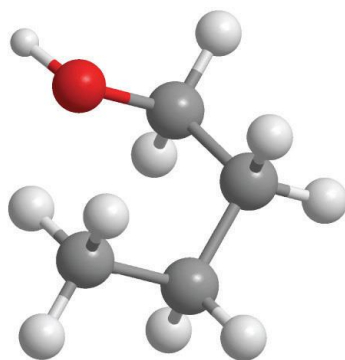
c.



d.

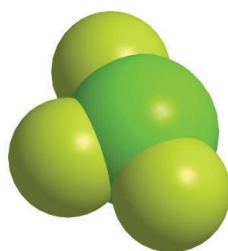


e.

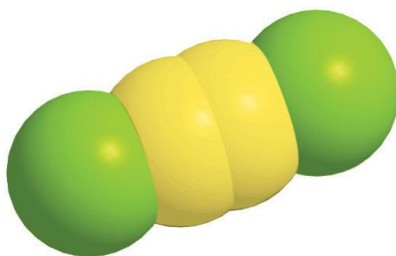


7. For each structural formula, write the condensed formula and the name of the compound.

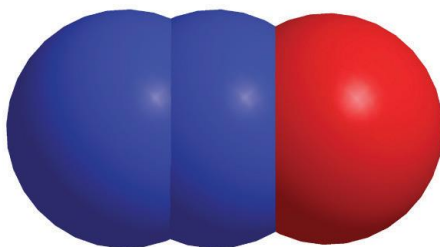
a.



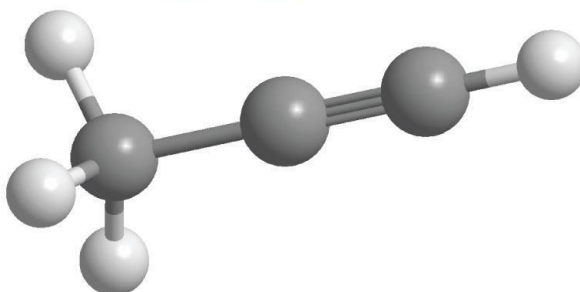
b.



c.



d.



1. Would you expect PCl_3 to be an ionic compound or a covalent compound? Explain your reasoning.

2. What distinguishes an aromatic hydrocarbon from an aliphatic hydrocarbon?
3. The following general formulas represent specific classes of hydrocarbons. Refer to Table 2.7 "The First 10 Straight-Chain Alkanes" and Table 2.8 "Some Common Acids That Do Not Contain Oxygen" and Figure 2.16 "Some Simple (a) Alkenes, (b) Alkynes, and (c) Cyclic Hydrocarbons" and identify the classes.
 - a. C_nH_{2n+2}
 - b. C_nH_{2n}
 - c. C_nH_{2n-2}
4. Using R to represent an alkyl or aryl group, show the general structure of an
 - a. alcohol.
 - b. phenol.

ANSWER

1.
 - a. ROH (where R is an alkyl group)
 - b. ROH (where R is an aryl group)

NUMERICAL PROBLEMS

1. Write the formula for each compound.
 - a. dinitrogen monoxide
 - b. silicon tetrafluoride
 - c. boron trichloride
 - d. nitrogen trifluoride
 - e. phosphorus tribromide
2. Write the formula for each compound.
 - a. dinitrogen trioxide
 - b. iodine pentafluoride
 - c. boron tribromide
 - d. oxygen difluoride
 - e. arsenic trichloride
3. Write the formula for each compound.
 - a. thallium(I) selenide

- b. neptunium(IV) oxide
 - c. iron(II) sulfide
 - d. copper(I) cyanide
 - e. nitrogen trichloride
4. Name each compound.
- a. RuO_4
 - b. PbO_2
 - c. MoF_6
 - d. $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$
 - e. WCl_4
5. Name each compound.
- a. NbO_2
 - b. MoS_2
 - c. P_4S_{10}
 - d. Cu_2O
 - e. ReF_5
6. Draw the structure of each compound.
- a. propyne
 - b. ethanol
 - c. *n*-hexane
 - d. cyclopropane
 - e. benzene
7. Draw the structure of each compound.
- a. 1-butene
 - b. 2-pentyne
 - c. cycloheptane
 - d. toluene
 - e. phenol

ANSWERS

1.

- a. N_2O
- b. SiF_4
- c. BCl_3
- d. NF_3
- e. PBr_3

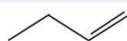
3.

- f. Tl_2Se
- g. NpO_2
- h. FeS
- i. CuCN
- j. NCl_3

5.

- k. niobium (IV) oxide
- l. molybdenum (IV) sulfide
- m. tetraphosphorus decasulfide
- n. copper(I) oxide
- o. rhenium(V) fluoride

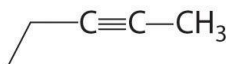
7. a.



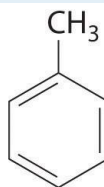
b.

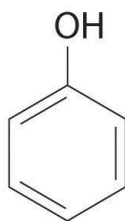


c.



d.





e.

2.5 Acids and Bases

LEARNING OBJECTIVE

1. To identify and name some common acids and bases.

For our purposes at this point in the text, we can define an acid as a substance with at least one hydrogen atom that can dissociate to form an anion and an H^+ ion (a proton) in aqueous solution, thereby forming an *acidic solution*. We can define bases as compounds that produce hydroxide ions (OH^-) and a cation when dissolved in water, thus forming a *basic solution*. Solutions that are neither basic nor acidic are *neutral*. We will discuss the chemistry of acids and bases in more detail in Chapter 4 "Reactions in Aqueous Solution", Chapter 8 "Ionic versus Covalent Bonding", and Chapter 16 "Aqueous Acid–Base Equilibria", but in this section we describe the nomenclature of common acids and identify some important bases so that you can recognize them in future discussions. Pure acids and bases and their concentrated aqueous solutions are commonly encountered in the laboratory. They are usually highly corrosive, so they must be handled with care.

Acids

The names of acids differentiate between (1) acids in which the H^+ ion is attached to an oxygen atom of a polyatomic anion (these are called oxoacids, or occasionally **oxyacids**) and (2) acids in which the H^+ ion is attached to some other element. In the latter case, the name of the acid begins with *hydro-* and ends in *-ic*, with the root of the name of the other element or ion in between. Recall that the name of the anion derived from this kind of acid always ends in *-ide*. Thus hydrogen chloride (HCl) gas dissolves in water to form hydrochloric acid (which contains H^+ and Cl^- ions), hydrogen cyanide (HCN) gas forms hydrocyanic acid (which contains H^+ and CN^- ions), and so forth (Table 2.8 "Some Common Acids That Do Not Contain Oxygen"). Examples of this kind of acid are commonly encountered and very important. For instance, your stomach contains a dilute solution of hydrochloric acid to help digest food. When the mechanisms that prevent the stomach from digesting itself malfunction, the acid destroys the lining of the stomach and an ulcer forms.

Note the Pattern

Acids are distinguished by whether the H^+ ion is attached to an oxygen atom of a polyatomic anion or some other element.

Table 2.8 Some Common Acids That Do Not Contain Oxygen

Formula	Name in Aqueous Solution	Name of Gaseous Species
HF	hydrofluoric acid	hydrogen fluoride
HCl	hydrochloric acid	hydrogen chloride
HBr	hydrobromic acid	hydrogen bromide
HI	hydroiodic acid	hydrogen iodide
HCN	hydrocyanic acid	hydrogen cyanide
H_2S	hydrosulfuric acid	hydrogen sulfide

If an acid contains one or more H^+ ions attached to oxygen, it is a derivative of one of the common oxoanions, such as sulfate (SO_4^{2-}) or nitrate (NO_3^-). These acids contain as many H^+ ions as are necessary to balance the negative charge on the anion, resulting in a neutral species such as H_2SO_4 and HNO_3 .

The names of acids are derived from the names of anions according to the following rules:

- If the name of the anion ends in *-ate*, then the name of the acid ends in *-ic*.** For example, because NO_3^- is the nitrate ion, HNO_3 is nitric acid. Similarly, ClO_4^- is the perchlorate ion, so HClO_4 is perchloric acid. Two important acids are sulfuric acid (H_2SO_4) from the sulfate ion (SO_4^{2-}) and phosphoric acid (H_3PO_4) from the phosphate ion (PO_4^{3-}). These two names use a slight variant of the root of the anion name: *sulfate* becomes *sulfuric* and *phosphate* becomes *phosphoric*.
- If the name of the anion ends in *-ite*, then the name of the acid ends in *-ous*.** For example, OCl^- is the hypochlorite ion, and HOCl is hypochlorous acid; NO_2^- is the nitrite ion, and HNO_2 is nitrous acid; and SO_3^{2-} is the sulfite ion, and H_2SO_3 is sulfurous acid. The same roots are used whether the acid name ends in *-ic* or *-ous*; thus, *sulfite* becomes *sulfurous*.

The relationship between the names of the oxoacids and the parent oxoanions is illustrated in Figure 2.20 "The Relationship between the Names of the Oxoacids and the Names of the Parent Oxoanions", and some common oxoacids are in Table 2.9 "Some Common Oxoacids".

Figure 2.20 *The Relationship between the Names of the Oxoacids and the Names of the Parent Oxoanions*

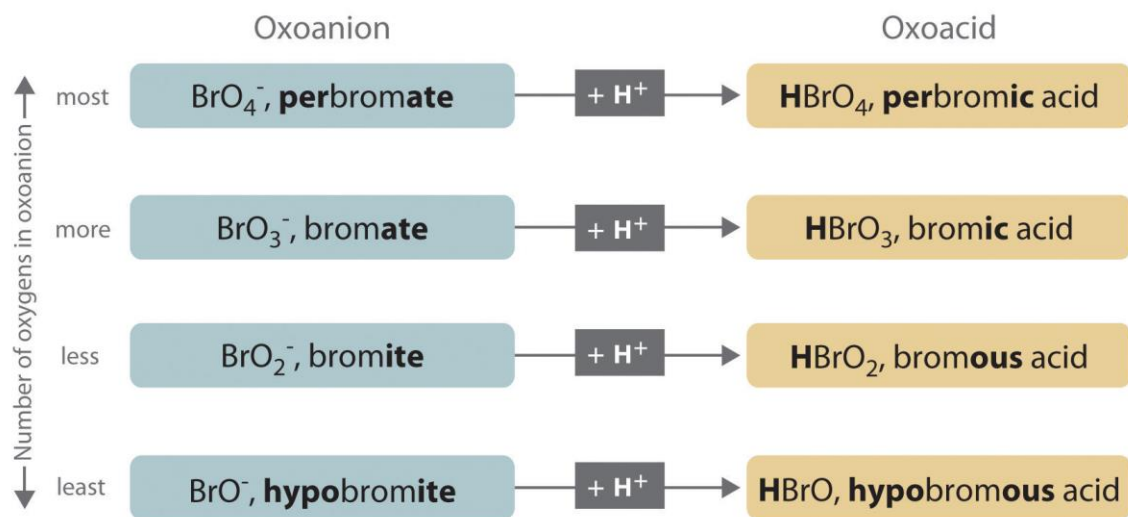


Table 2.9 Some Common Oxoacids

Formula	Name
HNO_2	nitrous acid
HNO_3	nitric acid
H_2SO_3	sulfurous acid
H_2SO_4	sulfuric acid
H_3PO_4	phosphoric acid
H_2CO_3	carbonic acid
HClO	hypochlorous acid
HClO_2	chlorous acid
HClO_3	chloric acid
HClO_4	perchloric acid

EXAMPLE 11

Name and give the formula for each acid.

- the acid formed by adding a proton to the hypobromite ion (OBr^-)
- the acid formed by adding two protons to the selenate ion (SeO_4^{2-})

Given: anion

Asked for: parent acid

Strategy:

Refer to Table 2.8 "Some Common Acids That Do Not Contain Oxygen" and Table 2.9 "Some Common Oxoacids" to find the name of the acid. If the acid is not listed, use the guidelines given previously.

Solution:

Neither species is listed in Table 2.8 "Some Common Acids That Do Not Contain Oxygen" or Table 2.9 "Some Common Oxoacids", so we must use the information given previously to derive the name of the acid from the name of the polyatomic anion.

- a. The anion name, *hypobromite*, ends in *-ite*, so the name of the parent acid ends in *-ous*. The acid is therefore hypobromous acid (HOBr).
- b. *Selenate* ends in *-ate*, so the name of the parent acid ends in *-ic*. The acid is therefore selenic acid (H₂SeO₄).

Exercise

Name and give the formula for each acid.

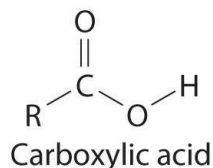
- a. the acid formed by adding a proton to the perbromate ion (BrO₄⁻)
- b. the acid formed by adding three protons to the arsenite ion (AsO₃³⁻)

Answer:

- a. perbromic acid; HBrO₄
- b. arsenous acid; H₃AsO₃

Many organic compounds contain the carbonyl group, in which there is a carbon–oxygen double bond.

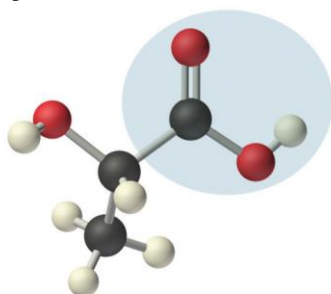
In carboxylic acids, an –OH group is covalently bonded to the carbon atom of the carbonyl group. Their general formula is RCO₂H, sometimes written as RCOOH:



where R can be an alkyl group, an aryl group, or a hydrogen atom. The simplest example, HCO₂H, is *formic acid*, so called because it is found in the secretions of stinging ants (from the Latin *formica*, meaning “ant”). Another example is *acetic acid* (CH₃CO₂H), which is found in vinegar. Like many acids, carboxylic acids tend to have sharp odors. For example, butyric acid (CH₃CH₂CH₂CO₂H), is responsible for the smell of rancid butter, and the characteristic odor of sour milk and vomit is due to lactic acid [CH₃CH(OH)CO₂H]. Some common carboxylic acids are shown in Figure 2.21 "Some Common Carboxylic Acids".

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Figure 2.21 Some Common Carboxylic Acids



Lactic acid, $\text{CH}_3\text{CH}(\text{OH})\text{CO}_2\text{H}$

Formula (Structure)	Name	Uses
HCO_2H	formic acid	tanning, dyeing
$\text{CH}_3\text{CO}_2\text{H}$	acetic acid	vinegar, food preservative
$\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$	propionic acid	food preservative
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$	butyric acid	varnishes
$\text{C}_6\text{H}_5\text{CO}_2\text{H}$ 	benzoic acid	food preservative, dyeing

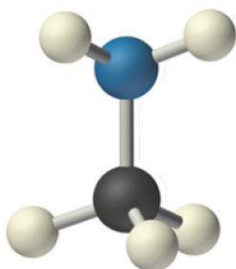
Although carboxylic acids are covalent compounds, when they dissolve in water, they dissociate to produce H^+ ions (just like any other acid) and RCO_2^- ions. Note that *only the hydrogen attached to the oxygen atom of the CO_2 group dissociates to form an H^+ ion*. In contrast, the hydrogen atom attached to the oxygen atom of an alcohol does *not* dissociate to form an H^+ ion when an alcohol is dissolved in water. The reasons for the difference in behavior between carboxylic acids and alcohols will be discussed in Chapter 8 "Ionic versus Covalent Bonding".

Note the Pattern

Only the hydrogen attached to the oxygen atom of the CO_2 group dissociates to form an H^+ ion.

Bases

We will present more comprehensive definitions of bases in later chapters, but virtually every base you encounter in the meantime will be an ionic compound, such as sodium hydroxide (NaOH) and barium hydroxide [$\text{Ba}(\text{OH})_2$], that contain the hydroxide ion and a metal cation. These have the general formula $\text{M}(\text{OH})_n$. It is important to recognize that alcohols, with the general formula ROH , are covalent compounds, not ionic compounds; consequently, they do *not* dissociate in water to form a basic solution (containing OH^- ions). When a base reacts with any of the acids we have discussed, it accepts a proton (H^+). For example, the hydroxide ion (OH^-) accepts a proton to form H_2O . Thus bases are also referred to as *proton acceptors*.



Methylamine

Concentrated aqueous solutions of ammonia (NH_3) contain significant amounts of the hydroxide ion, even though the dissolved substance is *not* primarily ammonium hydroxide (NH_4OH) as is often stated on the label. Thus aqueous ammonia solution is also a common base. Replacing a hydrogen atom of NH_3 with an alkyl group results in an amine (RNH_2), which is also a base. Amines have pungent odors—for example, methylamine (CH_3NH_2) is one of the compounds responsible for the foul odor associated with spoiled fish. The physiological importance of amines is suggested in the word *vitamin*, which is derived from the phrase *vital amines*. The word was coined to describe dietary substances that were effective at preventing scurvy, rickets, and other diseases because these substances were assumed to be amines. Subsequently, some vitamins have indeed been confirmed to be amines.

Note the Pattern

Metal hydroxides (MOH) yield OH^- ions and are bases, alcohols (ROH) do not yield OH^- or H^+ ions and are neutral, and carboxylic acids (RCO_2H) yield H^+ ions and are acids.

Summary

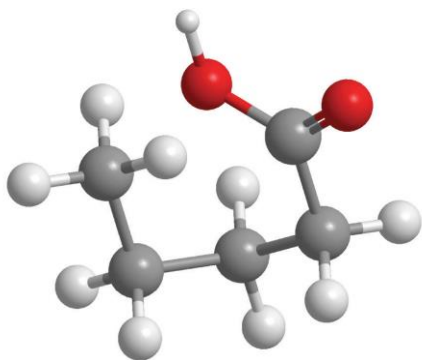
Common **acids** and the polyatomic anions derived from them have their own names and rules for nomenclature. The nomenclature of acids differentiates between **oxoacids**, in which the H^+ ion is attached to an oxygen atom of a polyatomic ion, and acids in which the H^+ ion is attached to another element. **Carboxylic acids** are an important class of organic acids. Ammonia is an important **base**, as are its organic derivatives, the **amines**.

KEY TAKEAWAY

- Common acids and polyatomic anions derived from them have their own names and rules for nomenclature.

CONCEPTUAL PROBLEMS

1. Name each acid.
 - a. HCl
 - b. HBrO_3
 - c. HNO_3
 - d. H_2SO_4
 - e. HIO_3
2. Name each acid.
 - a. HBr
 - b. H_2SO_3
 - c. HClO_3
 - d. HCN
 - e. H_3PO_4
3. Name the aqueous acid that corresponds to each gaseous species.
 - a. hydrogen bromide
 - b. hydrogen cyanide
 - c. hydrogen iodide
4. For each structural formula, write the condensed formula and the name of the compound.

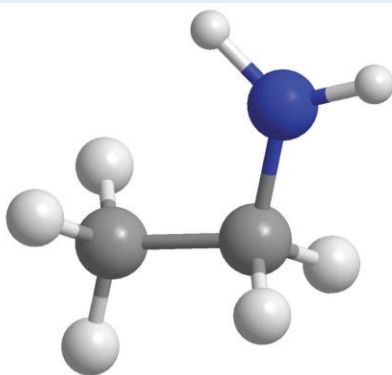


a.

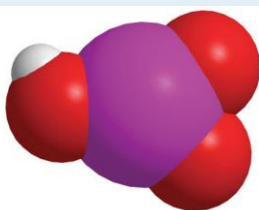


b.

5. For each structural formula, write the condensed formula and the name of the compound.



a.



b.

6. When each compound is added to water, is the resulting solution acidic, neutral, or basic?

- a. $\text{CH}_3\text{CH}_2\text{OH}$
- b. $\text{Mg}(\text{OH})_2$
- c. $\text{C}_6\text{H}_5\text{CO}_2\text{H}$
- d. LiOH
- e. $\text{C}_3\text{H}_7\text{CO}_2\text{H}$

f. H_2SO_4

7. Draw the structure of the simplest example of each type of compound.

a. alkane

b. alkene

c. alkyne

d. aromatic hydrocarbon

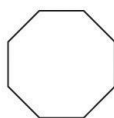
e. alcohol

f. carboxylic acid

g. amine

h. cycloalkane

8. Identify the class of organic compound represented by each compound.



a.

b. $\text{CH}_3\text{CH}_2\text{OH}$

c. $\text{HC}\equiv\text{CH}$



d.

e. $\text{C}_3\text{H}_7\text{NH}_2$

f. $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_3$



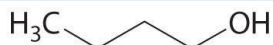
g.

9. Identify the class of organic compound represented by each compound.



a.

b.



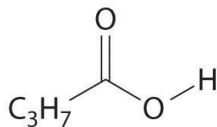
c.



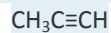
d.



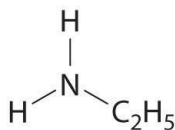
e.



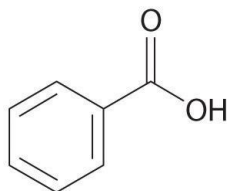
f.



g.



h.



NUMERICAL PROBLEMS

1. Write the formula for each compound.

- hypochlorous acid
- perbromic acid
- hydrobromic acid
- sulfurous acid
- sodium perbromate

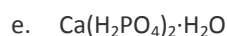
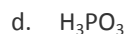
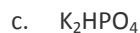
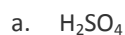
2. Write the formula for each compound.

- hydroiodic acid
- hydrogen sulfide
- phosphorous acid
- perchloric acid
- calcium hypobromite

3. Name each compound.

- HBr
- H_2SO_3
- HCN
- HClO_4
- NaHSO_4

4. Name each compound.



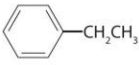
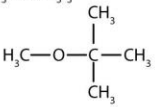
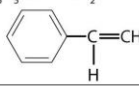
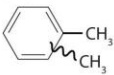
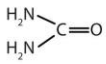
2.6 Industrially Important Chemicals

LEARNING OBJECTIVE

1. To appreciate the scope of the chemical industry and its contributions to modern society.

It isn't easy to comprehend the scale on which the chemical industry must operate to supply the huge amounts of chemicals required in modern industrial societies. Figure 2.22 "Top 25 Chemicals Produced in the United States in 2002*" lists the names and formulas of the chemical industry's "top 25" for 2002—the 25 chemicals produced in the largest quantity in the United States that year—along with the amounts produced, in *billions* of pounds. To put these numbers in perspective, consider that the 88.80 billion pounds of sulfuric acid produced in the United States in 2002 has a volume of 21.90 million cubic meters ($2.19 \times 10^7 \text{ m}^3$), enough to fill the Pentagon, probably the largest office building in the world, about 22 times.

Figure 2.22 Top 25 Chemicals Produced in the United States in 2002*

Rank	Name	Formula (Structure)	Billions of Pounds	Rank	Name	Formula (Structure)	Billions of Pounds
1	sulfuric acid	H_2SO_4	88.80	14	1,2-dichloroethane (ethylene dichloride)	$\text{ClCH}_2\text{CH}_2\text{Cl}$	15.94
2	nitrogen	N_2	58.70	15	ammonium nitrate	NH_4NO_3	15.33
3	oxygen	O_2	42.38	16	vinyl chloride	$\text{CH}_2=\text{CHCl}$	13.23
4	ethylene	$\text{H}_2\text{C}=\text{CH}_2$	40.41	17	benzene	C_6H_6	12.01
5	ammonia	NH_3	35.95	18	ethylbenzene	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$ 	10.99
6	calcium oxide (lime)	CaO	34.72	19	carbon dioxide	CO_2	10.91
7	phosphoric acid	H_3PO_4	25.36	20	methyl t-butyl ether	$\text{CH}_3\text{OC}(\text{CH}_3)_3$ 	10.86
8	sodium hydroxide	NaOH	24.02	21	styrene	$\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$ 	8.94
9	propylene (propene)	$\text{CH}_3\text{CH}=\text{CH}_2$	22.60	22	methanol	CH_3OH	8.73
10	chlorine	Cl_2	22.28	23	formaldehyde	$\text{H}_2\text{C}=\text{O}$ 	6.98
11	sodium carbonate	Na_2CO_3	20.89	24	xylenes (mixture)†	$(\text{CH}_3)_2\text{C}_6\text{H}_4$ 	6.38
12	urea	$(\text{NH}_2)_2\text{C}=\text{O}$ 	16.84	25	toluene	$\text{C}_6\text{H}_5\text{CH}_3$	6.03
13	nitric acid	HNO_3	16.08				

*Nonlinear structures not previously introduced are shown with their respective formulas.

†The squiggly line indicates that the second —CH_3 group can be attached to any of the other positions of the ring.

According to Figure 2.22 "Top 25 Chemicals Produced in the United States in 2002*", 11 of the top 15 compounds produced in the United States are inorganic, and the total mass of inorganic chemicals produced is almost twice the mass of organic chemicals. Yet the diversity of organic compounds used in industry is such that over half of the top 25 compounds (13 out of 25) are organic.

Why are such huge quantities of chemical compounds produced annually? They are used both directly as components of compounds and materials that we encounter on an almost daily basis and indirectly in the production of those compounds and materials. The single largest use of industrial chemicals is in the production of foods: 7 of the top 15

chemicals are either fertilizers (ammonia, urea, and ammonium nitrate) or used primarily in the production of fertilizers (sulfuric acid, nitric acid, nitrogen, and phosphoric acid). Many of the organic chemicals on the list are used primarily as ingredients in the plastics and related materials that are so prevalent in contemporary society. Ethylene and propylene, for example, are used to produce polyethylene and polypropylene, which are made into plastic milk bottles, sandwich bags, indoor-outdoor carpets, and other common items. Vinyl chloride, in the form of polyvinylchloride, is used in everything from pipes to floor tiles to trash bags. Though not listed in Figure 2.22 "Top 25 Chemicals Produced in the United States in 2002*", butadiene and carbon black are used in the manufacture of synthetic rubber for tires, and phenol and formaldehyde are ingredients in plywood, fiberglass, and many hard plastic items.

We do not have the space in this text to consider the applications of all these compounds in any detail, but we will return to many of them after we have developed the concepts necessary to understand their underlying chemistry. Instead, we conclude this chapter with a brief discussion of petroleum refining as it relates to gasoline and octane ratings and a look at the production and use of the topmost industrial chemical, sulfuric acid.

Petroleum

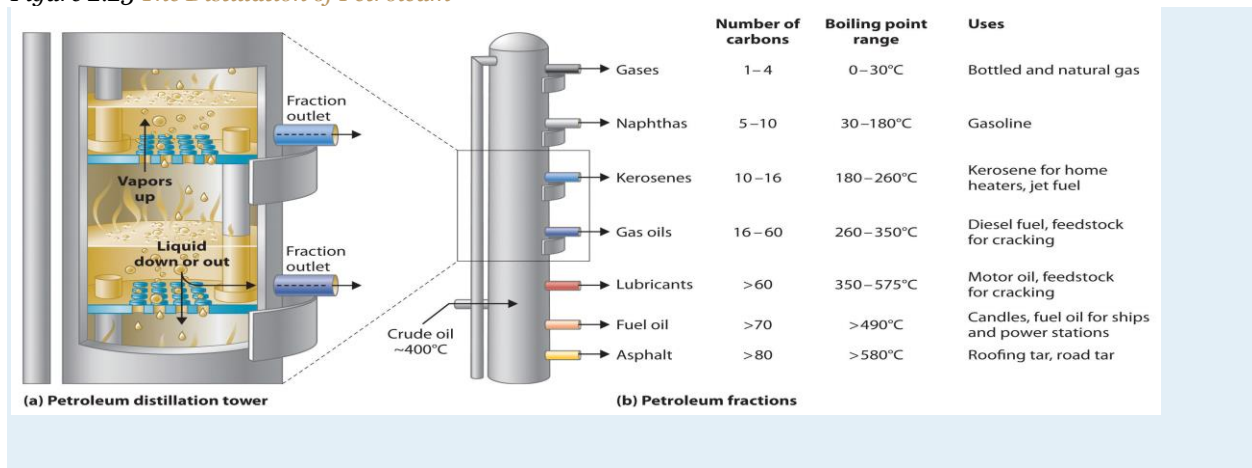
The petroleum that is pumped out of the ground at locations around the world is a complex mixture of several thousand organic compounds, including straight-chain alkanes, cycloalkanes, alkenes, and aromatic hydrocarbons with four to several hundred carbon atoms. The identities and relative abundances of the components vary depending on the source. So Texas crude oil is somewhat different from Saudi Arabian crude oil. In fact, the analysis of petroleum from different deposits can produce a "fingerprint" of each, which is useful in tracking down the sources of spilled crude oil. For example, Texas crude oil is "sweet," meaning that it contains a small amount of sulfur-containing molecules, whereas Saudi Arabian crude oil is "sour," meaning that it contains a relatively large amount of sulfur-containing molecules.

Gasoline

Petroleum is converted to useful products such as gasoline in three steps: distillation, cracking, and reforming. Recall from Chapter 1 "Introduction to Chemistry" that distillation separates compounds on the basis of their relative volatility, which is usually inversely proportional to their boiling points. Part (a) in Figure 2.23 "The Distillation of Petroleum" shows a cutaway drawing of a column used in the petroleum industry for separating the components of crude oil. The petroleum is heated to approximately

400°C (750°F), at which temperature it has become a mixture of liquid and vapor. This mixture, called the *feedstock*, is introduced into the refining tower. The most volatile components (those with the lowest boiling points) condense at the top of the column where it is cooler, while the less volatile components condense nearer the bottom. Some materials are so nonvolatile that they collect at the bottom without evaporating at all. Thus the composition of the liquid condensing at each level is different. These different fractions, each of which usually consists of a mixture of compounds with similar numbers of carbon atoms, are drawn off separately. Part (b) in Figure 2.23 "The Distillation of Petroleum" shows the typical fractions collected at refineries, the number of carbon atoms they contain, their boiling points, and their ultimate uses. These products range from gases used in natural and bottled gas to liquids used in fuels and lubricants to gummy solids used as tar on roads and roofs.

Figure 2.23 The Distillation of Petroleum



(a) This is a diagram of a distillation column used for separating petroleum fractions. (b) Petroleum fractions condense at different temperatures, depending on the number of carbon atoms in the molecules, and are drawn off from the column. The most volatile components (those with the lowest boiling points) condense at the top of the column, and the least volatile (those with the highest boiling points) condense at the bottom.

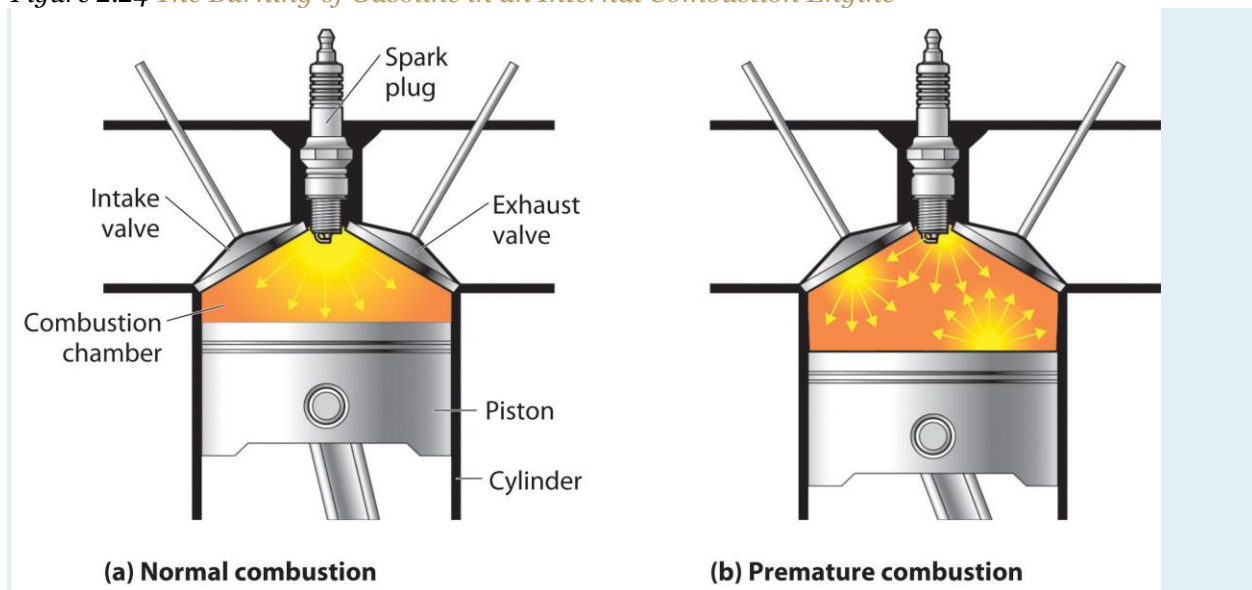
The economics of petroleum refining are complex. For example, the market demand for kerosene and lubricants is much lower than the demand for gasoline, yet all three fractions are obtained from the distillation column in comparable amounts. Furthermore, most gasolines and jet fuels are blends with very carefully controlled compositions that cannot vary as their original feedstocks did. To make petroleum refining more profitable, the less volatile, lower-value fractions must be converted to more volatile, higher-value mixtures that have carefully controlled formulas. The first process used to

accomplish this transformation is cracking, in which the larger and heavier hydrocarbons in the kerosene and higher-boiling-point fractions are heated to temperatures as high as 900°C. High-temperature reactions cause the carbon–carbon bonds to break, which converts the compounds to lighter molecules similar to those in the gasoline fraction. Thus in cracking, a straight-chain alkane with a number of carbon atoms corresponding to the kerosene fraction is converted to a mixture of hydrocarbons with a number of carbon atoms corresponding to the lighter gasoline fraction. The second process used to increase the amount of valuable products is called reforming; it is the chemical conversion of straight-chain alkanes to either branched-chain alkanes or mixtures of aromatic hydrocarbons. Using metals such as platinum brings about the necessary chemical reactions. The mixtures of products obtained from cracking and reforming are separated by fractional distillation.

Octane Ratings

The quality of a fuel is indicated by its octane rating, which is a measure of its ability to burn in a combustion engine without knocking or pinging. Knocking and pinging signal premature combustion (Figure 2.24 "The Burning of Gasoline in an Internal Combustion Engine"), which can be caused either by an engine malfunction or by a fuel that burns too fast. In either case, the gasoline-air mixture detonates at the wrong point in the engine cycle, which reduces the power output and can damage valves, pistons, bearings, and other engine components. The various gasoline formulations are designed to provide the mix of hydrocarbons least likely to cause knocking or pinging in a given type of engine performing at a particular level.

Figure 2.24 *The Burning of Gasoline in an Internal Combustion Engine*



(a) Normally, fuel is ignited by the spark plug, and combustion spreads uniformly outward. (b) Gasoline with an octane rating that is too low for the engine can ignite prematurely, resulting in uneven burning that causes knocking and pinging.

The octane scale was established in 1927 using a standard test engine and two pure compounds: *n*-heptane and isooctane (2,2,4-trimethylpentane). *n*-Heptane, which causes a great deal of knocking on combustion, was assigned an octane rating of 0, whereas isooctane, a very smooth-burning fuel, was assigned an octane rating of 100. Chemists assign octane ratings to different blends of gasoline by burning a sample of each in a test engine and comparing the observed knocking with the amount of knocking caused by specific mixtures of *n*-heptane and isooctane. For example, the octane rating of a blend of 89% isooctane and 11% *n*-heptane is simply the average of the octane ratings of the components weighted by the relative amounts of each in the blend. Converting percentages to decimals, we obtain the octane rating of the mixture:

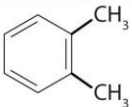
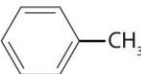
$$0.89(100) + 0.11(0) = 89$$

A gasoline that performs at the same level as a blend of 89% isooctane and 11% *n*-heptane is assigned an octane rating of 89; this represents an intermediate grade of gasoline. Regular gasoline typically has an octane rating of 87; premium has a rating of 93 or higher.

As shown in Figure 2.25 "The Octane Ratings of Some Hydrocarbons and Common Additives", many compounds that are now available have octane ratings greater than 100, which means they are better fuels than pure isooctane. In addition, antiknock agents, also called octane enhancers, have been developed. One of the most widely used for many

years was tetraethyllead $[(C_2H_5)_4Pb]$, which at approximately 3 g/gal gives a 10–15-point increase in octane rating. Since 1975, however, lead compounds have been phased out as gasoline additives because they are highly toxic. Other enhancers, such as methyl *t*-butyl ether (MTBE), have been developed to take their place. They combine a high octane rating with minimal corrosion to engine and fuel system parts. Unfortunately, when gasoline containing MTBE leaks from underground storage tanks, the result has been contamination of the groundwater in some locations, resulting in limitations or outright bans on the use of MTBE in certain areas. As a result, the use of alternative octane enhancers such as ethanol, which can be obtained from renewable resources such as corn, sugar cane, and, eventually, corn stalks and grasses, is increasing.

Figure 2.25 *The Octane Ratings of Some Hydrocarbons and Common Additives*

Name	Condensed Structural Formula	Octane Rating	Name	Condensed Structural Formula	Octane Rating
<i>n</i> -heptane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	0	<i>o</i> -xylene		107
<i>n</i> -hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$	25	ethanol	CH_3CH_2OH	108
<i>n</i> -pentane	$CH_3CH_2CH_2CH_2CH_3$	62	<i>t</i> -butyl alcohol	$(CH_3)_3COH$	113
isooctane	$(CH_3)_3CCH_2CH(CH_3)_2$	100	<i>p</i> -xylene		116
benzene		106	methyl <i>t</i> -butyl ether	$H_3COC(CH_3)_3$	116
methanol	CH_3OH	107	toluene		118

EXAMPLE 12

You have a crude (i.e., unprocessed or *straight-run*) petroleum distillate consisting of 10% *n*-heptane, 10% *n*-hexane, and 80% *n*-pentane by mass, with an octane rating of 52. What percentage of MTBE by mass would you need to increase the octane rating of the distillate to that of regular-grade gasoline (a rating of 87), assuming that the octane rating is directly proportional to the amounts of the compounds present? Use the information presented in Figure 2.25 "The Octane Ratings of Some Hydrocarbons and Common Additives".

Given: composition of petroleum distillate, initial octane rating, and final octane rating

Asked for: percentage of MTBE by mass in final mixture

Strategy:

A Define the unknown as the percentage of MTBE in the final mixture. Then subtract this unknown from 100% to obtain the percentage of petroleum distillate.

B Multiply the percentage of MTBE and the percentage of petroleum distillate by their respective octane ratings; add these values to obtain the overall octane rating of the new mixture.

C Solve for the unknown to obtain the percentage of MTBE needed.

Solution:

A The question asks what percentage of MTBE will give an overall octane rating of 87 when mixed with the straight-run fraction. From Figure 2.25 "The Octane Ratings of Some Hydrocarbons and Common Additives", the octane rating of MTBE is 116. Let x be the percentage of MTBE, and let $100 - x$ be the percentage of petroleum distillate.

B Multiplying the percentage of each component by its respective octane rating and setting the sum equal to the desired octane rating of the mixture (87) times 100 gives

$$\text{final octane rating of mixture} = 87 (100) = 52 (100 - x) + 116 x = 5200 - 52 x + 116 x = 5200 + 64 x$$

C Solving the equation gives $x = 55\%$. Thus the final mixture must contain 55% MTBE by mass.

To obtain a composition of 55% MTBE by mass, you would have to add more than an equal mass of MTBE (actually 0.55/0.45, or 1.2 times) to the straight-run fraction. This is 1.2 tons of MTBE per ton of straight-run gasoline, which would be prohibitively expensive. Thus there are sound economic reasons for reforming the kerosene fractions to produce toluene and other aromatic compounds, which have high octane ratings and are much cheaper than MTBE.

Exercise

As shown in Figure 2.25 "The Octane Ratings of Some Hydrocarbons and Common Additives", toluene is one of the fuels suitable for use in automobile engines. How much toluene would have to be added to a blend of the petroleum fraction in this example containing 15% MTBE by mass to increase the octane rating to that of premium gasoline (93)?

Answer: The final blend is 56% toluene by mass, which requires a ratio of 56/44, or 1.3 tons of toluene per ton of blend.

Sulfuric Acid

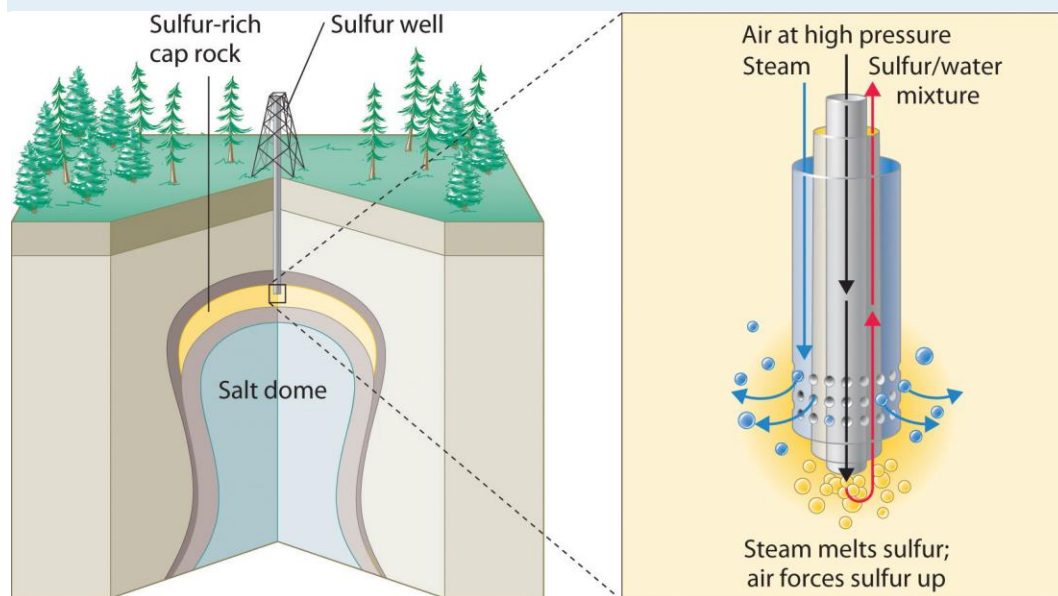
Sulfuric acid is one of the oldest chemical compounds known. It was probably first prepared by alchemists who burned sulfate salts such as $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, called green vitriol from its color and glassy appearance

(from the Latin *vitrum*, meaning “glass”). Because pure sulfuric acid was found to be useful for dyeing textiles, enterprising individuals looked for ways to improve its production. By the mid-18th century, sulfuric acid was being produced in multiton quantities by the *lead-chamber process*, which was invented by John Roebuck in 1746. In this process, sulfur was burned in a large room lined with lead, and the resulting fumes were absorbed in water.

Production

The production of sulfuric acid today is likely to start with elemental sulfur obtained through an ingenious technique called the *Frasch process*, which takes advantage of the low melting point of elemental sulfur (115.2°C). Large deposits of elemental sulfur are found in porous limestone rocks in the same geological formations that often contain petroleum. In the Frasch process, water at high temperature (160°C) and high pressure is pumped underground to melt the sulfur, and compressed air is used to force the liquid sulfur-water mixture to the surface (Figure 2.26 "Extraction of Elemental Sulfur from Underground Deposits"). The material that emerges from the ground is more than 99% pure sulfur. After it solidifies, it is pulverized and shipped in railroad cars to the plants that produce sulfuric acid, as shown here.

Figure 2.26 *Extraction of Elemental Sulfur from Underground Deposits*



In the Frasch process for extracting sulfur, very hot water at high pressure is injected into the sulfur-containing rock layer to melt the sulfur. The resulting mixture of liquid sulfur and hot water is forced up to the surface by compressed air.

An increasing number of sulfuric acid manufacturers have begun to use sulfur dioxide (SO_2) as a starting material instead of elemental sulfur. Sulfur dioxide is recovered from the burning of oil and gas, which contain small amounts of sulfur compounds. When not recovered, SO_2 is released into the atmosphere, where it is converted to an environmentally hazardous form that leads to *acid rain* (Chapter 4 "Reactions in Aqueous Solution").

If sulfur is the starting material, the first step in the production of sulfuric acid is the combustion of sulfur with oxygen to produce SO_2 . Next, SO_2 is converted to SO_3 by the *contact process*, in which SO_2 and O_2 react in the presence of V_2O_5 to achieve about 97% conversion to SO_3 . The SO_3 can then be treated with a small amount of water to produce sulfuric acid. Usually, however, the SO_3 is absorbed in concentrated sulfuric acid to produce *oleum*, a more potent form called *fuming sulfuric acid*. Because of its high SO_3 content (approximately 99% by mass), oleum is cheaper to ship than concentrated sulfuric acid. At the point of use, the oleum is diluted with water to give concentrated sulfuric acid (*very carefully* because dilution generates enormous amounts of heat). Because SO_2 is a pollutant, the small amounts of unconverted SO_2 are recovered and recycled to minimize the amount released into the air.

Uses

Two-thirds of the sulfuric acid produced in the United States is used to make fertilizers, most of which contain nitrogen, phosphorus, and potassium (in a form called *potash*). In earlier days, phosphate-containing rocks were simply ground up and spread on fields as fertilizer, but the extreme insolubility of many salts that contain the phosphate ion (PO_4^{3-}) limits the availability of phosphorus from these sources. Sulfuric acid serves as a source of protons (H^+ ions) that react with phosphate minerals to produce more soluble salts containing HPO_4^{2-} or H_2PO_4^- as the anion, which are much more readily taken up by plants. In this context, sulfuric acid is used in two principal ways: (1) the phosphate rocks are treated with concentrated sulfuric acid to produce "superphosphate," a mixture of 32% CaHPO_4 and $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, 50% $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, approximately 3% absorbed phosphoric acid, and other nutrients; and (2) sulfuric acid is used to produce phosphoric acid (H_3PO_4), which can then be used to convert phosphate rocks to "triple superphosphate," which is largely $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$.

Sulfuric acid is also used to produce potash, one of the other major ingredients in fertilizers. The name *potash* originally referred to potassium carbonate (obtained by boiling wood *ashes* with water in iron *pots*), but today it also refers to compounds such as potassium hydroxide (KOH) and potassium oxide

(K₂O). The usual source of potassium in fertilizers is actually potassium sulfate (K₂SO₄), which is produced by several routes, including the reaction of concentrated sulfuric acid with solid potassium chloride (KCl), which is obtained as the pure salt from mineral deposits.

Summary

Many chemical compounds are prepared industrially in huge quantities and used to produce foods, fuels, plastics, and other such materials. Petroleum refining takes a complex mixture of naturally occurring hydrocarbons as a feedstock and, through a series of steps involving distillation, **cracking**, and **reforming**, converts them to mixtures of simpler organic compounds with desirable properties. A major use of petroleum is in the production of motor fuels such as gasoline. The performance of such fuels in engines is described by their **octane rating**, which depends on the identity of the compounds present and their relative abundance in the blend.

Sulfuric acid is the compound produced in the largest quantity in the industrial world. Much of the sulfur used in the production of sulfuric acid is obtained via the Frasch process, in which very hot water forces liquid sulfur out of the ground in nearly pure form. Sulfuric acid is produced by the reaction of sulfur dioxide with oxygen in the presence of vanadium(V) oxide (the contact process), followed by absorption of the sulfur trioxide in concentrated sulfuric acid to produce oleum. Most sulfuric acid is used to prepare fertilizers.

KEY TAKEAWAY

- Many chemical compounds are prepared industrially in huge quantities to prepare the materials we need and use in our daily lives.

CONCEPTUAL PROBLEMS

1. Describe the processes used for converting crude oil to transportation fuels.
2. If your automobile engine is knocking, is the octane rating of your gasoline too low or too high? Explain your answer.
3. Tetraethyllead is no longer used as a fuel additive to prevent knocking. Instead, fuel is now marketed as “unleaded.” Why is tetraethyllead no longer used?
4. If you were to try to extract sulfur from an underground source, what process would you use? Describe briefly the essential features of this process.
5. Why are phosphate-containing minerals used in fertilizers treated with sulfuric acid?

ANSWER

1. Phosphate salts contain the highly-charged PO_4^{3-} ion, salts of which are often insoluble. Protonation of the PO_4^{3-} ion by strong acids such as H_2SO_4 leads to the formation of the HPO_4^{2-} and H_2PO_4^- ions. Because of their decreased negative charge, salts containing these anions are usually much more soluble, allowing the anions to be readily taken up by plants when they are applied as fertilizer.

NUMERICAL PROBLEM

1. In Example 12, the crude petroleum had an overall octane rating of 52. What is the composition of a solution of MTBE and *n*-heptane that has this octane rating?

2.7 End-of-Chapter Material

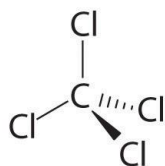
APPLICATION PROBLEMS

Problems marked with a ♦ involve multiple concepts.

1. Carbon tetrachloride (CCl_4) was used as a dry cleaning solvent until it was found to cause liver cancer. Based on the structure of chloroform given in Section 2.1 "Chemical Compounds", draw the structure of carbon tetrachloride.
2. Ammonium nitrate and ammonium sulfate are used in fertilizers as a source of nitrogen. The ammonium cation is tetrahedral. Refer to Section 2.1 "Chemical Compounds" to draw the structure of the ammonium ion.
3. The white light in fireworks displays is produced by burning magnesium in air, which contains oxygen. What compound is formed?
4. Sodium hydrogen sulfite, which is used for bleaching and swelling leather and to preserve flavor in almost all commercial wines, is made from sulfur dioxide. What are the formulas for these two sulfur-containing compounds?
5. Carbonic acid is used in carbonated drinks. When combined with lithium hydroxide, it produces lithium carbonate, a compound used to increase the brightness of pottery glazes and as a primary treatment for depression and bipolar disorder. Write the formula for both of these carbon-containing compounds.
6. Vinegar is a dilute solution of acetic acid, an organic acid, in water. What grouping of atoms would you expect to find in the structural formula for acetic acid?

7. ♦ Sodamide, or sodium amide, is prepared from sodium metal and gaseous ammonia. Sodamide contains the amide ion (NH_2^-), which reacts with water to form the hydroxide anion by removing an H^+ ion from water. Sodium amide is also used to prepare sodium cyanide.
- Write the formula for each of these sodium-containing compounds.
 - What are the products of the reaction of sodamide with water?
8. A mixture of isooctane, *n*-pentane, and *n*-heptane is known to have an octane rating of 87. Use the data in Figure 2.25 "The Octane Ratings of Some Hydrocarbons and Common Additives" to calculate how much isooctane and *n*-heptane are present if the mixture is known to contain 30% *n*-pentane.
9. A crude petroleum distillate consists of 60% *n*-pentane, 25% methanol, and the remainder *n*-hexane by mass (Figure 2.25 "The Octane Ratings of Some Hydrocarbons and Common Additives").
- What is the octane rating?
 - How much MTBE would have to be added to increase the octane rating to 93?
10. Premium gasoline sold in much of the central United States has an octane rating of 93 and contains 10% ethanol. What is the octane rating of the gasoline fraction before ethanol is added? (See Figure 2.25 "The Octane Ratings of Some Hydrocarbons and Common Additives".)

ANSWERS



1.

3. MgO , magnesium oxide

5. Carbonic acid is H_2CO_3 ; lithium carbonate is Li_2CO_3 .

7.

a. Sodamide is NaNH_2 , and sodium cyanide is NaCN .

b. Sodium hydroxide (NaOH) and ammonia (NH_3).

9.

a. 68

b. 52 g of MTBE must be added to 48 g of the crude distillate.

Chapter 3

Chemical Reactions

Chapter 2 "Molecules, Ions, and Chemical Formulas" introduced you to a wide variety of chemical compounds, many of which have interesting applications. For example, nitrous oxide, a mild anesthetic, is also used as the propellant in cans of whipped cream, while copper(I) oxide is used as both a red glaze for ceramics and in antifouling bottom paints for boats. In addition to the physical properties of substances, chemists are also interested in their chemical reactions, processes in which a substance is converted to one or more other substances with different compositions and properties. Our very existence depends on chemical reactions, such as those between oxygen in the air we breathe and nutrient molecules in the foods we eat. Other reactions cook those foods, heat our homes, and provide the energy to run our cars. Many of the materials and pharmaceuticals that we take for granted today, such as silicon nitride for the sharp edge of cutting tools and antibiotics such as amoxicillin, were unknown only a few years ago. Their development required that chemists understand how substances combine in certain ratios and under specific conditions to produce a new substance with particular properties.

Sodium. *The fourth most abundant alkali metal on Earth, sodium is a highly reactive element that is never found free in nature. When heated to 250°C, it bursts into flames if exposed to air.*

We begin this chapter by describing the relationship between the mass of a sample of a substance and its composition. We then develop methods for determining the quantities of compounds produced or consumed in chemical reactions, and we describe some fundamental types of chemical reactions. By applying the concepts and skills introduced in this chapter, you will be able to explain what happens to the sugar in a candy bar you eat, what reaction occurs in a battery when you start your car, what may be causing the "ozone hole" over Antarctica, and how we might prevent the hole's growth.

3.1 The Mole and Molar Masses

LEARNING OBJECTIVE

1. To calculate the molecular mass of a covalent compound and the formula mass of an ionic compound and to calculate the number of atoms, molecules, or formula units in a sample of a substance.

As you learned in Chapter 1 "Introduction to Chemistry", the **mass number** is the sum of the numbers of protons and neutrons present in the nucleus of an atom. The mass number is an integer that is approximately equal to the numerical value of the atomic mass. Although the mass number is unitless, it is assigned units called **atomic mass units (amu)**. Because a molecule or a polyatomic ion is an assembly of atoms whose identities are given in its molecular or ionic formula, we can calculate the average atomic mass of any molecule or polyatomic ion from its composition by adding together the masses of the constituent atoms. The average mass of a monatomic ion is the same as the average mass of an atom of the element because the mass of electrons is so small that it is insignificant in most calculations.

Molecular and Formula Masses

The molecular mass of a substance is the sum of the average masses of the atoms in one molecule of a substance. It is calculated by adding together the atomic masses of the elements in the substance, each multiplied by its subscript (written or implied) in the molecular formula. Because the units of atomic mass are atomic mass units, the units of molecular mass are also atomic mass units. The procedure for calculating molecular masses is illustrated in Example 1.

EXAMPLE 1

Calculate the molecular mass of ethanol, whose condensed structural formula is $\text{CH}_3\text{CH}_2\text{OH}$. Among its many uses, ethanol is a fuel for internal combustion engines.

Given: molecule

Asked for: molecular mass

Strategy:

A Determine the number of atoms of each element in the molecule.

B Obtain the atomic masses of each element from the periodic table and multiply the atomic mass of each element by the number of atoms of that element.

C Add together the masses to give the molecular mass.

Solution:

A The molecular formula of ethanol may be written in three different ways: $\text{CH}_3\text{CH}_2\text{OH}$ (which illustrates the presence of an ethyl group, CH_3CH_2- , and an $-\text{OH}$ group), $\text{C}_2\text{H}_5\text{OH}$, and $\text{C}_2\text{H}_6\text{O}$; all show that ethanol has two carbon atoms, six hydrogen atoms, and one oxygen atom.

B Taking the atomic masses from the periodic table, we obtain

$2 \times \text{atomic mass of carbon} = 2 \text{ atoms } (12.011 \text{ amu/atom}) = 24.022 \text{ amu}$
 $6 \times \text{atomic mass of hydrogen} = 6 \text{ atoms } (1.0079 \text{ amu/atom}) = 6.0474 \text{ amu}$
 $1 \times \text{atomic mass of oxygen} = 1 \text{ atom } (15.9994 \text{ amu/atom}) = 15.9994 \text{ amu}$

C Adding together the masses gives the molecular mass:

$24.022 \text{ amu} + 6.0474 \text{ amu} + 15.9994 \text{ amu} = 46.069 \text{ amu}$

Alternatively, we could have used unit conversions to reach the result in one step, as described in Essential

Skills 2 (Section 3.7 "Essential Skills 2"):

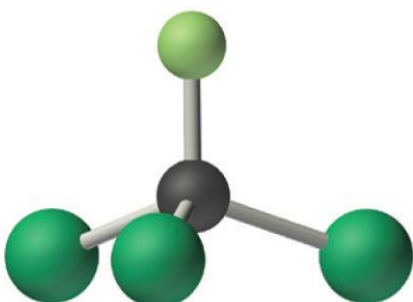
$[2 \text{ atoms C } (12.011 \text{ amu/atom})] + [6 \text{ atoms H } (1.0079 \text{ amu/atom})] + [1 \text{ atoms O } (15.9994 \text{ amu/atom})] = 46.069 \text{ amu}$

The same calculation can also be done in a tabular format, which is especially helpful for more complex molecules:

$2\text{C } (2 \text{ atoms})(12.011 \text{ amu/atom}) = 24.022 \text{ amu}$
 $6\text{H } (6 \text{ atoms})(1.0079 \text{ amu/atom}) = 6.0474 \text{ amu}$
 $1\text{O } (1 \text{ atom})(15.9994 \text{ amu/atom}) = 15.9994 \text{ amu}$
 $\text{C}_2\text{H}_6\text{O molecular mass of ethanol} = 46.069 \text{ amu}$

Exercise

Calculate the molecular mass of trichlorofluoromethane, also known as Freon-11, whose condensed structural formula is CCl_3F . Until recently, it was used as a refrigerant. The structure of a molecule of Freon-11 is as follows:



Freon-11, CCl_3F

Answer: 137.368 amu

Unlike molecules, which have covalent bonds, ionic compounds do not have a readily identifiable molecular unit. So for ionic compounds we use the *formula mass* (also called the empirical formula mass) of the compound rather than the molecular mass. The formula mass is the sum of the atomic masses of all the elements in the empirical formula, each multiplied by its subscript (written or implied). It is directly analogous to the molecular mass of a covalent compound. Once again, the units are atomic mass units.

Note the Pattern

Atomic mass, molecular mass, and formula mass all have the same units: atomic mass units.

EXAMPLE 2

Calculate the formula mass of $\text{Ca}_3(\text{PO}_4)_2$, commonly called calcium phosphate. This compound is the principal source of calcium found in bovine milk.

Given: ionic compound

Asked for: formula mass

Strategy:

A Determine the number of atoms of each element in the empirical formula.

B Obtain the atomic masses of each element from the periodic table and multiply the atomic mass of each element by the number of atoms of that element.

C Add together the masses to give the formula mass.

Solution:

A The empirical formula— $\text{Ca}_3(\text{PO}_4)_2$ —indicates that the simplest electrically neutral unit of calcium phosphate contains three Ca^{2+} ions and two PO_4^{3-} ions. The formula mass of this molecular unit is calculated by adding together the atomic masses of three calcium atoms, two phosphorus atoms, and eight oxygen atoms.

B Taking atomic masses from the periodic table, we obtain

$3 \times \text{atomic mass of calcium} = 3 \text{ atoms } (40.078 \text{ amu/atom}) = 120.234 \text{ amu}$
 $2 \times \text{atomic mass of phosphorus} = 2 \text{ atoms } (30.973761 \text{ amu/atom}) = 61.947522 \text{ amu}$
 $8 \times \text{atomic mass of oxygen} = 8 \text{ atoms } (15.9994 \text{ amu/atom}) = 127.9952 \text{ amu}$

C Adding together the masses gives the formula mass of $\text{Ca}_3(\text{PO}_4)_2$:

$120.234 \text{ amu} + 61.947522 \text{ amu} + 127.9952 \text{ amu} = 310.177 \text{ amu}$

We could also find the formula mass of $\text{Ca}_3(\text{PO}_4)_2$ in one step by using unit conversions or a tabular format:

$[3 \text{ atoms Ca } (40.078 \text{ amu/atom})] + [2 \text{ atoms P } (30.973761 \text{ amu/atom})] + [8 \text{ atoms O } (15.9994 \text{ amu/atom})] = 310.177 \text{ amu}$
 $3\text{Ca } (3 \text{ atoms})(40.078 \text{ amu/atom}) = 120.234 \text{ amu}$
 $2\text{P } (2 \text{ atoms})(30.973761 \text{ amu/atom}) = 61.947522 \text{ amu}$
 $+ 8\text{O } (8 \text{ atoms})(15.9994 \text{ amu/atom}) = 127.9952 \text{ amu}$
 $\text{mu Ca } 3 \text{ P } 2 \text{ O } 8 \text{ formula mass of Ca } 3 (\text{PO } 4) 2 = 310.177 \text{ amu}$

Exercise

Calculate the formula mass of Si_3N_4 , commonly called silicon nitride. It is an extremely hard and inert material that is used to make cutting tools for machining hard metal alloys.

Answer: 140.29 amu

The Mole

In Chapter 1 "Introduction to Chemistry", we described Dalton's theory that each chemical compound has a particular combination of atoms and that the ratios of the *numbers* of atoms of the elements present are

usually small whole numbers. We also described the **law of multiple proportions**, which states that the ratios of the masses of elements that form a series of compounds are small whole numbers. The problem for Dalton and other early chemists was to discover the quantitative relationship between the number of atoms in a chemical substance and its mass. Because the masses of individual atoms are so minuscule (on the order of 10^{-23}g/atom), chemists do not measure the mass of individual atoms or molecules. In the laboratory, for example, the masses of compounds and elements used by chemists typically range from milligrams to grams, while in industry, chemicals are bought and sold in kilograms and tons. To analyze the transformations that occur between individual atoms or molecules in a chemical reaction, it is therefore absolutely essential for chemists to know how many atoms or molecules are contained in a measurable quantity in the laboratory—a given mass of sample. The unit that provides this link is the mole (mol), from the Latin *moles*, meaning “pile” or “heap” (*not* from the small subterranean animal!).

Many familiar items are sold in numerical quantities that have unusual names. For example, cans of soda come in a six-pack, eggs are sold by the dozen (12), and pencils often come in a gross (12 dozen, or 144). Sheets of printer paper are packaged in reams of 500, a seemingly large number. Atoms are so small, however, that even 500 atoms are too small to see or measure by most common techniques. Any readily measurable mass of an element or compound contains an extraordinarily large number of atoms, molecules, or ions, so an extraordinarily large numerical unit is needed to count them. The mole is used for this purpose.

A **mole** is defined as the amount of a substance that contains the number of carbon atoms in exactly 12 g of isotopically pure carbon-12. According to the most recent experimental measurements, this mass of carbon-12 contains 6.022142×10^{23} atoms, but for most purposes 6.022×10^{23} provides an adequate number of significant figures. Just as 1 mol of atoms contains 6.022×10^{23} atoms, 1 mol of eggs contains 6.022×10^{23} eggs. The number in a mole is called Avogadro’s number, after the 19th-century Italian scientist who first proposed a relationship between the volumes of gases and the numbers of particles they contain.

It is not obvious why eggs come in dozens rather than 10s or 14s, or why a ream of paper contains 500 sheets rather than 400 or 600. The definition of a mole—that is, the decision to base it on 12 g of carbon-

12—is also arbitrary. The important point is that *1 mol of carbon—or of anything else, whether atoms, compact discs, or houses—always has the same number of objects: 6.022×10^{23} .*

Note the Pattern

One mole always has the same number of objects: 6.022×10^{23} .

To appreciate the magnitude of Avogadro's number, consider a mole of pennies. Stacked vertically, a mole of pennies would be 4.5×10^{17} mi high, or almost six times the diameter of the Milky Way galaxy. If a mole of pennies were distributed equally among the entire population on Earth, each person would get more than one trillion dollars. Clearly, the mole is so large that it is useful only for measuring very small objects, such as atoms.

The concept of the mole allows us to count a specific number of individual atoms and molecules by weighing measurable quantities of elements and compounds. To obtain 1 mol of carbon-12 atoms, we would weigh out 12 g of isotopically pure carbon-12. Because each element has a different atomic mass, however, a mole of each element has a different mass, even though it contains the same number of atoms (6.022×10^{23}). This is analogous to the fact that a dozen extra large eggs weighs more than a dozen small eggs, or that the total weight of 50 adult humans is greater than the total weight of 50 children. Because of the way in which the mole is defined, for every element the number of grams in a mole is the same as the number of atomic mass units in the atomic mass of the element. For example, the mass of 1 mol of magnesium (atomic mass = 24.305 amu) is 24.305 g. Because the atomic mass of magnesium (24.305 amu) is slightly more than twice that of a carbon-12 atom (12 amu), the mass of 1 mol of magnesium atoms (24.305 g) is slightly more than twice that of 1 mol of carbon-12 (12 g). Similarly, the mass of 1 mol of helium (atomic mass = 4.002602 amu) is 4.002602 g, which is about one-third that of 1 mol of carbon-12. Using the concept of the mole, we can now restate Dalton's theory: *1 mol of a compound is formed by combining elements in amounts whose mole ratios are small whole numbers.* For example, 1 mol of water (H₂O) has 2 mol of hydrogen atoms and 1 mol of oxygen atoms.

Molar Mass

The molar mass of a substance is defined as the mass in grams of 1 mol of that substance. One mole of isotopically pure carbon-12 has a mass of 12 g. For an element, the molar mass is the mass of 1 mol of atoms of that element; for a covalent molecular compound, it is the mass of 1 mol of molecules of that compound; for an ionic compound, it is the mass of 1 mol of formula units. That is, the molar mass of a

substance is the mass (in grams per mole) of 6.022×10^{23} atoms, molecules, or formula units of that substance. In each case, the number of grams in 1 mol is the same as the number of atomic mass units that describe the atomic mass, the molecular mass, or the formula mass, respectively.

Note the Pattern

The molar mass of any substance is its atomic mass, molecular mass, or formula mass in grams per mole.

The periodic table lists the atomic mass of carbon as 12.011 amu; the average molar mass of carbon—the mass of 6.022×10^{23} carbon atoms—is therefore 12.011 g/mol:

Substance (formula)	Atomic, Molecular, or Formula Mass (amu)	Molar Mass (g/mol)
carbon (C)	12.011 (atomic mass)	12.011
ethanol (C ₂ H ₅ OH)	46.069 (molecular mass)	46.069
calcium phosphate [Ca ₃ (PO ₄) ₂]	310.177 (formula mass)	310.177

The molar mass of naturally occurring carbon is different from that of carbon-12 and is not an integer because carbon occurs as a mixture of carbon-12, carbon-13, and carbon-14. One mole of carbon still has 6.022×10^{23} carbon atoms, but 98.89% of those atoms are carbon-12, 1.11% are carbon-13, and a trace (about 1 atom in 10^{12}) are carbon-14. (For more information, see Section 1.6 "Isotopes and Atomic Masses".) Similarly, the molar mass of uranium is 238.03 g/mol, and the molar mass of iodine is 126.90 g/mol. When we deal with elements such as iodine and sulfur, which occur as a diatomic molecule (I₂) and a polyatomic molecule (S₈), respectively, molar mass usually refers to the mass of 1 mol of *atoms* of the element—in this case I and S, *not* to the mass of 1 mol of *molecules* of the element (I₂ and S₈).

The molar mass of ethanol is the mass of ethanol (C₂H₅OH) that contains 6.022×10^{23} ethanol molecules.

As you calculated in Example 1, the molecular mass of ethanol is 46.069 amu. Because 1 mol of ethanol contains 2 mol of carbon atoms (2×12.011 g), 6 mol of hydrogen atoms (6×1.0079 g), and 1 mol of oxygen atoms (1×15.9994 g), its molar mass is 46.069 g/mol. Similarly, the formula mass of calcium phosphate [Ca₃(PO₄)₂] is 310.177 amu, so its molar mass is 310.177 g/mol. This is the mass of calcium phosphate that contains 6.022×10^{23} formula units. Figure 3.1 "Samples of 1 Mol of Some Common Substances" shows samples that contain precisely one molar mass of several common substances

The mole is the basis of quantitative chemistry. It provides chemists with a way to convert easily between the mass of a substance and the number of individual atoms, molecules, or formula units of that substance. Conversely, it enables

chemists to calculate the mass of a substance needed to obtain a desired number of atoms, molecules, or formula units. For example, to convert moles of a substance to mass, we use the relationship

Equation 3.1

$(\text{moles})(\text{molar mass}) \rightarrow \text{mass}$

or, more specifically,

Equation 3.2

$\text{moles (grams mole)} = \text{grams}$

Conversely, to convert the mass of a substance to moles, we use

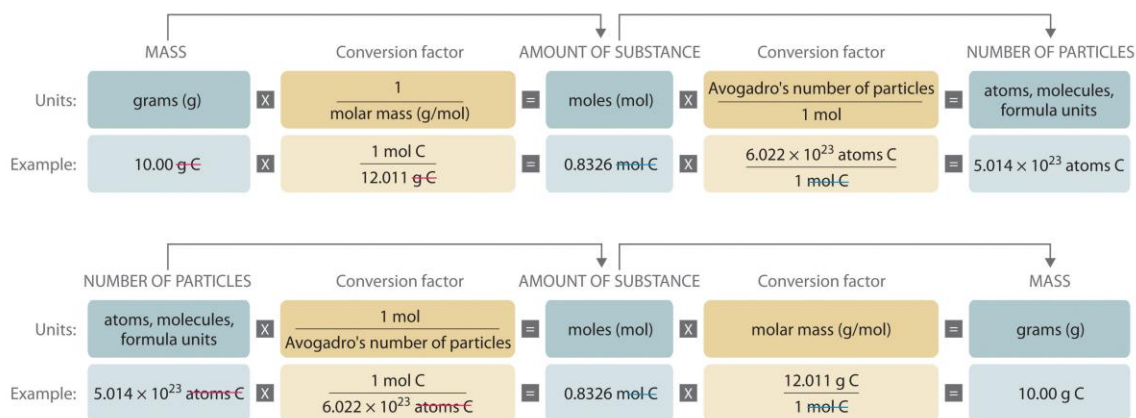
Equation 3.3

$(\text{ mass molar mass }) \rightarrow \text{moles (grams grams/mole)} = \text{grams (mole grams)} = \text{moles}$

Be sure to pay attention to the units when converting between mass and moles.

Figure 3.2 "A Flowchart for Converting between Mass; the Number of Moles; and the Number of Atoms, Molecules, or Formula Units" is a flowchart for converting between mass; the number of moles; and the number of atoms, molecules, or formula units. The use of these conversions is illustrated in Example 3 and Example 4.

Figure 3.2 A Flowchart for Converting between Mass; the Number of Moles; and the Number of Atoms, Molecules, or Formula Units



EXAMPLE 3

For 35.00 g of ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$), which is used in inks for ballpoint pens, calculate the number of

- moles.
- molecules.

Given: mass and molecular formula

Asked for: number of moles and number of molecules

Strategy:

A Use the molecular formula of the compound to calculate its molecular mass in grams per mole.

B Convert from mass to moles by dividing the mass given by the compound's molar mass.

C Convert from moles to molecules by multiplying the number of moles by Avogadro's number.

Solution:

- A** The molecular mass of ethylene glycol can be calculated from its molecular formula using the method illustrated in Example 1:

$2\text{C (2 atoms)}(12.011 \text{ amu/atom}) = 24.022 \text{ amu}$
 $6\text{H (6 atoms)}(1.0079 \text{ amu/atom}) = 6.0474 \text{ amu}$
 $+ 2\text{O (2 atoms)}(15.9994 \text{ amu/atom}) = 31.9988 \text{ amu}$
 $\text{C}_2\text{H}_6\text{O}_2 \text{ molecular mass of ethylene glycol} = 62.068 \text{ amu}$

The molar mass of ethylene glycol is 62.068 g/mol.

- The number of moles of ethylene glycol present in 35.00 g can be calculated by dividing the mass (in grams) by the molar mass (in grams per mole):

mass of ethylene glycol (g) / molar mass (g/mol) = moles ethylene glycol (mol)

So

$35.00 \text{ g ethylene glycol} / (62.068 \text{ g ethylene glycol} / 1 \text{ mol ethylene glycol}) = 0.5639 \text{ mol ethylene glycol}$

It is always a good idea to estimate the answer before you do the actual calculation. In this case, the mass given (35.00 g) is *less* than the molar mass, so the answer should be less than 1 mol. The calculated answer (0.5639 mol) is indeed less than 1 mol, so we have probably not made a major error in the calculations.

b. **C** To calculate the number of molecules in the sample, we multiply the number of moles by Avogadro's number:

molecules of ethylene glycol = $0.5639 \text{ mol} (6.022 \times 10^{23} \text{ molecules} / 1 \text{ mol}) = 3.396 \times 10^{23} \text{ molecules}$

Because we are dealing with slightly more than 0.5 mol of ethylene glycol, we expect the number of molecules present to be slightly more than one-half of Avogadro's number, or slightly more than 3×10^{23} molecules, which is indeed the case.

Exercise

For 75.0 g of CCl_3F (Freon-11), calculate the number of

- a. moles.
- b. molecules.

Answer:

- a. 0.546 mol
- b. 3.29×10^{23} molecules

EXAMPLE 4

Calculate the mass of 1.75 mol of each compound.

- a. S_2Cl_2 (common name: sulfur monochloride; systematic name: disulfur dichloride)
- b. $\text{Ca}(\text{ClO})_2$ (calcium hypochlorite)

Given: number of moles and molecular or empirical formula

Asked for: mass

Strategy:

A Calculate the molecular mass of the compound in grams from its molecular formula (if covalent) or empirical formula (if ionic).

B Convert from moles to mass by multiplying the moles of the compound given by its molar mass.

Solution:

We begin by calculating the molecular mass of S_2Cl_2 and the formula mass of $Ca(ClO)_2$.

A The molar mass of S_2Cl_2 is obtained from its molecular mass as follows:

$$2S (2 \text{ atoms})(32.065 \text{ amu/atom}) = 64.130 \text{ amu} + 2Cl (2 \text{ atoms})(35.453 \text{ amu/atom}) = 70.906 \text{ amu}$$

$$S_2Cl_2 \text{ molecular mass of } S_2Cl_2 = 135.036 \text{ amu}$$

The molar mass of S_2Cl_2 is 135.036 g/mol.

B The mass of 1.75 mol of S_2Cl_2 is calculated as follows:

$$\text{moles } S_2Cl_2 [\text{molar mass (g/mol)}] \rightarrow \text{mass of } S_2Cl_2 (g)$$

$$1.75 \text{ mol } S_2Cl_2 (135.036 \text{ g } S_2Cl_2 / 1 \text{ mol } S_2Cl_2) = 236 \text{ g } S_2Cl_2$$

A The formula mass of $Ca(ClO)_2$ is obtained as follows:

$$1Ca (1 \text{ atom})(40.078 \text{ amu/atom}) = 40.078 \text{ amu}$$

$$2Cl (2 \text{ atoms})(35.453 \text{ amu/atom}) = 70.906 \text{ amu}$$

$$+ 2O (2 \text{ atoms})(15.9994 \text{ amu/atom}) = 31.9988 \text{ amu}$$

$$Ca(ClO)_2 \text{ formula mass of } Ca(ClO)_2 = 142.983 \text{ amu}$$

The molar mass of $Ca(ClO)_2$ 142.983 g/mol.

B The mass of 1.75 mol of $Ca(ClO)_2$ is calculated as follows:

$$\text{moles } Ca(ClO)_2 [\text{molar mass } Ca(ClO)_2 / 1 \text{ mol } Ca(ClO)_2] = \text{mass } Ca(ClO)_2$$

$$1.75 \text{ mol } Ca(ClO)_2 [142.983 \text{ g } Ca(ClO)_2 / 1 \text{ mol } Ca(ClO)_2] = 250 \text{ g } Ca(ClO)_2$$

Because 1.75 mol is less than 2 mol, the final quantity in grams in both cases should be less than twice the molar mass, which it is.

Exercise

Calculate the mass of 0.0122 mol of each compound.

- Si_3N_4 (silicon nitride), used as bearings and rollers
- $(CH_3)_3N$ (trimethylamine), a corrosion inhibitor

Answer:

a. 1.71 g

b. 0.721 g

Summary

The **molecular mass** and the **formula mass** of a compound are obtained by adding together the atomic masses of the atoms present in the molecular formula or empirical formula, respectively; the units of both are atomic mass units (amu). The **mole** is a unit used to measure the number of atoms, molecules, or (in the case of ionic compounds) formula units in a given mass of a substance. The mole is defined as the amount of substance that contains the number of carbon atoms in exactly 12 g of carbon-12 and consists of **Avogadro's number** (6.022×10^{23}) of atoms of carbon-12. The **molar mass** of a substance is defined as the mass of 1 mol of that substance, expressed in grams per mole, and is equal to the mass of 6.022×10^{23} atoms, molecules, or formula units of that substance.

KEY TAKEAWAY

- To analyze chemical transformations, it is essential to use a standardized unit of measure called the mole.

CONCEPTUAL PROBLEMS

Please be sure you are familiar with the topics discussed in Essential Skills 2 (Section 3.7 "Essential Skills 2") before proceeding to the Conceptual Problems.

- Describe the relationship between an atomic mass unit and a gram.
- Is it correct to say that ethanol has a formula mass of 46? Why or why not?
- If 2 mol of sodium react completely with 1 mol of chlorine to produce sodium chloride, does this mean that 2 g of sodium reacts completely with 1 g of chlorine to give the same product? Explain your answer.
- Construct a flowchart to show how you would calculate the number of moles of silicon in a 37.0 g sample of orthoclase (KAlSi_3O_8), a mineral used in the manufacture of porcelain.
- Construct a flowchart to show how you would calculate the number of moles of nitrogen in a 22.4 g sample of nitroglycerin that contains 18.5% nitrogen by mass.

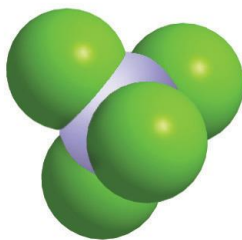
A = %N by mass, expressed as a

decimal $B = 1 \text{ molar mass of nitrogen in g nitroglycerin} \rightarrow \times A \text{ gN} \rightarrow \times B \text{ mol N}$

NUMERICAL PROBLEMS

Please be sure you are familiar with the topics discussed in Essential Skills 2 (Section 3.7 "Essential Skills 2") before proceeding to the Numerical Problems.

1. Derive an expression that relates the number of molecules in a sample of a substance to its mass and molecular mass.
2. Calculate the molecular mass or formula mass of each compound.
 - a. KCl (potassium chloride)
 - b. NaCN (sodium cyanide)
 - c. H₂S (hydrogen sulfide)
 - d. NaN₃ (sodium azide)
 - e. H₂CO₃ (carbonic acid)
 - f. K₂O (potassium oxide)
 - g. Al(NO₃)₃ (aluminum nitrate)
 - h. Cu(ClO₄)₂ [copper(II) perchlorate]
3. Calculate the molecular mass or formula mass of each compound.
 - a. V₂O₄ (vanadium(IV) oxide)
 - b. CaSiO₃ (calcium silicate)
 - c. BiOCl (bismuth oxychloride)
 - d. CH₃COOH (acetic acid)
 - e. Ag₂SO₄ (silver sulfate)
 - f. Na₂CO₃ (sodium carbonate)
 - g. (CH₃)₂CHOH (isopropyl alcohol)
4. Calculate the molar mass of each compound.

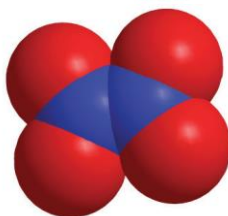


a.

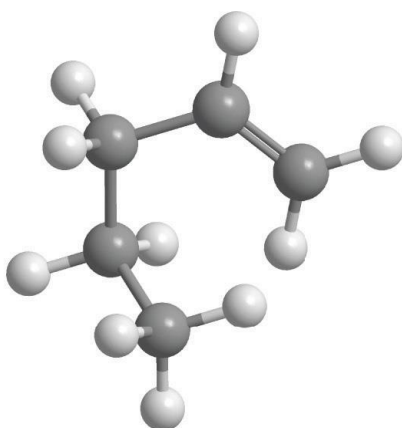
b.



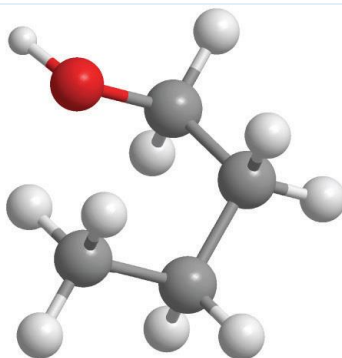
c.



d.

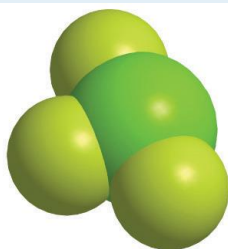


e.

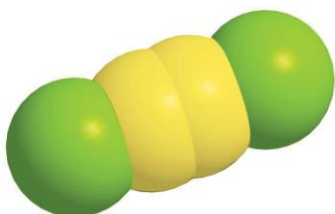


5. Calculate the molar mass of each compound.

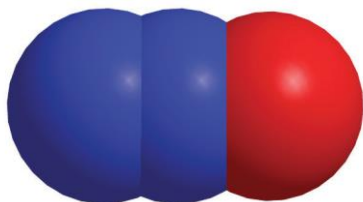
a.



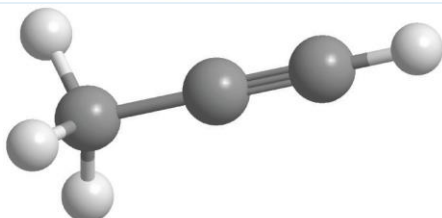
b.



c.

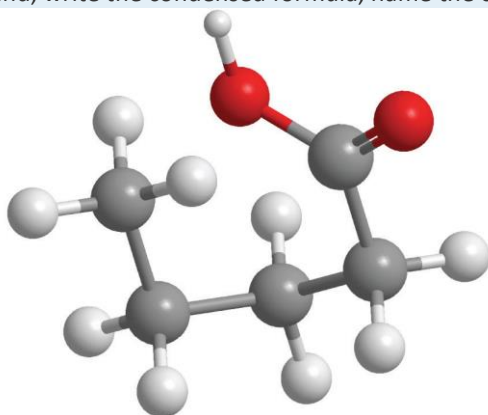


d.

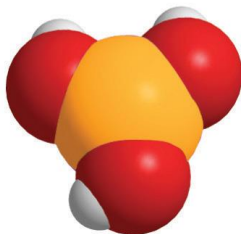


6. For each compound, write the condensed formula, name the compound, and give its molar mass.

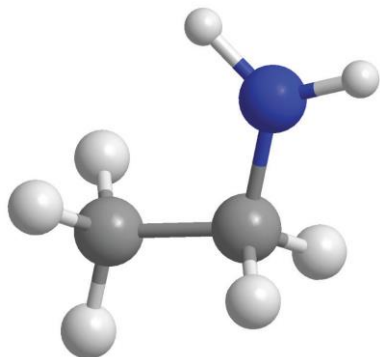
a.



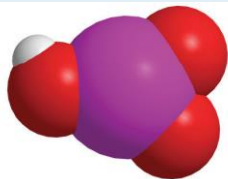
b.



7. For each compound, write the condensed formula, name the compound, and give its molar mass.



a.



b.

8. Calculate the number of moles in 5.00×10^2 g of each substance. How many molecules or formula units are present in each sample?

- a. CaO (lime)
- b. CaCO_3 (chalk)
- c. $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ [sucrose (cane sugar)]
- d. NaOCl (bleach)
- e. CO_2 (dry ice)

9. Calculate the mass in grams of each sample.

- a. 0.520 mol of N_2O_4
- b. 1.63 mol of $\text{C}_6\text{H}_4\text{Br}_2$
- c. 4.62 mol of $(\text{NH}_4)_2\text{SO}_3$

10. Give the number of molecules or formula units in each sample.

- a. 1.30×10^{-2} mol of SCl_2
- b. 1.03 mol of N_2O_5
- c. 0.265 mol of $\text{Ag}_2\text{Cr}_2\text{O}_7$

11. Give the number of moles in each sample.

- a. 9.58×10^{26} molecules of Cl_2
- b. 3.62×10^{27} formula units of KCl

c. 6.94×10^{28} formula units of $\text{Fe}(\text{OH})_2$

12. Solutions of iodine are used as antiseptics and disinfectants. How many iodine atoms correspond to 11.0 g of molecular iodine (I_2)?

13. What is the total number of atoms in each sample?

- a. 0.431 mol of Li
- b. 2.783 mol of methanol (CH_3OH)
- c. 0.0361 mol of CoCO_3
- d. 1.002 mol of SeBr_2O

14. What is the total number of atoms in each sample?

- a. 0.980 mol of Na
- b. 2.35 mol of O_2
- c. 1.83 mol of Ag_2S
- d. 1.23 mol of propane (C_3H_8)

15. What is the total number of atoms in each sample?

- a. 2.48 g of HBr
- b. 4.77 g of CS_2
- c. 1.89 g of NaOH
- d. 1.46 g of SrC_2O_4

16. Decide whether each statement is true or false and explain your reasoning.

- a. There are more molecules in 0.5 mol of Cl_2 than in 0.5 mol of H_2 .
- b. One mole of H_2 has 6.022×10^{23} hydrogen atoms.
- c. The molecular mass of H_2O is 18.0 amu.
- d. The formula mass of benzene is 78 amu.

17. Complete the following table.

Substance	Mass (g)	Number of Moles	Number of Molecules or Formula Units	Number of Atoms or Ions
MgCl_2	37.62			
AgNO_3		2.84		
BH_4Cl			8.93×10^{25}	
K_2S				7.69×10^{26}

Substance	Mass (g)	Number of Moles	Number of Molecules or Formula Units	Number of Atoms or Ions
H ₂ SO ₄		1.29		
C ₆ H ₁₄	11.84			
HClO ₃			2.45×10^{26}	

18. Give the formula mass or the molecular mass of each substance.

- PbClF
- Cu₂P₂O₇
- BiONO₃
- Tl₂SeO₄

19. Give the formula mass or the molecular mass of each substance.

- MoCl₅
- B₂O₃
- UO₂CO₃
- NH₄UO₂AsO₄

3.2 Determining Empirical and Molecular Formulas

LEARNING OBJECTIVES

- To determine the empirical formula of a compound from its composition by mass.
- To derive the molecular formula of a compound from its empirical formula.

When a new chemical compound, such as a potential new pharmaceutical, is synthesized in the laboratory or isolated from a natural source, chemists determine its elemental composition, its empirical formula, and its structure to understand its properties. In this section, we focus on how to determine the empirical formula of a compound and then use it to determine the molecular formula if the molar mass of the compound is known.

Calculating Mass Percentages

The law of definite proportions states that a chemical compound always contains the same proportion of elements by mass; that is, the percent composition—the percentage of each element present in a pure substance—is constant (although we now know there are exceptions to this law). For example, sucrose (cane sugar) is 42.11% carbon, 6.48% hydrogen, and 51.41% oxygen by mass. This means that 100.00 g of sucrose always contains 42.11 g of carbon, 6.48 g of hydrogen, and 51.41 g of oxygen. First we will use the

molecular formula of sucrose ($C_{12}H_{22}O_{11}$) to calculate the mass percentage of the component elements; then we will show how mass percentages can be used to determine an empirical formula.

According to its molecular formula, each molecule of sucrose contains 12 carbon atoms, 22 hydrogen atoms, and 11 oxygen atoms. A mole of sucrose molecules therefore contains 12 mol of carbon atoms, 22 mol of hydrogen atoms, and 11 mol of oxygen atoms. We can use this information to calculate the mass of each element in 1 mol of sucrose, which will give us the molar mass of sucrose. We can then use these masses to calculate the percent composition of sucrose. To three decimal places, the calculations are the following:

Equation 3.3

$$\begin{aligned} \text{mass of C/mol of sucrose} &= 12 \text{ mol C} \times 12.011 \text{ g C} / 1 \text{ mol C} = 144.132 \text{ g C} \\ \text{mass of H/mol of sucrose} &= 22 \text{ mol H} \times 1.008 \text{ g H} / 1 \text{ mol H} = 22.176 \text{ g H} \\ \text{mass of O/mol of sucrose} &= 11 \text{ mol O} \times 15.999 \text{ g O} / 1 \text{ mol O} = 175.989 \text{ g O} \end{aligned}$$

Thus 1 mol of sucrose has a mass of 342.297 g; note that more than half of the mass (175.989 g) is oxygen, and almost half of the mass (144.132 g) is carbon.

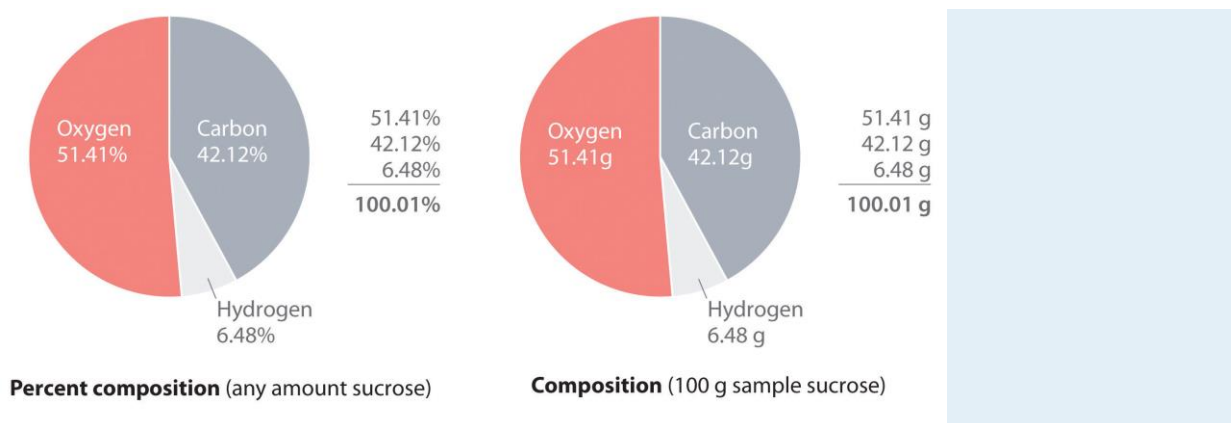
The mass percentage of each element in sucrose is the mass of the element present in 1 mol of sucrose divided by the molar mass of sucrose, multiplied by 100 to give a percentage. The result is shown to two decimal places:

$$\begin{aligned} \text{mass \% C in sucrose} &= \text{mass of C/mol sucrose} / \text{molar mass of sucrose} \times 100 = 144.132 \text{ g C} / 342.297 \text{ g/mol} \times 100 = 42.12 \% \\ \text{mass \% H in sucrose} &= \text{mass of H/mol sucrose} / \text{molar mass of sucrose} \times 100 = 22.176 \text{ g H} / 342.297 \text{ g/mol} \times 100 = 6.48 \% \\ \text{mass \% O in sucrose} &= \text{mass of O/mol sucrose} / \text{molar mass of sucrose} \times 100 = 175.989 \text{ g O} / 342.297 \text{ g/mol} \times 100 = 51.41 \% \end{aligned}$$

You can check your work by verifying that the sum of the percentages of all the elements in the compound is 100%:

$$42.12\% + 6.48\% + 51.41\% = 100.01\%$$

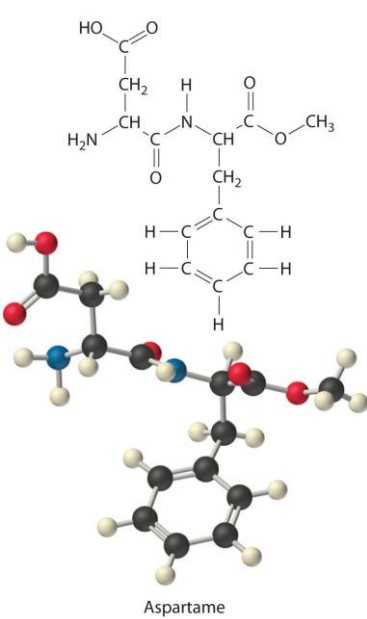
If the sum is not 100%, you have made an error in your calculations. (Rounding to the correct number of decimal places can, however, cause the total to be slightly different from 100%.) Thus 100.00 g of sucrose contains 42.12 g of carbon, 6.48 g of hydrogen, and 51.41 g of oxygen; to two decimal places, the percent composition of sucrose is indeed 42.12% carbon, 6.48% hydrogen, and 51.41% oxygen.



We could also calculate the mass percentages using atomic masses and molecular masses, with atomic mass units. Because the answer we are seeking is a ratio, expressed as a percentage, the units of mass cancel whether they are grams (using molar masses) or atomic mass units (using atomic and molecular masses).

EXAMPLE 5

Aspartame is the artificial sweetener sold as NutraSweet and Equal. Its molecular formula is $C_{14}H_{18}N_2O_5$.



- Calculate the mass percentage of each element in aspartame.
- Calculate the mass of carbon in a 1.00 g packet of Equal, assuming it is pure aspartame.

Given: molecular formula and mass of sample

Asked for: mass percentage of all elements and mass of one element in sample

Strategy:

A Use atomic masses from the periodic table to calculate the molar mass of aspartame.

B Divide the mass of each element by the molar mass of aspartame; then multiply by 100 to obtain percentages.

C To find the mass of an element contained in a given mass of aspartame, multiply the mass of aspartame by the mass percentage of that element, expressed as a decimal.

Solution:

A We calculate the mass of each element in 1 mol of aspartame and the molar mass of aspartame, here to three decimal places:

$$\begin{aligned}14\text{C } (14 \text{ mol C})(12.011 \text{ g/mol C}) &= 168.154 \text{ g} \\18\text{H } (18 \text{ mol H})(1.008 \text{ g/mol H}) &= 18.114 \text{ g} \\2\text{N } (2 \text{ mol N})(14.007 \text{ g/mol N}) &= 28.014 \text{ g} \\5\text{O } (5 \text{ mol O})(15.999 \text{ g/mol O}) &= 79.995 \text{ g} \\14\text{H } 18\text{N } 2\text{O } 5 \text{ molar mass of aspartame} &= 294.277 \text{ g/mol}\end{aligned}$$

Thus more than half the mass of 1 mol of aspartame (294.277 g) is carbon (168.154 g).

B To calculate the mass percentage of each element, we divide the mass of each element in the compound by the molar mass of aspartame and then multiply by 100 to obtain percentages, here reported to two decimal places:

$$\begin{aligned}\text{mass \% C} &= 168.154 \text{ g C} / 294.277 \text{ g aspartame} \times 100 = 57.14\% \\ \text{mass \% H} &= 18.114 \text{ g H} / 294.277 \text{ g aspartame} \times 100 = 6.16\% \\ \text{mass \% N} &= 28.014 \text{ g N} / 294.277 \text{ g aspartame} \times 100 = 9.52\% \\ \text{mass \% O} &= 79.995 \text{ g O} / 294.277 \text{ g aspartame} \times 100 = 27.18\%\end{aligned}$$

As a check, we can add the percentages together:

$$57.14\% + 6.16\% + 9.52\% + 27.18\% = 100.00\%$$

If you obtain a total that differs from 100% by more than about $\pm 1\%$, there must be an error somewhere in the calculation.

C The mass of carbon in 1.00 g of aspartame is calculated as follows:

$$\text{mass of C} = 1.00 \text{ g aspartame} \times 57.14 \text{ g C} / 100 \text{ g aspartame} = 0.571 \text{ g C}$$

Exercise

Calculate the mass percentage of each element in aluminum oxide (Al_2O_3). Then calculate the mass of aluminum in a 3.62 g sample of pure aluminum oxide.

Answer: 52.93% aluminum; 47.08% oxygen; 1.92 g Al

Determining the Empirical Formula of Penicillin

Just as we can use the empirical formula of a substance to determine its percent composition, we can use the percent composition of a sample to determine its empirical formula, which can then be used to determine its molecular formula. Such a procedure was actually used to determine the empirical and molecular formulas of the first antibiotic to be discovered: penicillin.

Antibiotics are chemical compounds that selectively kill microorganisms, many of which cause diseases. Although we may take antibiotics for granted today, penicillin was discovered only about 80 years ago. The subsequent development of a wide array of other antibiotics for treating many common diseases has contributed greatly to the substantial increase in life expectancy over the past 50 years. The discovery of penicillin is a historical detective story in which the use of mass percentages to determine empirical formulas played a key role.

In 1928, Alexander Fleming, a young microbiologist at the University of London, was working with a common bacterium that causes boils and other infections such as blood poisoning. For laboratory study, bacteria are commonly grown on the surface of a nutrient-containing gel in small, flat culture dishes. One day Fleming noticed that one of his cultures was contaminated by a bluish-green mold similar to the mold found on spoiled bread or fruit. Such accidents are rather common, and most laboratory workers would have simply thrown the cultures away. Fleming noticed, however, that the bacteria were growing everywhere on the gel *except* near the contaminating mold (part (a) in Figure 3.3 " "), and he hypothesized that the mold must be producing a substance that either killed the bacteria or prevented their growth. To test this hypothesis, he grew the mold in a liquid and then filtered the liquid and added it to various bacteria cultures. The liquid killed not only the bacteria Fleming had originally been studying but also a wide range of other disease-causing bacteria. Because the mold was a member of the *Penicillium* family (named for their pencil-shaped branches under the microscope) (part (b) in Figure 3.3 " "), Fleming called the active ingredient in the broth *penicillin*.

Although Fleming was unable to isolate penicillin in pure form, the medical importance of his discovery stimulated researchers in other laboratories. Finally, in 1940, two chemists at Oxford University, Howard Florey (1898–1968) and Ernst Chain (1906–1979), were able to isolate an active product, which they called penicillin G. Within three years, penicillin G was in widespread use for treating pneumonia, gangrene, gonorrhea, and other diseases, and its

use greatly increased the survival rate of wounded soldiers in World War II. As a result of their work, Fleming, Florey, and Chain shared the Nobel Prize in Medicine in 1945.

As soon as they had succeeded in isolating pure penicillin G, Florey and Chain subjected the compound to a procedure called combustion analysis (described later in this section) to determine what elements were present and in what quantities. The results of such analyses are usually reported as mass percentages. They discovered that a typical sample of penicillin G contains 53.9% carbon, 4.8% hydrogen, 7.9% nitrogen, 9.0% sulfur, and 6.5% sodium by mass. The sum of these numbers is only 82.1%, rather than 100.0%, which implies that there must be one or more additional elements. A reasonable candidate is oxygen, which is a common component of compounds that contain carbon and hydrogen;^[1] for technical reasons, however, it is difficult to analyze for oxygen directly. If we assume that all the missing mass is due to oxygen, then penicillin G contains $(100.0\% - 82.1\%) = 17.9\%$ oxygen. From these mass percentages, the empirical formula and eventually the molecular formula of the compound can be determined.

To determine the empirical formula from the mass percentages of the elements in a compound such as penicillin G, we need to convert the mass percentages to relative numbers of atoms. For convenience, we assume that we are dealing with a 100.0 g sample of the compound, even though the sizes of samples used for analyses are generally much smaller, usually in milligrams. This assumption simplifies the arithmetic because a 53.9% mass percentage of carbon corresponds to 53.9 g of carbon in a 100.0 g sample of penicillin G; likewise, 4.8% hydrogen corresponds to 4.8 g of hydrogen in 100.0 g of penicillin G; and so forth for the other elements. We can then divide each mass by the molar mass of the element to determine how many moles of each element are present in the 100.0 g sample:

Equation 3.4

$$\begin{aligned} \text{mass (g)} / \text{molar mass (g/mol)} &= (\text{g}) / (\text{mol g}) = \text{mol} \\ 53.9 \text{ g C} / (1 \text{ mol C } 12.011 \text{ g C}) &= 4.49 \text{ mol C} \\ 4.8 \text{ g H} / (1 \text{ mol H } 1.008 \text{ g H}) &= 4.8 \text{ mol H} \\ 7.9 \text{ g N} / (1 \text{ mol N } 14.007 \text{ g N}) &= 0.56 \text{ mol N} \\ 9.0 \text{ g S} / (1 \text{ mol S } 32.065 \text{ g S}) &= 0.28 \text{ mol S} \\ 6.5 \text{ g Na} / (1 \text{ mol Na } 22.990 \text{ g Na}) &= 0.28 \text{ mol Na} \\ 17.9 \text{ g O} / (1 \text{ mol O } 15.999 \text{ g O}) &= 1.12 \text{ mol O} \end{aligned}$$

Thus 100.0 g of penicillin G contains 4.49 mol of carbon, 4.8 mol of hydrogen, 0.56 mol of nitrogen, 0.28 mol of sulfur, 0.28 mol of sodium, and 1.12 mol of oxygen (assuming that all the missing mass was oxygen). The number of significant figures in the numbers of moles of elements varies between two and three because some of the analytical data were reported to only two significant figures.

These results tell us the ratios of the moles of the various elements in the sample (4.49 mol of carbon to 4.8 mol of hydrogen to 0.56 mol of nitrogen, and so forth), but they are not the whole-number ratios we need for the empirical formula—the empirical formula expresses the *relative* numbers of atoms in the *smallest whole numbers*

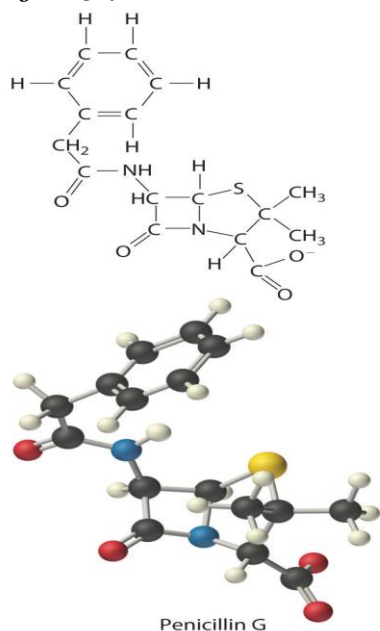
possible. To obtain whole numbers, we divide the numbers of moles of all the elements in the sample by the number of moles of the element present in the lowest relative amount, which in this example is sulfur or sodium. The results will be the subscripts of the elements in the empirical formula. To two significant figures, the results are

Equation 3.5

$$\begin{aligned} \text{C: } 4.49 / 0.28 &= 16 \quad \text{H: } 4.8 / 0.28 = 17 \quad \text{N: } 0.56 / 0.28 = 2 \quad \text{S: } 0.28 / 0.28 = 1 \quad \text{Na: } 0.28 / 0.28 = 1 \quad \text{O: } 1 \\ &.12 / 0.28 = 4 \end{aligned}$$

The empirical formula of penicillin G is therefore $\text{C}_{16}\text{H}_{17}\text{N}_2\text{NaO}_4\text{S}$. Other experiments have shown that penicillin G is actually an ionic compound that contains Na^+ cations and $[\text{C}_{16}\text{H}_{17}\text{N}_2\text{O}_4\text{S}]^-$ anions in a 1:1 ratio. The complex structure of penicillin G (Figure 3.4 "Structural Formula and Ball-and-Stick Model of the Anion of Penicillin G") was not determined until 1948.

Figure 3.4 *Structural Formula and Ball-and-Stick Model of the Anion of Penicillin G*



In some cases, one or more of the subscripts in a formula calculated using this procedure may not be integers. Does this mean that the compound of interest contains a nonintegral number of atoms? No; rounding errors in the calculations as well as experimental errors in the data can result in nonintegral ratios. When this happens, you must exercise some judgment in interpreting the results, as illustrated in Example 6. In particular, ratios of 1.50, 1.33, or 1.25 suggest that you should multiply *all* subscripts in the formula by 2, 3, or 4, respectively. Only if the ratio is within 5% of an integral value should you consider rounding to the nearest integer.

EXAMPLE 6

Calculate the empirical formula of the ionic compound calcium phosphate, a major component of fertilizer and a polishing agent in toothpastes. Elemental analysis indicates that it contains 38.77% calcium, 19.97% phosphorus, and 41.27% oxygen.

Given: percent composition

Asked for: empirical formula

Strategy:

A Assume a 100 g sample and calculate the number of moles of each element in that sample.

B Obtain the relative numbers of atoms of each element in the compound by dividing the number of moles of each element in the 100 g sample by the number of moles of the element present in the smallest amount.

C If the ratios are not integers, multiply all subscripts by the same number to give integral values.

D Because this is an ionic compound, identify the anion and cation and write the formula so that the charges balance.

Solution:

A A 100 g sample of calcium phosphate contains 38.77 g of calcium, 19.97 g of phosphorus, and 41.27 g of oxygen. Dividing the mass of each element in the 100 g sample by its molar mass gives the number of moles of each element in the sample:

moles Ca = $38.77 \text{ g Ca} \times \frac{1 \text{ mol Ca}}{40.078 \text{ g Ca}} = 0.9674 \text{ mol Ca}$ moles P = $19.97 \text{ g P} \times \frac{1 \text{ mol P}}{30.9738 \text{ g P}} = 0.6447 \text{ mol P}$ moles O = $41.27 \text{ g O} \times \frac{1 \text{ mol O}}{15.9994 \text{ g O}} = 2.5800 \text{ mol O}$

B To obtain the *relative* numbers of atoms of each element in the compound, divide the number of moles of each element in the 100-g sample by the number of moles of the element in the smallest amount, in this case phosphorus:

P: $0.6447 \text{ mol P} / 0.6447 \text{ mol P} = 1.000$ Ca: $0.9674 / 0.6447 = 1.501$ O: $2.5800 / 0.6447 = 4.002$

C We could write the empirical formula of calcium phosphate as $\text{Ca}_{1.501}\text{P}_{1.000}\text{O}_{4.002}$, but the empirical formula should show the ratios of the elements as small whole numbers. To convert the result to integral form, multiply all the subscripts by 2 to get $\text{Ca}_{3.002}\text{P}_{2.000}\text{O}_{8.004}$. The deviation from integral atomic ratios is small and can be attributed to minor experimental errors; therefore, the empirical formula is $\text{Ca}_3\text{P}_2\text{O}_8$.

D The calcium ion (Ca^{2+}) is a cation, so to maintain electrical neutrality, phosphorus and oxygen must form a polyatomic anion. We know from Chapter 2 "Molecules, Ions, and Chemical Formulas" that phosphorus and oxygen form the phosphate ion (PO_4^{3-} ; see Table 2.4 "Common Polyatomic Ions and Their Names").

Because there are two phosphorus atoms in the empirical formula, two phosphate ions must be present. So we write the formula of calcium phosphate as $\text{Ca}_3(\text{PO}_4)_2$.

Exercise

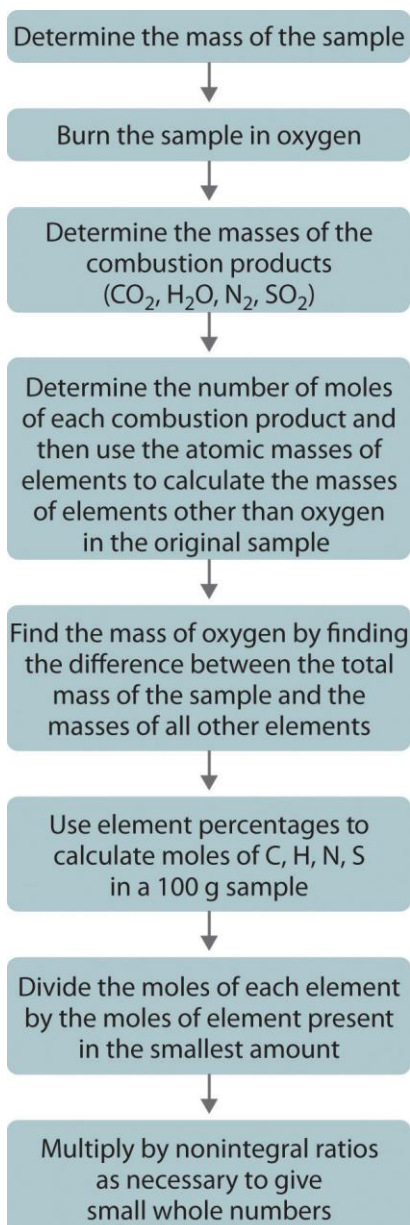
Calculate the empirical formula of ammonium nitrate, an ionic compound that contains 35.00% nitrogen, 5.04% hydrogen, and 59.96% oxygen by mass; refer to Table 2.4 "Common Polyatomic Ions and Their Names" if necessary. Although ammonium nitrate is widely used as a fertilizer, it can be dangerously explosive. For example, it was a major component of the explosive used in the 1995 Oklahoma City bombing.

Answer: $\text{N}_2\text{H}_4\text{O}_3$ is $\text{NH}_4^+\text{NO}_3^-$, written as NH_4NO_3

Combustion Analysis

One of the most common ways to determine the elemental composition of an unknown hydrocarbon is an analytical procedure called *combustion analysis*. A small, carefully weighed sample of an unknown compound that may contain carbon, hydrogen, nitrogen, and/or sulfur is burned in an oxygen atmosphere,^[2] and the quantities of the resulting gaseous products (CO_2 , H_2O , N_2 , and SO_2 , respectively) are determined by one of several possible methods. One procedure used in combustion analysis is outlined schematically in Figure 3.5 "Steps for Obtaining an Empirical Formula from Combustion Analysis", and a typical combustion analysis is illustrated in Example 7.

Figure 3.5 Steps for Obtaining an Empirical Formula from Combustion Analysis



EXAMPLE 7

Naphthalene, the active ingredient in one variety of mothballs, is an organic compound that contains carbon and hydrogen only. Complete combustion of a 20.10 mg sample of naphthalene in oxygen yielded 69.00 mg of CO₂ and 11.30 mg of H₂O. Determine the empirical formula of naphthalene.

Given: mass of sample and mass of combustion products

Asked for: empirical formula

Strategy:

A Use the masses and molar masses of the combustion products, CO_2 and H_2O , to calculate the masses of carbon and hydrogen present in the original sample of naphthalene.

B Use those masses and the molar masses of the elements to calculate the empirical formula of naphthalene.

Solution:

A Upon combustion, 1 mol of CO_2 is produced for each mole of carbon atoms in the original sample.

Similarly, 1 mol of H_2O is produced for every 2 mol of hydrogen atoms present in the sample. The masses of carbon and hydrogen in the original sample can be calculated from these ratios, the masses of CO_2 and H_2O , and their molar masses. Because the units of molar mass are grams per mole, we must first convert the masses from milligrams to grams:

$$\begin{aligned}\text{mass of C} &= 69.00 \text{ mg CO}_2 \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ mol CO}_2}{44.010 \text{ g CO}_2} \times \frac{1 \text{ mol C}}{1 \text{ mol CO}_2} \times 12.011 \text{ g C} = 1.883 \times 10^{-2} \text{ g C} \\ \text{mass of H} &= 11.30 \text{ mg H}_2\text{O} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ mol H}_2\text{O}}{18.015 \text{ g H}_2\text{O}} \times \frac{2 \text{ mol H}}{1 \text{ mol H}_2\text{O}} \times 1.0079 \text{ g H} = 1.264 \times 10^{-3} \text{ g H}\end{aligned}$$

B To obtain the *relative* numbers of atoms of both elements present, we need to calculate the number of moles of each and divide by the number of moles of the element present in the smallest amount:

$$\begin{aligned}\text{moles C} &= 1.883 \times 10^{-2} \text{ g C} \times \frac{1 \text{ mol C}}{12.011 \text{ g C}} = 1.568 \times 10^{-3} \text{ mol C} \\ \text{moles H} &= 1.264 \times 10^{-3} \text{ g H} \times \frac{1 \text{ mol H}}{1.0079 \text{ g H}} = 1.254 \times 10^{-3} \text{ mol H}\end{aligned}$$

Dividing each number by the number of moles of the element present in the smaller amount gives
H: $1.254 \times 10^{-3} / 1.254 \times 10^{-3} = 1.000$ C: $1.568 \times 10^{-3} / 1.254 \times 10^{-3} = 1.250$

Thus naphthalene contains a 1.25:1 ratio of moles of carbon to moles of hydrogen: $\text{C}_{1.25}\text{H}_{1.0}$. Because the ratios of the elements in the empirical formula must be expressed as small whole numbers, multiply both subscripts by 4, which gives C_5H_4 as the empirical formula of naphthalene. In fact, the molecular formula of naphthalene is C_{10}H_8 , which is consistent with our results.

Exercise

- Xylene, an organic compound that is a major component of many gasoline blends, contains carbon and hydrogen only. Complete combustion of a 17.12 mg sample of xylene in oxygen yielded 56.77 mg of CO_2 and 14.53 mg of H_2O . Determine the empirical formula of xylene.
- The empirical formula of benzene is CH (its molecular formula is C_6H_6). If 10.00 mg of benzene is subjected to combustion analysis, what mass of CO_2 and H_2O will be produced?

Answer:

- a. The empirical formula is C_4H_5 . (The molecular formula of xylene is actually C_8H_{10} .)
- b. 33.81 mg of CO_2 ; 6.92 mg of H_2O

From Empirical Formula to Molecular Formula

The empirical formula gives only the *relative* numbers of atoms in a substance in the smallest possible ratio. For a covalent substance, we are usually more interested in the molecular formula, which gives the actual number of atoms of each kind present per molecule. Without additional information, however, it is impossible to know whether the formula of penicillin G, for example, is $C_{16}H_{17}N_2NaO_4S$ or an integral multiple, such as $C_{32}H_{34}N_4Na_2O_8S_2$, $C_{48}H_{51}N_6Na_3O_{12}S_3$, or $(C_{16}H_{17}N_2NaO_4S)_n$, where n is an integer. (The actual structure of penicillin G is shown in Figure 3.4 "Structural Formula and Ball-and-Stick Model of the Anion of Penicillin G".)

Consider glucose, the sugar that circulates in our blood to provide fuel for our bodies and especially for our brains. Results from combustion analysis of glucose report that glucose contains 39.68% carbon and 6.58% hydrogen. Because combustion occurs in the presence of oxygen, it is impossible to directly determine the percentage of oxygen in a compound by using combustion analysis; other more complex methods are necessary. If we assume that the remaining percentage is due to oxygen, then glucose would contain 53.79% oxygen. A 100.0 g sample of glucose would therefore contain 39.68 g of carbon, 6.58 g of hydrogen, and 53.79 g of oxygen. To calculate the number of moles of each element in the 100.0 g sample, we divide the mass of each element by its molar mass:

Equation 3.6

$$\begin{aligned}\text{moles C} &= 39.68 \text{ g C} \times 1 \text{ mol C} / 12.011 \text{ g C} = 3.304 \text{ mol C} \\ \text{moles H} &= 6.58 \text{ g H} \times 1 \text{ mol H} / 1.0079 \text{ g H} = 6.53 \text{ mol H} \\ \text{moles O} &= 53.79 \text{ g O} \times 1 \text{ mol O} / 15.9994 \text{ g O} = 3.362 \text{ mol O}\end{aligned}$$

Once again, we find the subscripts of the elements in the empirical formula by dividing the number of moles of each element by the number of moles of the element present in the smallest amount:

C: $3.304 / 3.304 = 1.000$ H: $6.53 / 3.304 = 1.98$ O: $3.362 / 3.304 = 1.018$

The oxygen:carbon ratio is 1.018, or approximately 1, and the hydrogen:carbon ratio is approximately 2.

The empirical formula of glucose is therefore CH_2O , but what is its molecular formula?

Many known compounds have the empirical formula CH_2O , including formaldehyde, which is used to preserve biological specimens and has properties that are very different from the sugar circulating in our

blood. At this point, we cannot know whether glucose is CH_2O , $\text{C}_2\text{H}_4\text{O}_2$, or any other $(\text{CH}_2\text{O})_n$. We can, however, use the experimentally determined molar mass of glucose (180 g/mol) to resolve this dilemma. First, we calculate the **formula mass**, the molar mass of the formula unit, which is the sum of the atomic masses of the elements in the empirical formula multiplied by their respective subscripts. For glucose,

Equation 3.7

$$\text{formula mass of CH}_2\text{O} = [1 \text{ mol C} (12.011 \text{ g/mol C})] + [2 \text{ mol H} (1.0079 \text{ g/mol H})] + [1 \text{ mol O} (15.9994 \text{ g/mol O})] = 30.026 \text{ g}$$

This is much smaller than the observed molar mass of 180 g/mol.

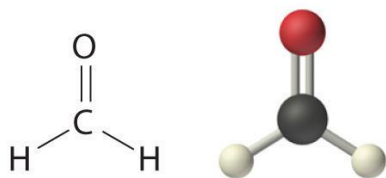
Second, we determine the number of formula units per mole. For glucose, we can calculate the number of (CH_2O) units—that is, the n in $(\text{CH}_2\text{O})_n$ —by dividing the molar mass of glucose by the formula mass of CH_2O :

Equation 3.8

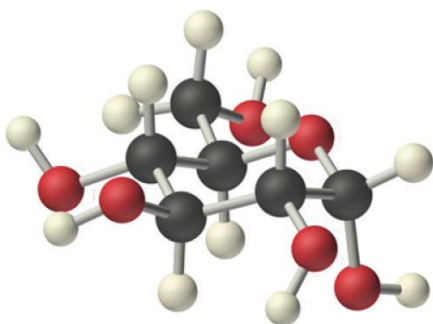
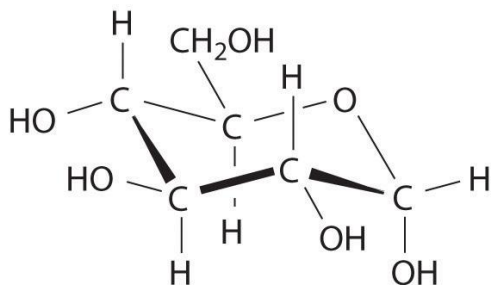
$$n = 180 \text{ g} / 30.026 \text{ g/CH}_2\text{O} = 5.99 \approx 6 \text{ CH}_2\text{O formula units}$$

Each glucose contains six CH_2O formula units, which gives a molecular formula for glucose of $(\text{CH}_2\text{O})_6$, which is more commonly written as $\text{C}_6\text{H}_{12}\text{O}_6$. The molecular structures of formaldehyde and glucose, both of which have the empirical formula CH_2O , are shown in Figure 3.6 "Structural Formulas and Ball-and-Stick Models of (a) Formaldehyde and (b) Glucose".

Figure 3.6 Structural Formulas and Ball-and-Stick Models of (a) Formaldehyde and (b) Glucose



(a) Formaldehyde, CH_2O



(b) Glucose, $(\text{CH}_2\text{O})_6$

EXAMPLE 8

Calculate the molecular formula of caffeine, a compound found in coffee, tea, and cola drinks that has a marked stimulatory effect on mammals. The chemical analysis of caffeine shows that it contains 49.18% carbon, 5.39% hydrogen, 28.65% nitrogen, and 16.68% oxygen by mass, and its experimentally determined molar mass is 196 g/mol.

Given: percent composition and molar mass

Asked for: molecular formula

Strategy:

A Assume 100 g of caffeine. From the percentages given, use the procedure given in Example 6 to calculate the empirical formula of caffeine.

B Calculate the formula mass and then divide the experimentally determined molar mass by the formula mass. This gives the number of formula units present.

C Multiply each subscript in the empirical formula by the number of formula units to give the molecular formula.

Solution:

A We begin by dividing the mass of each element in 100.0 g of caffeine (49.18 g of carbon, 5.39 g of hydrogen, 28.65 g

of nitrogen, 16.68 g of oxygen) by its molar mass. This gives the number of moles of each element in 100 g of caffeine.
moles C = $49.18 \text{ g C} \times \frac{1 \text{ mol C}}{12.011 \text{ g C}} = 4.095 \text{ mol C}$ moles H = $5.39 \text{ g H} \times \frac{1 \text{ mol H}}{1.0079 \text{ g H}} = 5.35 \text{ mol H}$ moles N = $28.65 \text{ g N} \times \frac{1 \text{ mol N}}{14.0067 \text{ g N}} = 2.045 \text{ mol N}$ moles O = $16.68 \text{ g O} \times \frac{1 \text{ mol O}}{15.9994 \text{ g O}} = 1.043 \text{ mol O}$

To obtain the relative numbers of atoms of each element present, divide the number of moles of each element by the number of moles of the element present in the least amount:

O: $1.043 / 1.043 = 1.000$ C: $4.095 / 1.043 = 3.926$ H: $5.35 / 1.043 = 5.13$ N: $2.045 / 1.043 = 1.960$

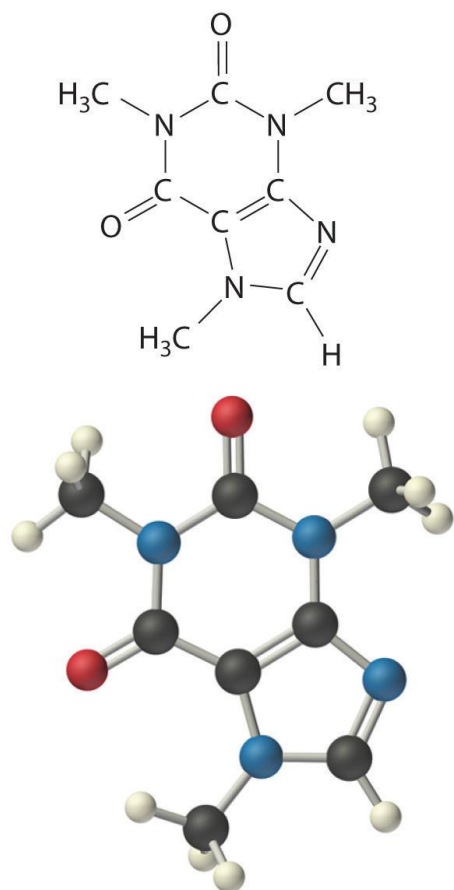
These results are fairly typical of actual experimental data. None of the atomic ratios is exactly integral but all are within 5% of integral values. Just as in Example 6, it is reasonable to assume that such small deviations from integral values are due to minor experimental errors, so round to the nearest integer. The empirical formula of caffeine is thus $\text{C}_4\text{H}_5\text{N}_2\text{O}$.

B The *molecular* formula of caffeine could be $\text{C}_4\text{H}_5\text{N}_2\text{O}$, but it could also be any integral multiple of this. To determine the actual molecular formula, we must divide the experimentally determined molar mass by the formula mass. The formula mass is calculated as follows:

$4\text{C (4 atoms C)(12.011 g/atom C)} = 48.044 \text{ g}$ $5\text{H (5 atoms H)(1.0079 g/atom H)} = 5.0395 \text{ g}$ $2\text{N (2 atoms N)(14.0067 g/atom N)} = 28.0134 \text{ g}$ $+ 1\text{O (1 atom O)(15.9994 g/atom O)} = 15.9994 \text{ g}$
C 4 H 5 N 2 O formula mass of caffeine = 97.096 g

Dividing the measured molar mass of caffeine (196 g/mol) by the calculated formula mass gives
 $196 \text{ g/mol} / 97.096 \text{ g/C}_4\text{H}_5\text{N}_2\text{O} = 2.02 \approx 2$ C 4 H 5 N 2 O empirical formula units

C There are two $\text{C}_4\text{H}_5\text{N}_2\text{O}$ formula units in caffeine, so the molecular formula must be $(\text{C}_4\text{H}_5\text{N}_2\text{O})_2 = \text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$. The structure of caffeine is as follows:



Caffeine

Exercise

Calculate the molecular formula of Freon-114, which has 13.85% carbon, 41.89% chlorine, and 44.06% fluorine. The experimentally measured molar mass of this compound is 171 g/mol. Like Freon-11, Freon-114 is a commonly used refrigerant that has been implicated in the destruction of the ozone layer.

Answer: C₂Cl₂F₄

Summary

The empirical formula of a substance can be calculated from the experimentally determined **percent composition**, the percentage of each element present in a pure substance by mass. In many cases, these percentages can be determined by *combustion analysis*. If the molar mass of the compound is known, the molecular formula can be determined from the empirical formula.

KEY TAKEAWAY

- The empirical formula of a substance can be calculated from its percent composition, and the molecular formula can be determined from the empirical formula and the compound's molar mass.

CONCEPTUAL PROBLEMS

1. What is the relationship between an empirical formula and a molecular formula?
2. Construct a flowchart showing how you would determine the empirical formula of a compound from its percent composition.

NUMERICAL PROBLEMS

Please be sure you are familiar with the topics discussed in Essential Skills 2 (Section 3.7 "Essential Skills 2") before proceeding to the Numerical Problems.

1. What is the mass percentage of water in each hydrate?
 - a. $\text{H}_3\text{AsO}_4 \cdot 0.5\text{H}_2\text{O}$
 - b. $\text{NH}_4\text{NiCl}_3 \cdot 6\text{H}_2\text{O}$
 - c. $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$
2. What is the mass percentage of water in each hydrate?
 - a. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
 - b. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$
 - c. $(\text{NH}_4)_3\text{ZrOH}(\text{CO}_3)_3 \cdot 2\text{H}_2\text{O}$
3. Which of the following has the greatest mass percentage of oxygen— KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, or Fe_2O_3 ?
4. Which of the following has the greatest mass percentage of oxygen— ThOCl_2 , MgCO_3 , or NO_2Cl ?
5. Calculate the percent composition of the element shown in bold in each compound.
 - a. SbBr_3
 - b. As_2I_4
 - c. AlPO_4
 - d. $\text{C}_6\text{H}_{10}\text{O}$
6. Calculate the percent composition of the element shown in bold in each compound.
 - a. HBrO_3
 - b. CsReO_4
 - c. $\text{C}_3\text{H}_8\text{O}$

d. FeSO_4

7. A sample of a chromium compound has a molar mass of 151.99 g/mol. Elemental analysis of the compound shows that it contains 68.43% chromium and 31.57% oxygen. What is the identity of the compound?
8. The percentages of iron and oxygen in the three most common binary compounds of iron and oxygen are given in the following table. Write the empirical formulas of these three compounds.

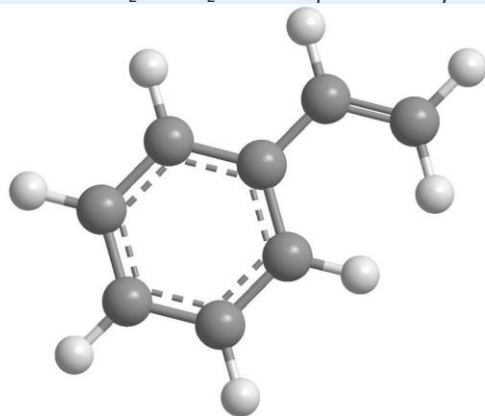
Compound	% Iron	% Oxygen	Empirical Formula
1	69.9	30.1	
2	77.7	22.3	
3	72.4	27.6	

9. What is the mass percentage of water in each hydrate?
- a. $\text{LiCl} \cdot \text{H}_2\text{O}$
- b. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
- c. $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$
10. What is the mass percentage of water in each hydrate?
- a. $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$
- b. $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$
- c. $\text{Mg}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$
11. Two hydrates were weighed, heated to drive off the waters of hydration, and then cooled. The residues were then reweighed. Based on the following results, what are the formulas of the hydrates?

Compound	Initial Mass (g)	Mass after Cooling (g)
$\text{NiSO}_4 \cdot x\text{H}_2\text{O}$	2.08	1.22
$\text{CoCl}_2 \cdot x\text{H}_2\text{O}$	1.62	0.88

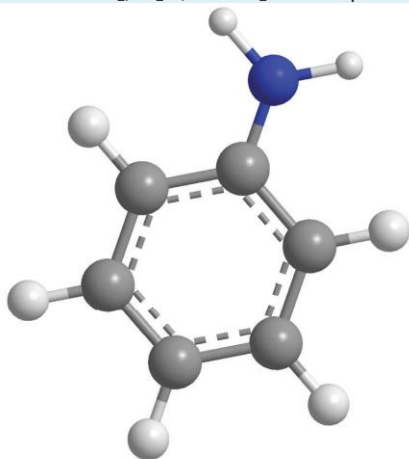
12. Which contains the greatest mass percentage of sulfur— FeS_2 , $\text{Na}_2\text{S}_2\text{O}_4$, or Na_2S ?
13. Given equal masses of each, which contains the greatest mass percentage of sulfur— NaHSO_4 or K_2SO_4 ?
14. Calculate the mass percentage of oxygen in each polyatomic ion.
- a. bicarbonate
- b. chromate
- c. acetate
- d. sulfite

15. Calculate the mass percentage of oxygen in each polyatomic ion.
- oxalate
 - nitrite
 - dihydrogen phosphate
 - thiocyanate
16. The empirical formula of garnet, a gemstone, is $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$. An analysis of a sample of garnet gave a value of 13.8% for the mass percentage of silicon. Is this consistent with the empirical formula?
17. A compound has the empirical formula $\text{C}_2\text{H}_4\text{O}$, and its formula mass is 88 g. What is its molecular formula?
18. Mirex is an insecticide that contains 22.01% carbon and 77.99% chlorine. It has a molecular mass of 545.59 g. What is its empirical formula? What is its molecular formula?
19. How many moles of CO_2 and H_2O will be produced by combustion analysis of 0.010 mol of styrene?



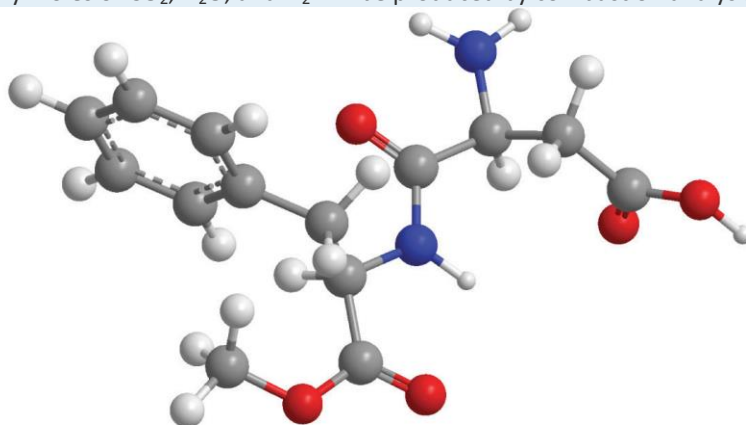
Styrene

20. How many moles of CO_2 , H_2O , and N_2 will be produced by combustion analysis of 0.0080 mol of aniline?



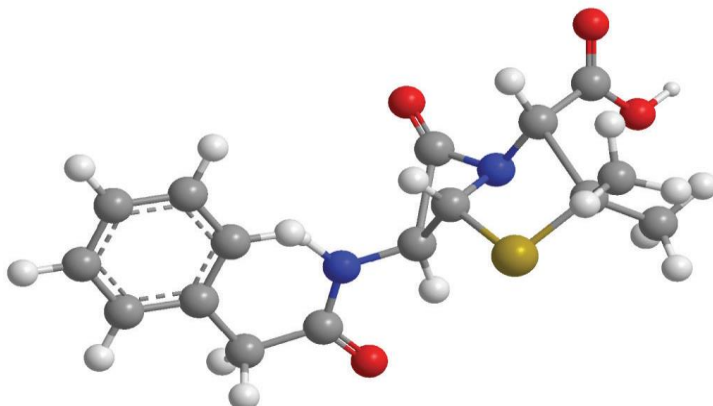
Aniline

21. How many moles of CO_2 , H_2O , and N_2 will be produced by combustion analysis of 0.0074 mol of aspartame?



Aspartame

22. How many moles of CO_2 , H_2O , N_2 , and SO_2 will be produced by combustion analysis of 0.0060 mol of penicillin G?



Penicillin G

1. Combustion of a 34.8 mg sample of benzaldehyde, which contains only carbon, hydrogen, and oxygen, produced 101 mg of CO_2 and 17.7 mg of H_2O .
 - a. What was the mass of carbon and hydrogen in the sample?
 - b. Assuming that the original sample contained only carbon, hydrogen, and oxygen, what was the mass of oxygen in the sample?
 - c. What was the mass percentage of oxygen in the sample?
 - d. What is the empirical formula of benzaldehyde?
 - e. The molar mass of benzaldehyde is 106.12 g/mol. What is its molecular formula?

2. Salicylic acid is used to make aspirin. It contains only carbon, oxygen, and hydrogen. Combustion of a 43.5 mg sample of this compound produced 97.1 mg of CO_2 and 17.0 mg of H_2O .
- What is the mass of oxygen in the sample?
 - What is the mass percentage of oxygen in the sample?
 - What is the empirical formula of salicylic acid?
 - The molar mass of salicylic acid is 138.12 g/mol. What is its molecular formula?
3. Given equal masses of the following acids, which contains the greatest amount of hydrogen that can dissociate to form H^+ —nitric acid, hydroiodic acid, hydrocyanic acid, or chloric acid?
4. Calculate the formula mass or the molecular mass of each compound.
- heptanoic acid (a seven-carbon carboxylic acid)
 - 2-propanol (a three-carbon alcohol)
 - KMnO_4
 - tetraethyllead
 - sulfurous acid
 - ethylbenzene (an eight-carbon aromatic hydrocarbon)
5. Calculate the formula mass or the molecular mass of each compound.
- MoCl_5
 - B_2O_3
 - bromobenzene
 - cyclohexene
 - phosphoric acid
 - ethylamine
6. Given equal masses of butane, cyclobutane, and propene, which contains the greatest mass of carbon?
7. Given equal masses of urea $[(\text{NH}_2)_2\text{CO}]$ and ammonium sulfate, which contains the most nitrogen for use as a fertilizer?

ANSWERS

1. To two decimal places, the percentages are:
- 5.97%
 - 37.12%

- c. 43.22%
2. % oxygen: KMnO_4 , 40.50%; $\text{K}_2\text{Cr}_2\text{O}_7$, 38.07%; Fe_2O_3 , 30.06%
3. To two decimal places, the percentages are:
- a. 66.32% Br
- b. 22.79% As
- c. 25.40% P
- d. 73.43% C
4. Cr_2O_3 .
5. To two decimal places, the percentages are:
- a. 29.82%
- b. 51.16%
- c. 25.40%
6. $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$
7. NaHSO_4
- 8.
- a. 72.71%
- b. 69.55%
- c. 65.99%
- d. 0%
9. $\text{C}_4\text{H}_8\text{O}_2$

23.

- a. 27.6 mg C and 1.98 mg H
- b. 5.2 mg O
- c. 15%
- d. C_7H_6O
- e. C_7H_6O

25. hydrocyanic acid, HCN

27. To two decimal places, the values are:

- a. 273.23 amu
- b. 69.62 amu
- c. 157.01 amu
- d. 82.14 amu
- e. 98.00 amu
- f. 45.08 amu

29. Urea

[1] Do not assume that the “missing” mass is always due to oxygen. It could be any other element.

[2] Other elements, such as metals, can be determined by other methods.

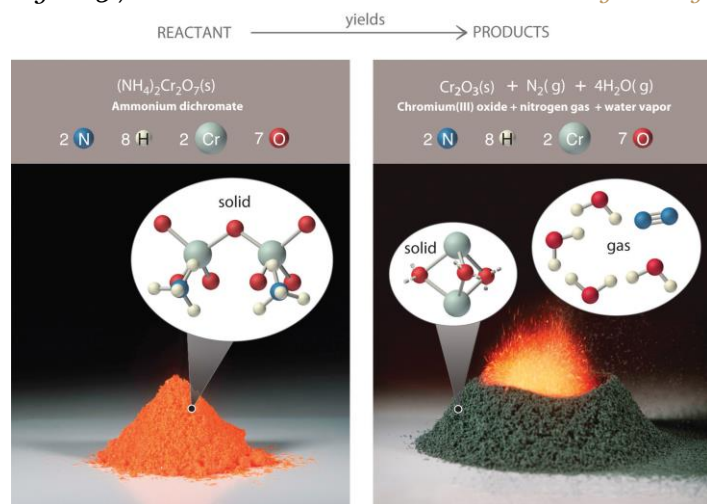
3.3 Chemical Equations

LEARNING OBJECTIVES

- 1. To describe a chemical reaction.
- 2. To calculate the quantities of compounds produced or consumed in a chemical reaction.

As shown in Figure 3.7 "An Ammonium Dichromate Volcano: Change during a Chemical Reaction", applying a small amount of heat to a pile of orange ammonium dichromate powder results in a vigorous reaction known as the ammonium dichromate volcano. Heat, light, and gas are produced as a large pile of fluffy green chromium(III) oxide forms. We can describe this reaction with a chemical equation, an expression that gives the identities and quantities of the substances in a chemical reaction. Chemical formulas and other symbols are used to indicate the starting material(s), or reactant(s), which by convention are written on the left side of the equation, and the final compound(s), or product(s), which are written on the right. An arrow points from the reactant to the products:

Figure 3.7 *An Ammonium Dichromate Volcano: Change during a Chemical Reaction*



The starting material (left) is solid ammonium dichromate. A chemical reaction (right) transforms it to solid chromium(III) oxide, depicted showing a portion of its chained structure, nitrogen gas, and water vapor. (In addition, energy in the form of heat and light is released.) During the reaction, the distribution of atoms changes, but the number of atoms of each element does not change. Because the numbers of each type of atom are the same in the reactants and the products, the chemical equation is balanced.

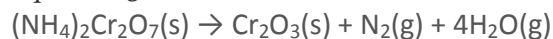
Equation 3.9



The arrow is read as “yields” or “reacts to form.” So Equation 3.9 tells us that ammonium dichromate (the reactant) yields chromium(III) oxide, nitrogen, and water (the products).

The equation for this reaction is even more informative when written as

Equation 3.10



Equation 3.10 is identical to Equation 3.9 except for the addition of abbreviations in parentheses to indicate the physical state of each species. The abbreviations are (s) for solid, (l) for liquid, (g) for gas, and (aq) for an *aqueous solution*, a solution of the substance in water.

Consistent with the law of conservation of mass, the numbers of each type of atom are the same on both sides of Equation 3.9 and Equation 3.10. (For more information on the law of conservation of mass, see Section 1.4 “A Brief History of Chemistry”.) As illustrated in Figure 3.7 “An Ammonium Dichromate Volcano: Change during a Chemical Reaction”, each side has two chromium atoms, seven oxygen atoms, two nitrogen atoms, and eight hydrogen atoms. In a *balanced chemical equation*, both the numbers of each type of atom and the total charge are the same on both

sides. Equation 3.9 and Equation 3.10 are balanced chemical equations. What is different on each side of the equation is how the atoms are arranged to make molecules or ions. *A chemical reaction represents a change in the distribution of atoms but not in the number of atoms.* In this reaction, and in most chemical reactions, bonds are broken in the reactants (here, Cr–O and N–H bonds), and new bonds are formed to create the products (here, O–H and N≡N bonds). If the numbers of each type of atom are different on the two sides of a chemical equation, then the equation is unbalanced, and it cannot correctly describe what happens during the reaction. To proceed, *the equation must first be balanced.*

Note the Pattern

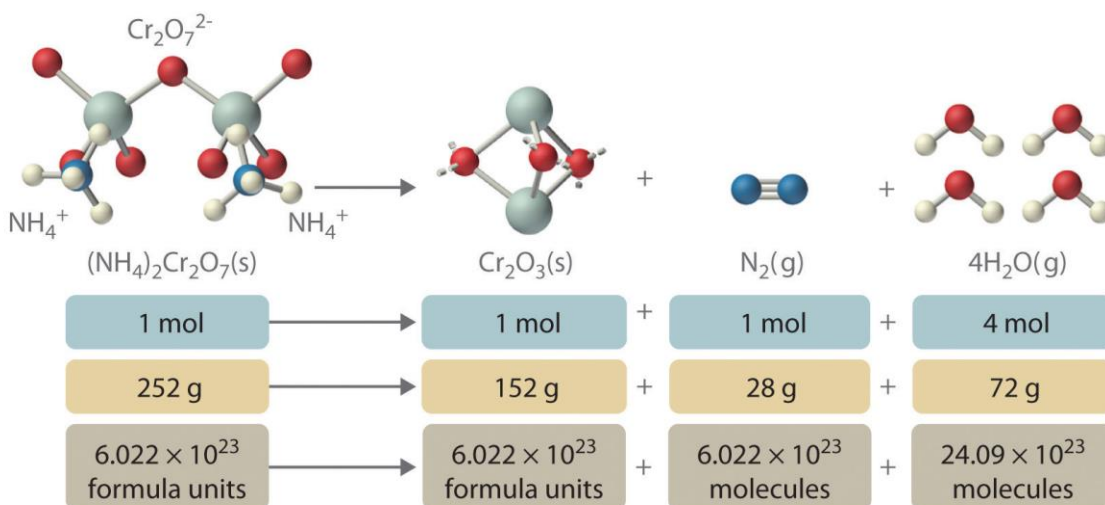
A chemical reaction changes only the distribution of atoms, *not* the number of atoms.

Interpreting Chemical Equations

In addition to providing qualitative information about the identities and physical states of the reactants and products, a balanced chemical equation provides *quantitative* information. Specifically, it tells the relative amounts of reactants and products consumed or produced in a reaction. The number of atoms, molecules, or formula units of a reactant or a product in a balanced chemical equation is the coefficient of that species (e.g., the 4 preceding H₂O in Equation 3.9). When no coefficient is written in front of a species, the coefficient is assumed to be 1. As illustrated in Figure 3.8 "The Relationships among Moles, Masses, and Formula Units of Compounds in the Balanced Chemical Reaction for the Ammonium Dichromate Volcano", the coefficients allow us to interpret Equation 3.9 in any of the following ways:

- Two NH₄⁺ ions and one Cr₂O₇²⁻ ion yield 1 formula unit of Cr₂O₃, 1 N₂ molecule, and 4 H₂O molecules.
- One mole of (NH₄)₂Cr₂O₇ yields 1 mol of Cr₂O₃, 1 mol of N₂, and 4 mol of H₂O.
- A mass of 252 g of (NH₄)₂Cr₂O₇ yields 152 g of Cr₂O₃, 28 g of N₂, and 72 g of H₂O.
- A total of 6.022×10^{23} formula units of (NH₄)₂Cr₂O₇ yields 6.022×10^{23} formula units of Cr₂O₃, 6.022×10^{23} molecules of N₂, and 24.09×10^{23} molecules of H₂O.

Figure 3.8 The Relationships among Moles, Masses, and Formula Units of Compounds in the Balanced Chemical Reaction for the Ammonium Dichromate Volcano



These are all *chemically equivalent* ways of stating the information given in the balanced chemical equation, using the concepts of the mole, molar or formula mass, and Avogadro's number. The ratio of the number of moles of one substance to the number of moles of another is called the mole ratio. For example, the mole ratio of H_2O to N_2 in Equation 3.9 is 4:1. The total mass of reactants equals the total mass of products, as predicted by Dalton's law of conservation of mass: 252 g of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ yields $152 + 28 + 72 = 252$ g of products. The chemical equation does *not*, however, show the rate of the reaction (rapidly, slowly, or not at all) or whether energy in the form of heat or light is given off. We will consider these issues in more detail in later chapters.

An important chemical reaction was analyzed by Antoine Lavoisier, an 18th-century French chemist, who was interested in the chemistry of living organisms as well as simple chemical systems. In a classic series of experiments, he measured the carbon dioxide and heat produced by a guinea pig during respiration, in which organic compounds are used as fuel to produce energy, carbon dioxide, and water. Lavoisier found that the ratio of heat produced to carbon dioxide exhaled was similar to the ratio observed for the reaction of charcoal with oxygen in the air to produce carbon dioxide—a process chemists call *combustion*. Based on these experiments, he proposed that “Respiration is a combustion, slow it is true, but otherwise perfectly similar to that of charcoal.” Lavoisier was correct, although the organic compounds consumed in respiration are substantially different from those found in charcoal. One of the most important fuels in the human body is glucose ($\text{C}_6\text{H}_{12}\text{O}_6$), which is virtually the only fuel used in the brain. Thus combustion and respiration are examples of chemical reactions.

EXAMPLE 9

The balanced chemical equation for the combustion of glucose in the laboratory (or in the brain) is as follows:

$$\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + 6\text{O}_2(\text{g}) \rightarrow 6\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l})$$

Construct a table showing how to interpret the information in this equation in terms of

- a single molecule of glucose.
- moles of reactants and products.
- grams of reactants and products represented by 1 mol of glucose.
- numbers of molecules of reactants and products represented by 1 mol of glucose.

Given: balanced chemical equation

Asked for: molecule, mole, and mass relationships

Strategy:

A Use the coefficients from the balanced chemical equation to determine both the molecular and mole ratios.

B Use the molar masses of the reactants and products to convert from moles to grams.

C Use Avogadro's number to convert from moles to the number of molecules.

Solution:

This equation is balanced as written: each side has 6 carbon atoms, 18 oxygen atoms, and 12 hydrogen atoms.

We can therefore use the coefficients directly to obtain the desired information.

- A** One molecule of glucose reacts with 6 molecules of O_2 to yield 6 molecules of CO_2 and 6 molecules of H_2O .
- One mole of glucose reacts with 6 mol of O_2 to yield 6 mol of CO_2 and 6 mol of H_2O .

B To interpret the equation in terms of masses of reactants and products, we need their molar masses and the mole ratios from part b. The molar masses in grams per mole are as follows: glucose, 180.16; O_2 , 31.9988; CO_2 , 44.010; and H_2O , 18.015.

mass of reactants = mass of products
 $g \text{ glucose} + g \text{ } O_2 = g \text{ } CO_2 + g \text{ } H_2O$
 $1 \text{ mol glucose (180.16 g)} + 6 \text{ mol } O_2 (6 \times 31.9988 \text{ g}) = 6 \text{ mol } CO_2 (6 \times 44.010 \text{ g}) + 6 \text{ mol } H_2O (6 \times 18.015 \text{ g})$
 $372.15 \text{ g} = 372.15 \text{ g}$

C One mole of glucose contains Avogadro's number (6.022×10^{23}) of glucose molecules. Thus 6.022×10^{23} glucose molecules react with $(6 \times 6.022 \times 10^{23}) = 3.613 \times 10^{24}$ oxygen molecules to yield $(6 \times 6.022 \times 10^{23}) = 3.613 \times 10^{24}$ molecules each of CO_2 and H_2O .

In tabular form:

	$C_6H_{12}O_6(s)$	+	$6O_2(g)$	$\rightarrow$	$6CO_2(g)$	+	$6H_2O(l)$
a.	1 molecule		6 molecules		6 molecules		6 molecules

	$\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$	+	$6\text{O}_2(\text{g})$	$\rightarrow$	$6\text{CO}_2(\text{g})$	+	$6\text{H}_2\text{O}(\text{l})$
b.	1 mol		6 mol		6 mol		6 mol
c.	180.16 g		191.9928 g		264.06 g		108.09 g
d.	6.022×10^{23} molecules		3.613×10^{24} molecules		3.613×10^{24} molecules		3.613×10^{24} molecules

Exercise

Ammonium nitrate is a common fertilizer, but under the wrong conditions it can be hazardous. In 1947, a ship loaded with ammonium nitrate caught fire during unloading and exploded, destroying the town of Texas City, Texas. The explosion resulted from the following reaction:

$$2\text{NH}_4\text{NO}_3(\text{s}) \rightarrow 2\text{N}_2(\text{g}) + 4\text{H}_2\text{O}(\text{g}) + \text{O}_2(\text{g})$$

Construct a table showing how to interpret the information in the equation in terms of

- individual molecules and ions.
- moles of reactants and products.
- grams of reactants and products given 2 mol of ammonium nitrate.
- numbers of molecules or formula units of reactants and products given 2 mol of ammonium nitrate.

Answer:

	$2\text{NH}_4\text{NO}_3(\text{s})$	$\rightarrow$	$2\text{N}_2(\text{g})$	+	$4\text{H}_2\text{O}(\text{g})$	+	$\text{O}_2(\text{g})$
a.	2NH_4^+ ions and 2NO_3^- ions		2 molecules		4 molecules		1 molecule
b.	2 mol		2 mol		4 mol		1 mol
c.	160.0864 g		56.0268 g		72.0608 g		31.9988 g
d.	1.204×10^{24} formula units		1.204×10^{24} molecules		2.409×10^{24} molecules		6.022×10^{23} molecules

Balancing Simple Chemical Equations

When a chemist encounters a new reaction, it does not usually come with a label that shows the balanced chemical equation. Instead, the chemist must identify the reactants and products and then write them in the form of a chemical equation that may or may not be balanced as first written. Consider, for example, the combustion of *n*-heptane (C_7H_{16}), an important component of gasoline:

Equation 3.11



The complete combustion of any hydrocarbon with sufficient oxygen *always* yields carbon dioxide and water (Figure 3.9 "An Example of a Combustion Reaction").

Equation 3.11 is not balanced: the numbers of each type of atom on the reactant side of the equation (7 carbon atoms, 16 hydrogen atoms, and 2 oxygen atoms) is not the same as the numbers of each type of atom on the product side (1 carbon atom, 2 hydrogen atoms, and 3 oxygen atoms). Consequently, we must adjust the coefficients of the reactants and products to give the same numbers of atoms of each type on both sides of the equation. Because the identities of the reactants and products are fixed, we *cannot* balance the equation by changing the subscripts of the reactants or the products. To do so would change the chemical identity of the species being described, as illustrated in Figure 3.10 "Balancing Equations".

Steps in Balancing a Chemical Equation

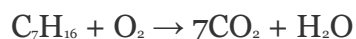
1. Identify the most complex substance.
2. Beginning with that substance, choose an element that appears in only one reactant and one product, if possible. Adjust the coefficients to obtain the same number of atoms of this element on both sides.
3. Balance polyatomic ions (if present) as a unit.
4. Balance the remaining atoms, usually ending with the least complex substance and using fractional coefficients if necessary. If a fractional coefficient has been used, multiply both sides of the equation by the denominator to obtain whole numbers for the coefficients.
5. Count the numbers of atoms of each kind on both sides of the equation to be sure that the chemical equation is balanced.

To demonstrate this approach, let's use the combustion of *n*-heptane (Equation 3.11) as an example.

1. **Identify the most complex substance.** The most complex substance is the one with the largest number of different atoms, which is C_7H_{16} . We will assume initially that the final balanced chemical equation contains 1 molecule or formula unit of this substance.

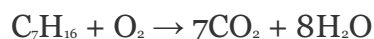
2. **Adjust the coefficients.** Try to adjust the coefficients of the molecules on the other side of the equation to obtain the same numbers of atoms on both sides. Because one molecule of *n*-heptane contains 7 carbon atoms, we need 7 CO₂ molecules, each of which contains 1 carbon atom, on the right side:

Equation 3.12



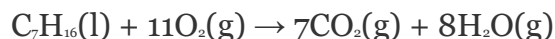
3. **Balance polyatomic ions as a unit.** There are no polyatomic ions to be considered in this reaction.
4. **Balance the remaining atoms.** Because one molecule of *n*-heptane contains 16 hydrogen atoms, we need 8 H₂O molecules, each of which contains 2 hydrogen atoms, on the right side:

Equation 3.13



The carbon and hydrogen atoms are now balanced, but we have 22 oxygen atoms on the right side and only 2 oxygen atoms on the left. We can balance the oxygen atoms by adjusting the coefficient in front of the least complex substance, O₂, on the reactant side:

Equation 3.14



5. **Check your work.** The equation is now balanced, and there are no fractional coefficients: there are 7 carbon atoms, 16 hydrogen atoms, and 22 oxygen atoms on each side. *Always check to be sure that a chemical equation is balanced.*

The assumption that the final balanced chemical equation contains only one molecule or formula unit of the most complex substance is not always valid, but it is a good place to start. Consider, for example, a similar reaction, the combustion of isooctane (C₈H₁₈). Because the combustion of any hydrocarbon with oxygen produces carbon dioxide and water, the unbalanced chemical equation is as follows:

Equation 3.15



EXAMPLE 10

The reaction of the mineral hydroxyapatite [Ca₅(PO₄)₃(OH)] with phosphoric acid and water gives Ca(H₂PO₄)₂·H₂O (calcium dihydrogen phosphate monohydrate). Write and balance the equation for this reaction.

Given: reactants and product

Asked for: balanced chemical equation

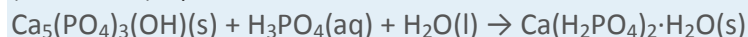
Strategy:

A Identify the product and the reactants and then write the unbalanced chemical equation.

B Follow the steps for balancing a chemical equation.

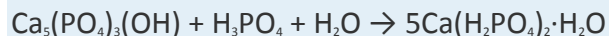
Solution:

A We must first identify the product and reactants and write an equation for the reaction. The formulas for hydroxyapatite and calcium dihydrogen phosphate monohydrate are given in the problem. Recall from Chapter 2 "Molecules, Ions, and Chemical Formulas" that phosphoric acid is H_3PO_4 . The initial (unbalanced) equation is as follows:

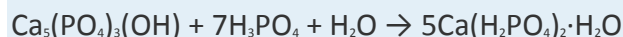


1. **B Identify the most complex substance.** We start by assuming that only one molecule or formula unit of the most complex substance, $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$, appears in the balanced chemical equation.

Adjust the coefficients. Because calcium is present in only one reactant and one product, we begin with it. One formula unit of $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ contains 5 calcium atoms, so we need 5 $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ on the right side:

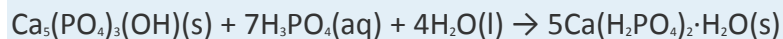


Balance polyatomic ions as a unit. It is usually easier to balance an equation if we recognize that certain combinations of atoms occur on both sides. In this equation, the polyatomic phosphate ion (PO_4^{3-}), shows up in three places.^[1] Thus it is easier to balance PO_4 as a unit rather than counting individual phosphorus and oxygen atoms. There are 10 PO_4 units on the right side but only 4 on the left. The simplest way to balance the PO_4 units is to place a coefficient of 7 in front of H_3PO_4 :



Although OH^- is also a polyatomic ion, it does not appear on both sides of the equation. So oxygen and hydrogen must be balanced separately.

Balance the remaining atoms. We now have 30 hydrogen atoms on the right side but only 24 on the left. We can balance the hydrogen atoms using the least complex substance, H_2O , by placing a coefficient of 4 in front of H_2O on the left side, giving a total of 4 H_2O molecules:



The equation is now balanced. Even though we have not explicitly balanced the oxygen atoms, there are 45 oxygen atoms on each side.

2. **Check your work.** Both sides of the equation contain 5 calcium atoms, 7 phosphorus atoms, 30 hydrogen atoms, and 45 oxygen atoms.

Exercise

Fermentation is a biochemical process that enables yeast cells to live in the absence of oxygen. Humans have exploited it for centuries to produce wine and beer and make bread rise. In fermentation, sugars such as glucose are converted to ethanol and carbon dioxide. Write a balanced chemical reaction for the fermentation of glucose.

Answer: $\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) \rightarrow 2\text{C}_2\text{H}_5\text{OH}(\text{l}) + 2\text{CO}_2(\text{g})$

Summary

In a chemical reaction, one or more substances are transformed to new substances. A chemical reaction is described by a **chemical equation**, an expression that gives the identities and quantities of the substances involved in a reaction. A chemical equation shows the starting compound(s)—the **reactants**—on the left and the final compound(s)—the **products**—on the right, separated by an arrow. In a *balanced chemical equation*, the numbers of atoms of each element and the total charge are the same on both sides of the equation. The number of atoms, molecules, or formula units of a reactant or product in a balanced chemical equation is the **coefficient** of that species. The **mole ratio** of two substances in a chemical reaction is the ratio of their coefficients in the balanced chemical equation.

KEY TAKEAWAY

- A chemical reaction is described by a chemical equation that gives the identities and quantities of the reactants and the products.

CONCEPTUAL PROBLEMS

1. How does a balanced chemical equation agree with the law of definite proportions?
2. What is the difference between S_8 and 8S ? Use this example to explain why subscripts in a formula must not be changed.
3. What factors determine whether a chemical equation is balanced?

4. What information can be obtained from a balanced chemical equation? Does a balanced chemical equation give information about the rate of a reaction?

NUMERICAL PROBLEMS

1. Balance each chemical equation.
 - a. $\text{KI(aq)} + \text{Br}_2(\text{l}) \rightarrow \text{KBr(aq)} + \text{I}_2(\text{s})$
 - b. $\text{MnO}_2(\text{s}) + \text{HCl(aq)} \rightarrow \text{MnCl}_2(\text{aq}) + \text{Cl}_2(\text{g}) + \text{H}_2\text{O(l)}$
 - c. $\text{Na}_2\text{O(s)} + \text{H}_2\text{O(l)} \rightarrow \text{NaOH(aq)}$
 - d. $\text{Cu(s)} + \text{AgNO}_3(\text{aq}) \rightarrow \text{Cu(NO}_3)_2(\text{aq}) + \text{Ag(s)}$
 - e. $\text{SO}_2(\text{g}) + \text{H}_2\text{O(l)} \rightarrow \text{H}_2\text{SO}_3(\text{aq})$
 - f. $\text{S}_2\text{Cl}_2(\text{l}) + \text{NH}_3(\text{l}) \rightarrow \text{S}_4\text{N}_4(\text{s}) + \text{S}_8(\text{s}) + \text{NH}_4\text{Cl(s)}$
2. Balance each chemical equation.
 - a. $\text{Be(s)} + \text{O}_2(\text{g}) \rightarrow \text{BeO(s)}$
 - b. $\text{N}_2\text{O}_3(\text{g}) + \text{H}_2\text{O(l)} \rightarrow \text{HNO}_2(\text{aq})$
 - c. $\text{Na(s)} + \text{H}_2\text{O(l)} \rightarrow \text{NaOH(aq)} + \text{H}_2(\text{g})$
 - d. $\text{CaO(s)} + \text{HCl(aq)} \rightarrow \text{CaCl}_2(\text{aq}) + \text{H}_2\text{O(l)}$
 - e. $\text{CH}_3\text{NH}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O(g)} + \text{CO}_2(\text{g}) + \text{N}_2(\text{g})$
 - f. $\text{Fe(s)} + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{FeSO}_4(\text{aq}) + \text{H}_2(\text{g})$
3. Balance each chemical equation.
 - a. $\text{N}_2\text{O}_5(\text{g}) \rightarrow \text{NO}_2(\text{g}) + \text{O}_2(\text{g})$
 - b. $\text{NaNO}_3(\text{s}) \rightarrow \text{NaNO}_2(\text{s}) + \text{O}_2(\text{g})$
 - c. $\text{Al(s)} + \text{NH}_4\text{NO}_3(\text{s}) \rightarrow \text{N}_2(\text{g}) + \text{H}_2\text{O(l)} + \text{Al}_2\text{O}_3(\text{s})$
 - d. $\text{C}_3\text{H}_5\text{N}_3\text{O}_9(\text{l}) \rightarrow \text{CO}_2(\text{g}) + \text{N}_2(\text{g}) + \text{H}_2\text{O(g)} + \text{O}_2(\text{g})$
 - e. reaction of butane with excess oxygen
 - f. $\text{IO}_2\text{F(s)} + \text{BrF}_3(\text{l}) \rightarrow \text{IF}_5(\text{l}) + \text{Br}_2(\text{l}) + \text{O}_2(\text{g})$
4. Balance each chemical equation.
 - a. $\text{H}_2\text{S(g)} + \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O(l)} + \text{S}_8(\text{s})$
 - b. $\text{KCl(aq)} + \text{HNO}_3(\text{aq}) + \text{O}_2(\text{g}) \rightarrow \text{KNO}_3(\text{aq}) + \text{Cl}_2(\text{g}) + \text{H}_2\text{O(l)}$
 - c. $\text{NH}_3(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{NO(g)} + \text{H}_2\text{O(g)}$
 - d. $\text{CH}_4(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{CO(g)} + \text{H}_2(\text{g})$

- e. $\text{NaF(aq)} + \text{Th(NO}_3)_4\text{(aq)} \rightarrow \text{NaNO}_3\text{(aq)} + \text{ThF}_4\text{(s)}$
 - f. $\text{Ca}_5(\text{PO}_4)_3\text{F(s)} + \text{H}_2\text{SO}_4\text{(aq)} + \text{H}_2\text{O(l)} \rightarrow \text{H}_3\text{PO}_4\text{(aq)} + \text{CaSO}_4 \cdot 2\text{H}_2\text{O(s)} + \text{HF(aq)}$
5. Balance each chemical equation.
- a. $\text{NaCl(aq)} + \text{H}_2\text{SO}_4\text{(aq)} \rightarrow \text{Na}_2\text{SO}_4\text{(aq)} + \text{HCl(g)}$
 - b. $\text{K(s)} + \text{H}_2\text{O(l)} \rightarrow \text{KOH(aq)} + \text{H}_2\text{(g)}$
 - c. reaction of octane with excess oxygen
 - d. $\text{S}_8\text{(s)} + \text{Cl}_2\text{(g)} \rightarrow \text{S}_2\text{Cl}_2\text{(l)}$
 - e. $\text{CH}_3\text{OH(l)} + \text{I}_2\text{(s)} + \text{P}_4\text{(s)} \rightarrow \text{CHI}_3\text{(l)} + \text{H}_3\text{PO}_4\text{(aq)} + \text{H}_2\text{O(l)}$
 - f. $(\text{CH}_3)_3\text{Al(s)} + \text{H}_2\text{O(l)} \rightarrow \text{CH}_4\text{(g)} + \text{Al(OH)}_3\text{(s)}$
6. Write a balanced chemical equation for each reaction.
- a. Aluminum reacts with bromine.
 - b. Sodium reacts with chlorine.
 - c. Aluminum hydroxide and acetic acid react to produce aluminum acetate and water.
 - d. Ammonia and oxygen react to produce nitrogen monoxide and water.
 - e. Nitrogen and hydrogen react at elevated temperature and pressure to produce ammonia.
 - f. An aqueous solution of barium chloride reacts with a solution of sodium sulfate.
7. Write a balanced chemical equation for each reaction.
- a. Magnesium burns in oxygen.
 - b. Carbon dioxide and sodium oxide react to produce sodium carbonate.
 - c. Aluminum reacts with hydrochloric acid.
 - d. An aqueous solution of silver nitrate reacts with a solution of potassium chloride.
 - e. Methane burns in oxygen.
 - f. Sodium nitrate and sulfuric acid react to produce sodium sulfate and nitric acid.

[1] In H_3PO_4 , the phosphate ion is combined with three H^+ ions to make phosphoric acid (H_3PO_4), whereas in $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ it is combined with two H^+ ions to give the dihydrogen phosphate ion.

3.4 Mass Relationships in Chemical Equations

LEARNING OBJECTIVE

1. To calculate the quantities of compounds produced or consumed in a chemical reaction.

A balanced chemical equation gives the identity of the reactants and the products as well as the accurate number of molecules or moles of each that are consumed or produced. Stoichiometry is a collective term for the quantitative relationships between the masses, the numbers of moles, and the numbers of particles (atoms, molecules, and ions) of the reactants and the products in a balanced chemical equation. A stoichiometric quantity is the amount of product or reactant specified by the coefficients in a balanced chemical equation. In , for example, you learned how to express the stoichiometry of the reaction for the ammonium dichromate volcano in terms of the atoms, ions, or molecules involved and the numbers of moles, grams, and formula units of each (recognizing, for instance, that 1 mol of ammonium dichromate produces 4 mol of water). This section describes how to use the stoichiometry of a reaction to answer questions like the following: How much oxygen is needed to ensure complete combustion of a given amount of isooctane? (This information is crucial to the design of nonpolluting and efficient automobile engines.) How many grams of pure gold can be obtained from a ton of low-grade gold ore? (The answer determines whether the ore deposit is worth mining.) If an industrial plant must produce a certain number of tons of sulfuric acid per week, how much elemental sulfur must arrive by rail each week?

All these questions can be answered using the concepts of the mole and molar and formula masses, along with the coefficients in the appropriate balanced chemical equation.

Stoichiometry Problems

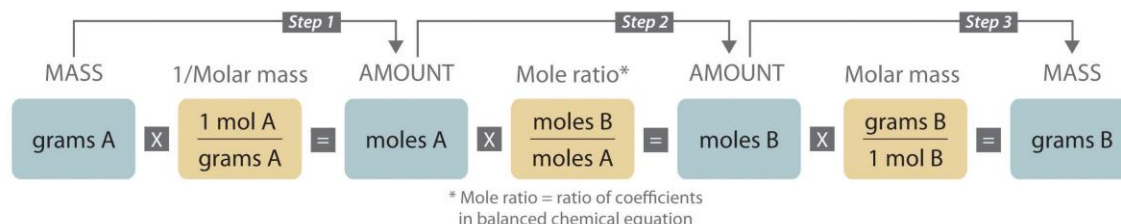
When we carry out a reaction in either an industrial setting or a laboratory, it is easier to work with *masses* of substances than with the numbers of molecules or moles. The general method for converting from the mass of any reactant or product to the mass of any other reactant or product using a balanced chemical equation is outlined in and described in the following text.

Steps in Converting between Masses of Reactant and Product

1. Convert the mass of one substance (substance A) to the corresponding number of moles using its molar mass.
2. From the balanced chemical equation, obtain the number of moles of another substance (B) from the number of moles of substance A using the appropriate mole ratio (the ratio of their coefficients).
3. Convert the number of moles of substance B to mass using its molar mass. It is important to remember that some species are in excess by virtue of the reaction conditions. For example, if a substance reacts with the oxygen in air, then oxygen is in obvious (but unstated) excess.

Converting amounts of substances to moles—and vice versa—is the key to all stoichiometry problems, whether the amounts are given in units of mass (grams or kilograms), weight (pounds or tons), or volume (liters or gallons).

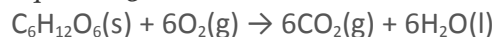
Figure 3.11 A Flowchart for Stoichiometric Calculations Involving Pure Substances



The molar masses of the reactants and the products are used as conversion factors so that you can calculate the mass of product from the mass of reactant and vice versa.

To illustrate this procedure, let's return to the combustion of glucose. We saw earlier that glucose reacts with oxygen to produce carbon dioxide and water:

Equation 3.20



Just before a chemistry exam, suppose a friend reminds you that glucose is the major fuel used by the human brain.

You therefore decide to eat a candy bar to make sure that your brain doesn't run out of energy during the exam (even though there is no direct evidence that consumption of candy bars improves performance on chemistry exams). If a typical 2 oz candy bar contains the equivalent of 45.3 g of glucose and the glucose is completely converted to carbon dioxide during the exam, how many grams of carbon dioxide will you produce and exhale into the exam room?

The initial step in solving a problem of this type must be to write the balanced chemical equation for the reaction.

Inspection of shows that it is balanced as written, so we can proceed to the strategy outlined in , adapting it as follows:

1. Use the molar mass of glucose (to one decimal place, 180.2 g/mol) to determine the number of moles of glucose in the candy bar:

$$\text{moles glucose} = 45.3 \text{ g glucose} \times \frac{1 \text{ mol glucose}}{180.2 \text{ g glucose}} = 0.251 \text{ mol glucose}$$
2. According to the balanced chemical equation, 6 mol of CO_2 is produced per mole of glucose; the mole ratio of CO_2 to glucose is therefore 6:1. The number of moles of CO_2 produced is thus

$$\text{moles CO}_2 = \text{mol glucose} \times \frac{6 \text{ mol CO}_2}{1 \text{ mol glucose}} = 0.251 \text{ mol glucose} \times \frac{6 \text{ mol CO}_2}{1 \text{ mol glucose}} = 1.51 \text{ mol CO}_2$$
3. Use the molar mass of CO_2 (44.010 g/mol) to calculate the mass of CO_2 corresponding to 1.51 mol of CO_2 :

$$\text{mass of CO}_2 = 1.51 \text{ mol CO}_2 \times 44.010 \text{ g CO}_2 / 1 \text{ mol CO}_2 = 66.5 \text{ g CO}_2$$

We can summarize these operations as follows:

$$45.3 \text{ g glucose} \times 1 \text{ mol glucose} / 180.2 \text{ g glucose} \times 6 \text{ mol CO}_2 / 1 \text{ mol glucose} \times 44.010 \text{ g CO}_2 / 1 \text{ mol CO}_2 = 66.4 \text{ g CO}_2$$

Discrepancies between the two values are attributed to rounding errors resulting from using stepwise calculations in steps 1–3. (For more information about rounding and significant digits, see Essential Skills 1 in , .) In , you will discover that this amount of gaseous carbon dioxide occupies an enormous volume—more than 33 L. We could use similar methods to calculate the amount of oxygen consumed or the amount of water produced.

We just used the balanced chemical equation to calculate the mass of product that is formed from a certain amount of reactant. We can also use the balanced chemical equation to determine the masses of reactants that are necessary to form a certain amount of product or, as shown in Example 11, the mass of one reactant that is required to consume a given mass of another reactant.

EXAMPLE 11

The combustion of hydrogen with oxygen to produce gaseous water is extremely vigorous, producing one of the hottest flames known. Because so much energy is released for a given mass of hydrogen or oxygen, this reaction was used to fuel the NASA (National Aeronautics and Space Administration) space shuttles, which have recently been retired from service. NASA engineers calculated the exact amount of each reactant needed for the flight to make sure that the shuttles did not carry excess fuel into orbit. Calculate how many tons of hydrogen a space shuttle needed to carry for each 1.00 tn of oxygen (1 tn = 2000 lb).

Given: reactants, products, and mass of one reactant

Asked for: mass of other reactant

Strategy:

A Write the balanced chemical equation for the reaction.

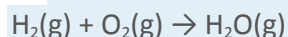
B Convert mass of oxygen to moles. From the mole ratio in the balanced chemical equation, determine the number of moles of hydrogen required. Then convert the moles of hydrogen to the equivalent mass in tons.

Solution:

We use the same general strategy for solving stoichiometric calculations as in the preceding example.

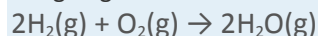
Because the amount of oxygen is given in tons rather than grams, however, we also need to convert tons to units of mass in grams. Another conversion is needed at the end to report the final answer in tons.

A We first use the information given to write a balanced chemical equation. Because we know the identity of both the reactants and the product, we can write the reaction as follows:



This equation is not balanced because there are two oxygen atoms on the left side and only one on the right.

Assigning a coefficient of 2 to both H_2O and H_2 gives the balanced chemical equation:



Thus 2 mol of H_2 react with 1 mol of O_2 to produce 2 mol of H_2O .

B To convert tons of oxygen to units of mass in grams, we multiply by the appropriate conversion factors:

$$\text{mass of O}_2 = 1.00 \text{ tn} \times 2000 \text{ lb tn} \times 453.6 \text{ g lb} = 9.07 \times 10^5 \text{ g O}_2$$

Using the molar mass of O_2 (32.00 g/mol, to four significant figures), we can calculate the number of moles of O_2 contained in this mass of O_2 :

$$\text{mol O}_2 = 9.07 \times 10^5 \text{ g O}_2 \times \frac{1 \text{ mol O}_2}{32.00 \text{ g O}_2} = 2.83 \times 10^4 \text{ mol O}_2$$

Now use the coefficients in the balanced chemical equation to obtain the number of moles of H_2 needed to react with this number of moles of O_2 :

$$\text{mol H}_2 = \text{mol O}_2 \times \frac{2 \text{ mol H}_2}{1 \text{ mol O}_2} = 2.83 \times 10^4 \text{ mol O}_2 \times \frac{2 \text{ mol H}_2}{1 \text{ mol O}_2} = 5.66 \times 10^4 \text{ mol H}_2$$

The molar mass of H_2 (2.016 g/mol) allows us to calculate the corresponding mass of H_2 :

$$\text{mass of H}_2 = 5.66 \times 10^4 \text{ mol H}_2 \times 2.016 \text{ g H}_2 \text{ mol H}_2 = 1.14 \times 10^5 \text{ g H}_2$$

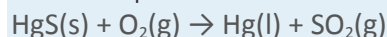
Finally, convert the mass of H_2 to the desired units (tons) by using the appropriate conversion factors:

$$\text{tons H}_2 = 1.14 \times 10^5 \text{ g H}_2 \times \frac{1 \text{ lb}}{453.6 \text{ g}} \times \frac{1 \text{ tn}}{2000 \text{ lb}} = 0.126 \text{ tn H}_2$$

The space shuttle had to be designed to carry 0.126 tn of H_2 for each 1.00 tn of O_2 . Even though 2 mol of H_2 are needed to react with each mole of O_2 , the molar mass of H_2 is so much smaller than that of O_2 that only a relatively small mass of H_2 is needed compared to the mass of O_2 .

Exercise

Alchemists produced elemental mercury by roasting the mercury-containing ore cinnabar (HgS) in air:



The volatility and toxicity of mercury make this a hazardous procedure, which likely shortened the life span of many alchemists. Given 100 g of cinnabar, how much elemental mercury can be produced from this reaction?

Answer: 86.2 g

Limiting Reactants

In all the examples discussed thus far, the reactants were assumed to be present in stoichiometric quantities. Consequently, none of the reactants was left over at the end of the reaction. This is often desirable, as in the case of a space shuttle, where excess oxygen or hydrogen was not only extra freight to be hauled into orbit but also an explosion hazard. More often, however, reactants are present in mole ratios that are not the same as the ratio of the coefficients in the balanced chemical equation. As a result, one or more of them will not be used up completely but will be left over when the reaction is completed. In this situation, the amount of product that can be obtained is limited by the amount of only one of the reactants. The reactant that restricts the amount of product obtained is called the limiting reactant. The reactant that remains after a reaction has gone to completion is *in excess*.

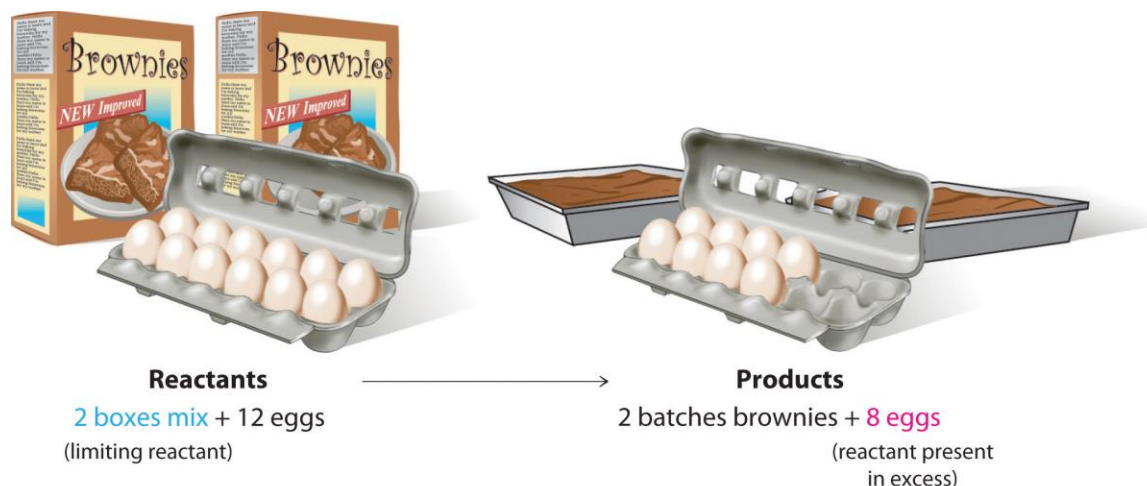
To be certain you understand these concepts, let's first consider a nonchemical example. Assume you have invited some friends for dinner and want to bake brownies for dessert. You find two boxes of brownie mix in your pantry and see that each package requires two eggs. The balanced equation for brownie preparation is thus

Equation 3.21

1 box mix + 2 eggs $\rightarrow$ 1 batch brownies

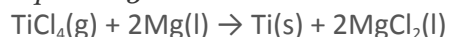
If you have a dozen eggs, which ingredient will determine the number of batches of brownies that you can prepare? Because each box of brownie mix requires two eggs and you have two boxes, you need four eggs. Twelve eggs is eight more eggs than you need. Although the ratio of eggs to boxes is 2:1, the ratio in your possession is 6:1. Hence the eggs are the ingredient (reactant) present in excess, and the brownie mix is the limiting reactant (). Even if you had a refrigerator full of eggs, you could make only two batches of brownies.

Figure 3.12 The Concept of a Limiting Reactant in the Preparation of Brownies



Let's now turn to a chemical example of a limiting reactant: the production of pure titanium. This metal is fairly light (45% lighter than steel and only 60% heavier than aluminum) and has great mechanical strength (as strong as steel and twice as strong as aluminum). Because it is also highly resistant to corrosion and can withstand extreme temperatures, titanium has many applications in the aerospace industry. Titanium is also used in medical implants and portable computer housings because it is light and resistant to corrosion. Although titanium is the ninth most common element in Earth's crust, it is relatively difficult to extract from its ores. In the first step of the extraction process, titanium-containing oxide minerals react with solid carbon and chlorine gas to form titanium tetrachloride (TiCl_4) and carbon dioxide. Titanium tetrachloride is then converted to metallic titanium by reaction with magnesium metal at high temperature:

Equation 3.22



Because titanium ores, carbon, and chlorine are all rather inexpensive, the high price of titanium (about \$100 per kilogram) is largely due to the high cost of magnesium metal. Under these circumstances, magnesium metal is the limiting reactant in the production of metallic titanium.

Suppose you have 1.00 kg of titanium tetrachloride and 200 g of magnesium metal. How much titanium metal can you produce according to ? Solving this type of problem requires that you carry out the following steps:

1. Determine the number of moles of each reactant.
2. Compare the mole ratio of the reactants with the ratio in the balanced chemical equation to determine which reactant is limiting.
3. Calculate the number of moles of product that can be obtained from the limiting reactant.

- Convert the number of moles of product to mass of product.

- To determine the number of moles of reactants present, you must calculate or look up their molar masses: 189.679 g/mol for titanium tetrachloride and 24.305 g/mol for magnesium. The number of moles of each is calculated as follows:

$$\begin{aligned}\text{moles TiCl}_4 &= \frac{\text{mass TiCl}_4}{\text{molar mass TiCl}_4} = \frac{1000 \text{ g TiCl}_4}{189.679 \text{ g TiCl}_4} = 5.272 \text{ mol TiCl}_4 \\ \text{moles Mg} &= \frac{\text{mass Mg}}{\text{molar mass Mg}} = \frac{200 \text{ g Mg}}{24.305 \text{ g Mg}} = 8.23 \text{ mol Mg}\end{aligned}$$

- You have more moles of magnesium than of titanium tetrachloride, but the ratio is only

$$\frac{\text{mol Mg}}{\text{mol TiCl}_4} = \frac{8.23 \text{ mol}}{5.272 \text{ mol}} = 1.56$$

Because the ratio of the coefficients in the balanced chemical equation is

$$2 \text{ mol Mg} : 1 \text{ mol TiCl}_4 = 2$$

you do not have enough magnesium to react with all the titanium tetrachloride. If this point is not clear

from the mole ratio, you should calculate the number of moles of one reactant that is required for

complete reaction of the other reactant. For example, you have 8.23 mol of Mg, so you need $(8.23 \div 2) =$

4.12 mol of TiCl_4 for complete reaction. Because you have 5.272 mol of TiCl_4 , titanium tetrachloride is

present in excess. Conversely, 5.272 mol of TiCl_4 requires $2 \times 5.272 = 10.54$ mol of Mg, but you have only 8.23 mol. So *magnesium is the limiting reactant*.

- Because magnesium is the limiting reactant, the number of moles of magnesium determines the number of moles of titanium that can be formed:

$$\text{moles Ti} = \frac{\text{mol Mg}}{2} = \frac{8.23 \text{ mol Mg}}{2} = 4.12 \text{ mol Ti}$$

Thus only 4.12 mol of Ti can be formed.

- To calculate the mass of titanium metal that you can obtain, multiply the number of moles of titanium by the molar mass of titanium (47.867 g/mol):

$$\text{moles Ti} = \text{mass Ti} \times \frac{1 \text{ mol Ti}}{47.867 \text{ g Ti}} = 4.12 \text{ mol Ti} \times 47.867 \text{ g Ti} = 197 \text{ g Ti}$$

Here is a simple and reliable way to identify the limiting reactant in any problem of this sort:

- Calculate the number of moles of each reactant present: 5.272 mol of TiCl_4 and 8.23 mol of Mg.
- Divide the actual number of moles of each reactant by its stoichiometric coefficient in the balanced chemical equation:

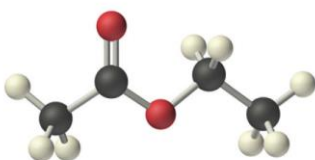
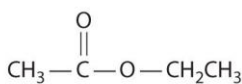
$$\frac{\text{TiCl}_4}{5} : \frac{5.272 \text{ mol (actual)}}{1 \text{ mol (stoich)}} = 5.272 \quad \frac{\text{Mg}}{2} : \frac{8.23 \text{ mol (actual)}}{2 \text{ mol (stoich)}} = 4.12$$

3. The reactant with the smallest mole ratio is limiting. Magnesium, with a calculated stoichiometric mole ratio of 4.12, is the limiting reactant.

As you learned in , density is the mass per unit volume of a substance. If we are given the density of a substance, we can use it in stoichiometric calculations involving liquid reactants and/or products, as Example 12 demonstrates.

EXAMPLE 12

Ethyl acetate ($\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$) is the solvent in many fingernail polish removers and is used to decaffeinate coffee beans and tea leaves. It is prepared by reacting ethanol ($\text{C}_2\text{H}_5\text{OH}$) with acetic acid ($\text{CH}_3\text{CO}_2\text{H}$); the other product is water. A small amount of sulfuric acid is used to accelerate the reaction, but the sulfuric acid is not consumed and does not appear in the balanced chemical equation. Given 10.0 mL each of acetic acid and ethanol, how many grams of ethyl acetate can be prepared from this reaction? The densities of acetic acid and ethanol are 1.0492 g/mL and 0.7893 g/mL, respectively.



Ethyl acetate

Given: reactants, products, and volumes and densities of reactants

Asked for: mass of product

Strategy:

A Balance the chemical equation for the reaction.

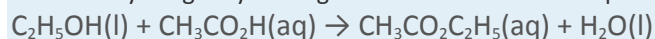
B Use the given densities to convert from volume to mass. Then use each molar mass to convert from mass to moles.

C Using mole ratios, determine which substance is the limiting reactant. After identifying the limiting reactant, use mole ratios based on the number of moles of limiting reactant to determine the number of moles of product.

D Convert from moles of product to mass of product.

Solution:

A We always begin by writing the balanced chemical equation for the reaction:



B We need to calculate the number of moles of ethanol and acetic acid that are present in 10.0 mL of each.

Recall from that the density of a substance is the mass divided by the volume:

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

Rearranging this expression gives $\text{mass} = (\text{density})(\text{volume})$. We can replace mass by the product of the density and the volume to calculate the number of moles of each substance in 10.0 mL (remember, 1 mL = 1 cm³):

$\text{moles C}_2\text{H}_5\text{OH} = \frac{\text{mass C}_2\text{H}_5\text{OH}}{\text{molar mass C}_2\text{H}_5\text{OH}} = \frac{\text{volume C}_2\text{H}_5\text{OH} \times \text{density C}_2\text{H}_5\text{OH}}{\text{molar mass C}_2\text{H}_5\text{OH}} = \frac{10.0 \text{ mL C}_2\text{H}_5\text{OH} \times 0.7893 \text{ g C}_2\text{H}_5\text{OH} / 1 \text{ mL C}_2\text{H}_5\text{OH}}{46.07 \text{ g C}_2\text{H}_5\text{OH} / \text{mol C}_2\text{H}_5\text{OH}} = 0.171 \text{ mol C}_2\text{H}_5\text{OH}$
 $\text{moles CH}_3\text{CO}_2\text{H} = \frac{\text{mass CH}_3\text{CO}_2\text{H}}{\text{molar mass CH}_3\text{CO}_2\text{H}} = \frac{\text{volume CH}_3\text{CO}_2\text{H} \times \text{density CH}_3\text{CO}_2\text{H}}{\text{molar mass CH}_3\text{CO}_2\text{H}} = \frac{10.0 \text{ mL CH}_3\text{CO}_2\text{H} \times 1.0492 \text{ g CH}_3\text{CO}_2\text{H} / 1 \text{ mL CH}_3\text{CO}_2\text{H}}{60.05 \text{ g CH}_3\text{CO}_2\text{H} / \text{mol CH}_3\text{CO}_2\text{H}} = 0.175 \text{ mol CH}_3\text{CO}_2\text{H}$

C The number of moles of acetic acid exceeds the number of moles of ethanol. Because the reactants both have coefficients of 1 in the balanced chemical equation, the mole ratio is 1:1. We have 0.171 mol of ethanol and 0.175 mol of acetic acid, so ethanol is the limiting reactant and acetic acid is in excess. The coefficient in the balanced chemical equation for the product (ethyl acetate) is also 1, so the mole ratio of ethanol and ethyl acetate is also 1:1. This means that given 0.171 mol of ethanol, the amount of ethyl acetate produced must also be 0.171 mol:

$\text{moles ethyl acetate} = \text{mol ethanol} \times \frac{1 \text{ mol ethyl acetate}}{1 \text{ mol ethanol}} = 0.171 \text{ mol C}_2\text{H}_5\text{OH} \times \frac{1 \text{ mol CH}_3\text{CO}_2\text{C}_2\text{H}_5}{1 \text{ mol C}_2\text{H}_5\text{OH}} = 0.171 \text{ mol CH}_3\text{CO}_2\text{C}_2\text{H}_5$

D The final step is to determine the mass of ethyl acetate that can be formed, which we do by multiplying the number of moles by the molar mass:

$\text{mass of ethyl acetate} = \text{mol ethyl acetate} \times \text{molar mass ethyl acetate} = 0.171 \text{ mol CH}_3\text{CO}_2\text{C}_2\text{H}_5 \times 88.11 \text{ g CH}_3\text{CO}_2\text{C}_2\text{H}_5 / \text{mol CH}_3\text{CO}_2\text{C}_2\text{H}_5 = 15.1 \text{ g CH}_3\text{CO}_2\text{C}_2\text{H}_5$

Thus 15.1 g of ethyl acetate can be prepared in this reaction. If necessary, you could use the density of ethyl acetate (0.9003 g/cm³) to determine the volume of ethyl acetate that could be produced:

$\text{volume of ethyl acetate} = \frac{15.1 \text{ g CH}_3\text{CO}_2\text{C}_2\text{H}_5}{0.9003 \text{ g CH}_3\text{CO}_2\text{C}_2\text{H}_5 / \text{mL CH}_3\text{CO}_2\text{C}_2\text{H}_5} = 16.8 \text{ mL CH}_3\text{CO}_2\text{C}_2\text{H}_5$

Exercise

Under appropriate conditions, the reaction of elemental phosphorus and elemental sulfur produces the compound P₄S₁₀. How much P₄S₁₀ can be prepared starting with 10.0 g of P₄ and 30.0 g of S₈?

Answer: 35.9 g

Percent Yield

You have learned that when reactants are not present in stoichiometric quantities, the limiting reactant determines the maximum amount of product that can be formed from the reactants. The amount of product calculated in this way is the theoretical yield, the amount you would obtain if the reaction occurred perfectly and your method of purifying the product were 100% efficient.

In reality, you almost always obtain less product than is theoretically possible because of mechanical losses (such as spilling), separation procedures that are not 100% efficient, competing reactions that form undesired products, and reactions that simply do not go all the way to completion, thus resulting in a mixture of products and reactants. This last possibility is a common occurrence and is the subject of . So the actual yield, the measured mass of products obtained from a reaction, is almost always less than the theoretical yield (often much less). The percent yield of a reaction is the ratio of the actual yield to the theoretical yield, multiplied by 100 to give a percentage:

Equation 3.23

$$\text{percent yield} = \frac{\text{actual yield (g)}}{\text{theoretical yield (g)}} \times 100$$

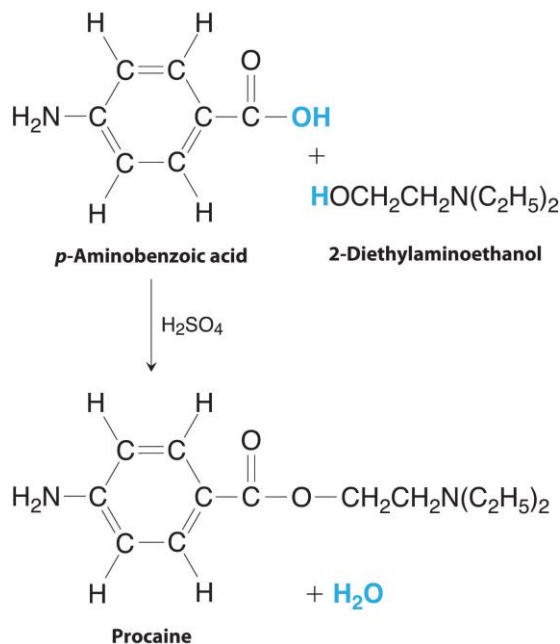
The method used to calculate the percent yield of a reaction is illustrated in Example 13.

EXAMPLE 13

Procaine is a key component of Novocain, an injectable local anesthetic used in dental work and minor surgery. Procaine can be prepared in the presence of H_2SO_4 (indicated above the arrow) by the reaction

$$\text{C}_7\text{H}_7\text{NO}_2 \text{ } p\text{-aminobenzoic acid} + \text{C}_6\text{H}_{15}\text{NO}_2 \text{ } 2\text{-diethylaminoethanol} \rightarrow \text{H}_2\text{SO}_4 \text{ } \text{C}_{13}\text{H}_{20}\text{N}_2\text{O}_2 \text{ } \text{procaine} + \text{H}_2\text{O}$$

If we carried out this reaction using 10.0 g of *p*-aminobenzoic acid and 10.0 g of 2-diethylaminoethanol, and we isolated 15.7 g of procaine, what was the percent yield?



Given: masses of reactants and product

Asked for: percent yield

Strategy:

A Write the balanced chemical equation.

B Convert from mass of reactants and product to moles using molar masses and then use mole ratios to determine which is the limiting reactant. Based on the number of moles of the limiting reactant, use mole ratios to determine the theoretical yield.

C Calculate the percent yield by dividing the actual yield by the theoretical yield and multiplying by 100.

Solution:

A From the formulas given for the reactants and the products, we see that the chemical equation is balanced as written. According to the equation, 1 mol of each reactant combines to give 1 mol of product plus 1 mol of water.

B To determine which reactant is limiting, we need to know their molar masses, which are calculated from their structural formulas: *p*-aminobenzoic acid ($\text{C}_7\text{H}_7\text{NO}_2$), 137.14 g/mol; diethylaminoethanol ($\text{C}_6\text{H}_{15}\text{NO}$), 117.19 g/mol. Thus the reaction used the following numbers of moles of reactants:

moles *p*-aminobenzoic acid = $10.0 \text{ g} \times \frac{1 \text{ mol}}{137.14 \text{ g}} = 0.0729 \text{ mol}$ *p*-aminobenzoic acid

moles 2-diethylaminoethanol = $10.0 \text{ g} \times \frac{1 \text{ mol}}{117.19 \text{ g}} = 0.0853 \text{ mol}$ 2-diethylaminoethanol

The reaction requires a 1:1 mole ratio of the two reactants, so *p*-aminobenzoic acid is the limiting reactant. Based on the coefficients in the balanced chemical equation, 1 mol of *p*-aminobenzoic acid yields 1 mol of procaine. We can therefore obtain only a maximum of 0.0729 mol of procaine. To calculate the corresponding mass of procaine, we use its structural formula ($C_{13}H_{20}N_2O_2$) to calculate its molar mass, which is 236.31 g/mol.

theoretical yield of procaine = $0.0729 \text{ mol} \times 236.31 \text{ g/mol} = 17.2 \text{ g}$

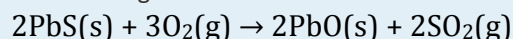
C The actual yield was only 15.7 g of procaine, so the percent yield was

percent yield = $15.7 \text{ g} / 17.2 \text{ g} \times 100 = 91.3 \%$

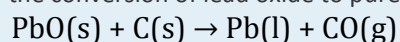
(If the product were pure and dry, this yield would indicate that we have very good lab technique!)

Exercise

Lead was one of the earliest metals to be isolated in pure form. It occurs as concentrated deposits of a distinctive ore called galena (PbS), which is easily converted to lead oxide (PbO) in 100% yield by roasting in air via the following reaction:



The resulting PbO is then converted to the pure metal by reaction with charcoal. Because lead has such a low melting point (327°C), it runs out of the ore-charcoal mixture as a liquid that is easily collected. The reaction for the conversion of lead oxide to pure lead is as follows:



If 93.3 kg of PbO is heated with excess charcoal and 77.3 kg of pure lead is obtained, what is the percent yield?

Answer: 89.2%

Percent yield can range from 0% to 100%.^[1] A 100% yield means that everything worked perfectly, and you obtained all the product that could have been produced. Anyone who has tried to do something as simple as fill a salt shaker or add oil to a car's engine without spilling knows how unlikely a 100% yield is. At the other extreme, a yield of 0% means that *no* product was obtained. A percent yield of 80%–90% is usually considered good to excellent; a yield of 50% is only fair. In part because of the problems and costs of waste disposal, industrial production facilities face considerable pressures to optimize the yields of products and make them as close to 100% as possible.

Summary

The **stoichiometry** of a reaction describes the relative amounts of reactants and products in a balanced chemical equation. A **stoichiometric quantity** of a reactant is the amount necessary to react completely with the other reactant(s). If a quantity of a reactant remains unconsumed after complete reaction has occurred, it is *in excess*. The reactant that is consumed first and limits the amount of product(s) that can be obtained is the **limiting reactant**. To identify the limiting reactant, calculate the number of moles of each reactant present and compare this ratio to the mole ratio of the reactants in the balanced chemical equation. The maximum amount of product(s) that can be obtained in a reaction from a given amount of reactant(s) is the **theoretical yield** of the reaction. The **actual yield** is the amount of product(s) actually obtained in the reaction; it cannot exceed the theoretical yield. The **percent yield** of a reaction is the ratio of the actual yield to the theoretical yield, expressed as a percentage.

KEY TAKEAWAY

- The stoichiometry of a balanced chemical equation identifies the maximum amount of product that can be obtained.

CONCEPTUAL PROBLEMS

1. Engineers use conservation of mass, called a “mass balance,” to determine the amount of product that can be obtained from a chemical reaction. Mass balance assumes that the total mass of reactants is equal to the total mass of products. Is this a chemically valid practice? Explain your answer.
2. Given the equation $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g})$, is it correct to say that 10 g of hydrogen will react with 10 g of oxygen to produce 20 g of water vapor?
3. What does it mean to say that a reaction is *stoichiometric*?
4. When sulfur is burned in air to produce sulfur dioxide, what is the limiting reactant? Explain your answer.
5. Is it possible for the percent yield to be greater than the theoretical yield? Justify your answer.

NUMERICAL PROBLEMS

Please be sure you are familiar with the topics discussed in Essential Skills 2 () before proceeding to the Numerical Problems.

1. What is the formula mass of each species?
 - a. ammonium chloride
 - b. sodium cyanide
 - c. magnesium hydroxide

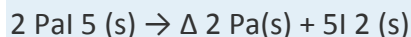
- d. calcium phosphate
 - e. lithium carbonate
 - f. hydrogen sulfite ion
2. What is the molecular or formula mass of each compound?
- a. potassium permanganate
 - b. sodium sulfate
 - c. hydrogen cyanide
 - d. potassium thiocyanate
 - e. ammonium oxalate
 - f. lithium acetate
3. How many moles are in each of the following?
- a. 10.76 g of Si
 - b. 8.6 g of Pb
 - c. 2.49 g of Mg
 - d. 0.94 g of La
 - e. 2.68 g of chlorine gas
 - f. 0.089 g of As
4. How many moles are in each of the following?
- a. 8.6 g of CO_2
 - b. 2.7 g of CaO
 - c. 0.89 g of KCl
 - d. 4.3 g of SrBr_2
 - e. 2.5 g of NaOH
 - f. 1.87 g of Ca(OH)_2
5. Convert the following to moles and millimoles.
- a. 1.68 g of Ba(OH)_2
 - b. 0.792 g of H_3PO_4
 - c. 3.21 g of K_2S
 - d. 0.8692 g of $\text{Cu(NO}_3)_2$

- e. 10.648 g of $\text{Ba}_3(\text{PO}_4)_2$
 - f. 5.79 g of $(\text{NH}_4)_2\text{SO}_4$
 - g. 1.32 g of $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$
 - h. 4.29 g of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$
6. Convert the following to moles and millimoles.
- a. 0.089 g of silver nitrate
 - b. 1.62 g of aluminum chloride
 - c. 2.37 g of calcium carbonate
 - d. 1.004 g of iron(II) sulfide
 - e. 2.12 g of dinitrogen pentoxide
 - f. 2.68 g of lead(II) nitrate
 - g. 3.02 g of ammonium phosphate
 - h. 5.852 g of sulfuric acid
 - i. 4.735 g of potassium dichromate
7. What is the mass of each substance in grams and milligrams?
- a. 5.68 mol of Ag
 - b. 2.49 mol of Sn
 - c. 0.0873 mol of Os
 - d. 1.74 mol of Si
 - e. 0.379 mol of H_2
 - f. 1.009 mol of Zr
8. What is the mass of each substance in grams and milligrams?
- a. 2.080 mol of CH_3OH
 - b. 0.288 mol of P_4
 - c. 3.89 mol of ZnCl_2
 - d. 1.800 mol of $\text{Fe}(\text{CO})_5$
 - e. 0.798 mol of S_8
 - f. 4.01 mol of NaOH
9. What is the mass of each compound in kilograms?

- a. 6.38 mol of P_4O_{10}
 - b. 2.26 mol of $\text{Ba}(\text{OH})_2$
 - c. 4.35 mol of K_3PO_4
 - d. 2.03 mol of $\text{Ni}(\text{ClO}_3)_2$
 - e. 1.47 mol of NH_4NO_3
 - f. 0.445 mol of $\text{Co}(\text{NO}_3)_3$
10. How many atoms are contained in each?
- a. 2.32 mol of Bi
 - b. 0.066 mol of V
 - c. 0.267 mol of Ru
 - d. 4.87 mol of C
 - e. 2.74 g of I_2
 - f. 1.96 g of Cs
 - g. 7.78 g of O_2
11. Convert each number of atoms to milligrams.
- a. 5.89×10^{22} Pt atoms
 - b. 2.899×10^{21} Hg atoms
 - c. 4.826×10^{22} atoms of chlorine
12. Write a balanced chemical equation for each reaction and then determine which reactant is in excess.
- a. 2.46 g barium(s) plus 3.89 g bromine(l) in water to give barium bromide
 - b. 1.44 g bromine(l) plus 2.42 g potassium iodide(s) in water to give potassium bromide and iodine
 - c. 1.852 g of Zn metal plus 3.62 g of sulfuric acid in water to give zinc sulfate and hydrogen gas
 - d. 0.147 g of iron metal reacts with 0.924 g of silver acetate in water to give iron(II) acetate and silver metal
 - e. 3.142 g of ammonium phosphate reacts with 1.648 g of barium hydroxide in water to give ammonium hydroxide and barium phosphate

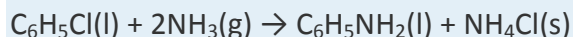
13. Under the proper conditions, ammonia and oxygen will react to form dinitrogen monoxide (nitrous oxide, also called laughing gas) and water. Write a balanced chemical equation for this reaction. Determine which reactant is in excess for each combination of reactants.
- 24.6 g of ammonia and 21.4 g of oxygen
 - 3.8 mol of ammonia and 84.2 g of oxygen
 - 3.6×10^{24} molecules of ammonia and 318 g of oxygen
 - 2.1 mol of ammonia and 36.4 g of oxygen
14. When a piece of zinc metal is placed in aqueous hydrochloric acid, zinc chloride is produced, and hydrogen gas is evolved. Write a balanced chemical equation for this reaction. Determine which reactant is in excess for each combination of reactants.
- 12.5 g of HCl and 7.3 g of Zn
 - 6.2 mol of HCl and 100 g of Zn
 - 2.1×10^{23} molecules of Zn and 26.0 g of HCl
 - 3.1 mol of Zn and 97.4 g of HCl
15. Determine the mass of each reactant needed to give the indicated amount of product. Be sure that the chemical equations are balanced.
- $\text{NaI(aq)} + \text{Cl}_2(\text{g}) \rightarrow \text{NaCl(aq)} + \text{I}_2(\text{s})$; 1.0 mol of NaCl
 - $\text{NaCl(aq)} + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{HCl(g)} + \text{Na}_2\text{SO}_4(\text{aq})$; 0.50 mol of HCl
 - $\text{NO}_2(\text{g}) + \text{H}_2\text{O(l)} \rightarrow \text{HNO}_2(\text{aq}) + \text{HNO}_3(\text{aq})$; 1.5 mol of HNO_3
16. Determine the mass of each reactant needed to give the indicated amount of product. Be sure that the chemical equations are balanced.
- $\text{AgNO}_3(\text{aq}) + \text{CaCl}_2(\text{s}) \rightarrow \text{AgCl(s)} + \text{Ca(NO}_3)_2(\text{aq})$; 1.25 mol of AgCl
 - $\text{Pb(s)} + \text{PbO}_2(\text{s}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{PbSO}_4(\text{s}) + \text{H}_2\text{O(l)}$; 3.8 g of PbSO_4
 - $\text{H}_3\text{PO}_4(\text{aq}) + \text{MgCO}_3(\text{s}) \rightarrow \text{Mg}_3(\text{PO}_4)_2(\text{s}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O(l)}$; 6.41 g of $\text{Mg}_3(\text{PO}_4)_2$
17. Determine the percent yield of each reaction. Be sure that the chemical equations are balanced. Assume that any reactants for which amounts are not given are in excess. (The symbol Δ indicates that the reactants are heated.)
- $\text{KClO}_3(\text{s}) \xrightarrow{\Delta} \text{KCl(s)} + \text{O}_2(\text{g})$; 2.14 g of KClO_3 produces 0.67 g of O_2

- b. $\text{Cu(s)} + \text{H}_2\text{SO}_4\text{(aq)} \rightarrow \text{CuSO}_4\text{(aq)} + \text{SO}_2\text{(g)} + \text{H}_2\text{O(l)}$; 4.00 g of copper gives 1.2 g of sulfur dioxide
- c. $\text{AgC}_2\text{H}_3\text{O}_2\text{(aq)} + \text{Na}_3\text{PO}_4\text{(aq)} \rightarrow \text{Ag}_3\text{PO}_4\text{(s)} + \text{NaC}_2\text{H}_3\text{O}_2\text{(aq)}$; 5.298 g of silver acetate produces 1.583 g of silver phosphate
18. Each step of a four-step reaction has a yield of 95%. What is the percent yield for the overall reaction?
19. A three-step reaction yields of 87% for the first step, 94% for the second, and 55% for the third. What is the percent yield of the overall reaction?
20. Give a general expression relating the theoretical yield (in grams) of product that can be obtained from x grams of B, assuming neither A nor B is limiting.
- $\text{A} + 3\text{B} \rightarrow 2\text{C}$
21. Under certain conditions, the reaction of hydrogen with carbon monoxide can produce methanol.
- Write a balanced chemical equation for this reaction.
 - Calculate the percent yield if exactly 200 g of methanol is produced from exactly 300 g of carbon monoxide.
22. Chlorine dioxide is a bleaching agent used in the paper industry. It can be prepared by the following reaction:
- $\text{NaClO}_2\text{(s)} + \text{Cl}_2\text{(g)} \rightarrow \text{ClO}_2\text{(aq)} + \text{NaCl(aq)}$
- What mass of chlorine is needed for the complete reaction of 30.5 g of NaClO_2 ?
 - Give a general equation for the conversion of x grams of sodium chlorite to chlorine dioxide.
23. The reaction of propane gas ($\text{CH}_3\text{CH}_2\text{CH}_3$) with chlorine gas (Cl_2) produces two monochloride products: $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ and $\text{CH}_3\text{CHClCH}_3$. The first is obtained in a 43% yield and the second in a 57% yield.
- If you use 2.78 g of propane gas, how much chlorine gas would you need for the reaction to go to completion?
 - How many grams of each product could theoretically be obtained from the reaction starting with 2.78 g of propane?
 - Use the actual percent yield to calculate how many grams of each product would actually be obtained.
24. Protactinium (Pa), a highly toxic metal, is one of the rarest and most expensive elements. The following reaction is one method for preparing protactinium metal under relatively extreme conditions:



- Given 15.8 mg of reactant, how many milligrams of protactinium could be synthesized?
- If 3.4 mg of Pa was obtained, what was the percent yield of this reaction?
- If you obtained 3.4 mg of Pa and the percent yield was 78.6%, how many grams of PaI_5 were used in the preparation?

25. Aniline ($\text{C}_6\text{H}_5\text{NH}_2$) can be produced from chlorobenzene ($\text{C}_6\text{H}_5\text{Cl}$) via the following reaction:



Assume that 20.0 g of chlorobenzene at 92% purity is mixed with 8.30 g of ammonia.

- Which is the limiting reactant?
 - Which reactant is present in excess?
 - What is the theoretical yield of ammonium chloride in grams?
 - If 4.78 g of NH_4Cl was recovered, what was the percent yield?
 - Derive a general expression for the theoretical yield of ammonium chloride in terms of grams of chlorobenzene reactant, if ammonia is present in excess.
26. A stoichiometric quantity of chlorine gas is added to an aqueous solution of NaBr to produce an aqueous solution of sodium chloride and liquid bromine. Write the chemical equation for this reaction. Then assume an 89% yield and calculate the mass of chlorine given the following:
- 9.36×10^{24} formula units of NaCl
 - 8.5×10^4 mol of Br_2
 - 3.7×10^8 g of NaCl

ANSWERS

- 53.941 amu
 - 49.0072 amu
 - 58.3197 amu
 - 310.177 amu
 - 73.891 amu
 - 81.071 amu
-

3.

- a. 0.3831 mol Si
- b. 4.2×10^{-2} mol Pb
- c. 0.102 mol Mg
- d. 6.8×10^{-3} mol La
- e. 3.78×10^{-2} mol Cl_2
- f. 1.2×10^{-3} mol As

4.

5.

- a. 9.80×10^{-3} mol or 9.80 mmole $\text{Ba}(\text{OH})_2$
- b. 8.08×10^{-3} mol or 8.08 mmole H_3PO_4
- c. 2.91×10^{-2} mol or 29.1 mmole K_2S
- d. 4.634×10^{-3} mol or 4.634 mmole $\text{Cu}(\text{NO}_3)_2$
- e. 1.769×10^{-2} mol 17.69 mmole $\text{Ba}_3(\text{PO}_4)_2$
- f. 4.38×10^{-2} mol or 43.8 mmole $(\text{NH}_4)_2\text{SO}_4$
- g. 4.06×10^{-3} mol or 4.06 mmole $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$
- h. 1.96×10^{-2} mol or 19.6 mmole $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$

6.

7.

- a. 613 g or 6.13×10^5 mg Ag
- b. 296 g or 2.96×10^5 mg Sn
- c. 16.6 g or 1.66×10^4 mg Os
- d. 48.9 g or 4.89×10^4 mg Si
- e. 0.764 g or 764 mg H_2
- f. 92.05 g or 9.205×10^4 mg Zr

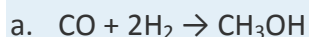
8.

9.

- a. 1.81 kg P_4O_{10}
- b. 0.387 kg $\text{Ba}(\text{OH})_2$

- c. 0.923 kg K_3PO_4
- d. 0.458 kg $\text{Ni}(\text{ClO}_3)_2$
- e. 0.118 kg $(\text{NH}_4)\text{NO}_3$
- f. 0.109 kg $\text{Co}(\text{NO}_3)_3$
- 10.
- 11.
- a. 1.91×10^4 mg Pt
- b. 965.6 mg Hg
- c. 2841 mg Cl
- 12.
13. The balanced chemical equation for this reaction is
- $$2\text{NH}_3 + 2\text{O}_2 \rightarrow \text{N}_2\text{O} + 3\text{H}_2\text{O}$$
- a. NH_3
- b. NH_3
- c. O_2
- d. NH_3
- 14.
- 15.
- a. 150 g NaI and 35 g Cl_2
- b. 29 g NaCl and 25 g H_2SO_4
- c. 140 g NO_2 and 27 g H_2O
- 16.
- 17.
- a. 80%
- b. 30%
- c. 35.7%
- 18.
19. 45%.
- 20.

21.



b. 58.28%

22.

23.

a. 2.24 g Cl_2

b. 4.95 g

c. 2.13 g $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ plus 2.82 g $\text{CH}_3\text{CHClCH}_3$

24.

25.

a. chlorobenzene

b. ammonia

c. 8.74 g ammonium chloride.

d. 55%

e.

Theoretical yield (NH_4Cl)

= mass of chlorobenzene (g) $\times$ 0.92 $\times$ 53.49 g/mol / 112.55 g/mol

[1] In the laboratory, a student will occasionally obtain a yield that appears to be greater than 100%. This usually happens when the product is impure or is wet with a solvent such as water. If this is not the case, then the student *must* have made an error in weighing either the reactants or the products. The law of conservation of mass applies even to undergraduate chemistry laboratory experiments!

3.5 Classifying Chemical Reactions

LEARNING OBJECTIVES

1. To identify fundamental types of chemical reactions.
2. To predict the types of reactions substances will undergo.

The chemical reactions we have described are only a tiny sampling of the infinite number of chemical reactions possible. How do chemists cope with this overwhelming diversity? How do they predict which compounds will react with one another and what products will be formed? The key to success is to find useful ways to categorize reactions.

Familiarity with a few basic types of reactions will help you to predict the products that form when certain kinds of compounds or elements come in contact.

Most chemical reactions can be classified into one or more of five basic types: acid–base reactions, exchange reactions, condensation reactions (and the reverse, cleavage reactions), and oxidation–reduction reactions. The general forms of these five kinds of reactions are summarized in Table 3.1 "Basic Types of Chemical Reactions", along with examples of each. It is important to note, however, that many reactions can be assigned to more than one classification, as you will see in our discussion. The classification scheme is only for convenience; the same reaction can be classified in different ways, depending on which of its characteristics is most important. Oxidation–reduction reactions, in which there is a net transfer of electrons from one atom to another, and condensation reactions are discussed in this section. Acid–base reactions and one kind of exchange reaction—the formation of an insoluble salt such as barium sulfate when solutions of two soluble salts are mixed together—will be discussed in Chapter 4 "Reactions in Aqueous Solution".

Table 3.1 Basic Types of Chemical Reactions

Table 3.1 Basic Types of Chemical Reactions		
Name of Reaction	General Form	Example(s)
oxidation–reduction (redox)	oxidant + reductant → reduced oxidant + oxidized reductant	$\text{C}_7\text{H}_{16}(\text{l}) + 11\text{O}_2(\text{g}) \rightarrow 7\text{CO}_2(\text{g}) + 8\text{H}_2\text{O}(\text{g})$
acid–base	acid + base → salt	$\text{NH}_3(\text{aq}) + \text{HNO}_3(\text{aq}) \rightarrow \text{NH}_4^+(\text{aq}) + \text{NO}_3^-(\text{aq})$
exchange	$\text{AB} + \text{C} \rightarrow \text{AC} + \text{B}$	$\text{CH}_3\text{Cl} + \text{OH}^- \rightarrow \text{CH}_3\text{OH} + \text{Cl}^-$
	$\text{AB} + \text{CD} \rightarrow \text{AD} + \text{CB}$	$\text{BaCl}_2(\text{aq}) + \text{Na}_2\text{SO}_4(\text{aq}) \rightarrow \text{BaSO}_4(\text{s}) + 2\text{NaCl}(\text{aq})$
condensation	$\text{A} + \text{B} \rightarrow \text{AB}$	$\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{CO}_3(\text{aq})$
		$\text{HBr} + \text{H}_2\text{C}=\text{CH}_2 \rightarrow \text{CH}_3\text{CH}_2\text{Br}^*$
cleavage	$\text{AB} \rightarrow \text{A} + \text{B}$	$\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
		$\text{CH}_3\text{CH}_2\text{Cl} \rightarrow \text{H}_2\text{C}=\text{CH}_2 + \text{HCl}^{**}$
* In more advanced chemistry courses you will learn that this reaction is also called an <i>addition</i> reaction.		
** In more advanced chemistry courses you will learn that this reaction is also called an <i>elimination</i> reaction.		

Oxidation–Reduction Reactions

The term oxidation was first used to describe reactions in which metals react with oxygen in air to produce metal oxides. When iron is exposed to air in the presence of water, for example, the iron turns to rust—an iron oxide. When

exposed to air, aluminum metal develops a continuous, coherent, transparent layer of aluminum oxide on its surface. In both cases, the metal acquires a positive charge by transferring electrons to the neutral oxygen atoms of an oxygen molecule. As a result, the oxygen atoms acquire a negative charge and form oxide ions (O^{2-}). Because the metals have lost electrons to oxygen, they have been *oxidized*; oxidation is therefore the loss of electrons. Conversely, because the oxygen atoms have gained electrons, they have been *reduced*, so reduction is the gain of electrons. For every oxidation, there must be an associated reduction.

Note the Pattern

Any oxidation *must* be accompanied by a reduction and vice versa.

Originally, the term reduction referred to the decrease in mass observed when a metal oxide was heated with carbon monoxide, a reaction that was widely used to extract metals from their ores. When solid copper(I) oxide is heated with hydrogen, for example, its mass decreases because the formation of pure copper is accompanied by the loss of oxygen atoms as a volatile product (water). The reaction is as follows:

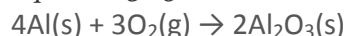
Equation 3.24



Oxidation and reduction reactions are now defined as reactions that exhibit a change in the oxidation states of one or more elements in the reactants, which follows the mnemonic *oxidation is loss reduction is gain*, or *oil rig*.

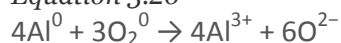
The oxidation state of each atom in a compound is the charge an atom would have if all its bonding electrons were transferred to the atom with the greater attraction for electrons. Atoms in their elemental form, such as O_2 or H_2 , are assigned an oxidation state of zero. For example, the reaction of aluminum with oxygen to produce aluminum oxide is

Equation 3.25



Each neutral oxygen atom gains two electrons and becomes negatively charged, forming an oxide ion; thus, oxygen has an oxidation state of -2 in the product and has been reduced. Each neutral aluminum atom loses three electrons to produce an aluminum ion with an oxidation state of $+3$ in the product, so aluminum has been oxidized. In the formation of Al_2O_3 , electrons are transferred as follows (the superscript 0 emphasizes the oxidation state of the elements):

Equation 3.26



Equation 3.24 and Equation 3.25 are examples of oxidation–reduction (redox) reactions. In redox reactions, there is a net transfer of electrons from one reactant to another. In any redox reaction, the total number of electrons lost must

equal the total of electrons gained to preserve electrical neutrality. In Equation 3.26, for example, the total number of electrons lost by aluminum is equal to the total number gained by oxygen:

Equation 3.27

electrons lost = 4 Al atoms $\times$ 3 e⁻ lost Al atom = 12 e⁻ lost electrons gained = 6 O atoms $\times$ 2 e⁻ gained O atom = 12 e⁻ gained

The same pattern is seen in all oxidation–reduction reactions: the number of electrons lost must equal the number of electrons gained.

An additional example of a redox reaction, the reaction of sodium metal with oxygen in air, is illustrated in Figure 3.1 "Samples of 1 Mol of Some Common Substances".

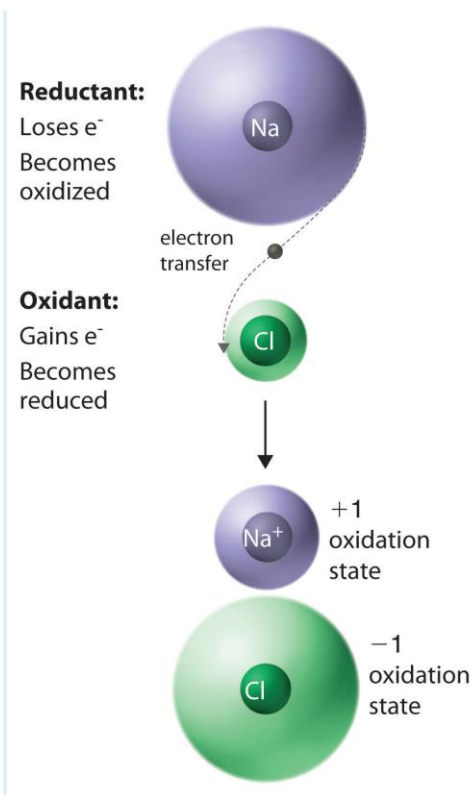
Note the Pattern

In all oxidation–reduction (redox) reactions, the number of electrons lost equals the number of electrons gained.

Assigning Oxidation States

Assigning oxidation states to the elements in binary ionic compounds is straightforward: the oxidation states of the elements are identical to the charges on the monatomic ions. In Chapter 2 "Molecules, Ions, and Chemical Formulas", you learned how to predict the formulas of simple ionic compounds based on the sign and magnitude of the charge on monatomic ions formed by the neutral elements. Examples of such compounds are sodium chloride (NaCl; Figure 3.13 "The Reaction of a Neutral Sodium Atom with a Neutral Chlorine Atom"), magnesium oxide (MgO), and calcium chloride (CaCl₂). In covalent compounds, in contrast, atoms share electrons. Oxidation states in covalent compounds are somewhat arbitrary, but they are useful bookkeeping devices to help you understand and predict many reactions.

Figure 3.13 The Reaction of a Neutral Sodium Atom with a Neutral Chlorine Atom



A set of rules for assigning oxidation states to atoms in chemical compounds follows. As we discuss atomic and molecular structure in Chapter 6 "The Structure of Atoms", Chapter 7 "The Periodic Table and Periodic Trends", Chapter 8 "Ionic versus Covalent Bonding", and Chapter 9 "Molecular Geometry and Covalent Bonding Models", the principles underlying these rules will be described more fully.

Rules for Assigning Oxidation States^[1]

1. The oxidation state of an atom in any pure element, whether monatomic, diatomic, or polyatomic, is zero.
2. The oxidation state of a monatomic ion is the same as its charge—for example, $Na^+ = +1$, $Cl^- = -1$.
3. The oxidation state of fluorine in chemical compounds is always -1 . Other halogens usually have oxidation states of -1 as well, except when combined with oxygen or other halogens.
4. Hydrogen is assigned an oxidation state of $+1$ in its compounds with nonmetals and -1 in its compounds with metals.
5. Oxygen is normally assigned an oxidation state of -2 in compounds, with two exceptions: in compounds that contain oxygen–fluorine or oxygen–oxygen bonds, the

oxidation state of oxygen is determined by the oxidation states of the other elements present.

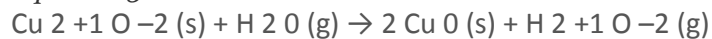
6. The sum of the oxidation states of all the atoms in a neutral molecule or ion must equal the charge on the molecule or ion.

In any chemical reaction, the net charge must be conserved; that is, in a chemical reaction, the total number of electrons is constant, just like the total number of atoms. Consistent with this, rule 1 states that the sum of the individual oxidation states of the atoms in a molecule or ion must equal the net charge on that molecule or ion. In NaCl, for example, Na has an oxidation state of +1 and Cl is -1 . The net charge is zero, as it must be for any compound.

Rule 3 is required because fluorine attracts electrons more strongly than any other element, for reasons you will discover in Chapter 6 "The Structure of Atoms". Hence fluorine provides a reference for calculating the oxidation states of other atoms in chemical compounds. Rule 4 reflects the difference in chemistry observed for compounds of hydrogen with nonmetals (such as chlorine) as opposed to compounds of hydrogen with metals (such as sodium). For example, NaH contains the H^- ion, whereas HCl forms H^+ and Cl^- ions when dissolved in water. Rule 5 is necessary because fluorine has a greater attraction for electrons than oxygen does; this rule also prevents violations of rule 2. So the oxidation state of oxygen is +2 in OF_2 but $-1/2$ in KO_2 . Note that an oxidation state of $-1/2$ for O in KO_2 is perfectly acceptable.

The reduction of copper(I) oxide shown in Equation 3.28 demonstrates how to apply these rules. Rule 1 states that atoms in their elemental form have an oxidation state of zero, which applies to H_2 and Cu. From rule 4, hydrogen in H_2O has an oxidation state of +1, and from rule 5, oxygen in both Cu_2O and H_2O has an oxidation state of -2 . Rule 6 states that the sum of the oxidation states in a molecule or formula unit must equal the net charge on that compound. This means that each Cu atom in Cu_2O must have a charge of +1: $2(+1) + (-2) = 0$. So the oxidation states are as follows:

Equation 3.28



Assigning oxidation states allows us to see that there has been a net transfer of electrons from hydrogen ($0 \rightarrow +1$) to copper ($+1 \rightarrow 0$). So this is a redox reaction. Once again, the number of electrons lost equals the number of electrons gained, and there is a net conservation of charge:

Equation 3.29

electrons lost = 2 H atoms $\times$ 1 e⁻ – lost H atom = 2 e⁻ – lost electrons gained = 2 Cu atoms $\times$ 1 e⁻ – gained Cu atom = 2 e⁻ – gained

Remember that oxidation states are useful for visualizing the transfer of electrons in oxidation–reduction reactions, but the oxidation state of an atom and its actual charge are the same only for simple ionic compounds. Oxidation states are a convenient way of assigning electrons to atoms, and they are useful for predicting the types of reactions that substances undergo.

EXAMPLE 14

Assign oxidation states to all atoms in each compound.

1. sulfur hexafluoride (SF₆)
 - a. methanol (CH₃OH)
 - b. ammonium sulfate [(NH₄)₂SO₄]
 - c. magnetite (Fe₃O₄)
 - d. ethanoic (acetic) acid (CH₃CO₂H)

Given: molecular or empirical formula

Asked for: oxidation states

Strategy:

Begin with atoms whose oxidation states can be determined unambiguously from the rules presented (such as fluorine, other halogens, oxygen, and monatomic ions). Then determine the oxidation states of other atoms present according to rule 1.

Solution:

- a. We know from rule 3 that fluorine always has an oxidation state of –1 in its compounds. The six fluorine atoms in sulfur hexafluoride give a total negative charge of –6. Because rule 1 requires that the sum of the oxidation states of all atoms be zero in a neutral molecule (here SF₆), the oxidation state of sulfur must be +6:

$$[(6 \text{ F atoms})(-1)] + [(1 \text{ S atom})(+6)] = 0$$

- a. According to rules 4 and 5, hydrogen and oxygen have oxidation states of +1 and –2, respectively. Because methanol has no net charge, carbon must have an oxidation state of –2:

$$[(4 \text{ H atoms})(+1)] + [(1 \text{ O atom})(-2)] + [(1 \text{ C atom})(-2)] = 0$$

b. Note that $(\text{NH}_4)_2\text{SO}_4$ is an ionic compound that consists of both a polyatomic cation (NH_4^+) and a polyatomic anion (SO_4^{2-}) (see Table 2.4 "Common Polyatomic Ions and Their Names"). We assign oxidation states to the atoms in each polyatomic ion separately. For NH_4^+ , hydrogen has an oxidation state of +1 (rule 4), so nitrogen must have an oxidation state of -3:

$$[(4 \text{ H atoms})(+1)] + [(1 \text{ N atom})(-3)] = +1, \text{ the charge on the } \text{NH}_4^+ \text{ ion}$$

For SO_4^{2-} , oxygen has an oxidation state of -2 (rule 5), so sulfur must have an oxidation state of +6:

$$[(4 \text{ O atoms})(-2)] + [(1 \text{ S atom})(+6)] = -2, \text{ the charge on the sulfate ion}$$

a. Oxygen has an oxidation state of -2 (rule 5), giving an overall charge of -8 per formula unit. This must be balanced by the positive charge on three iron atoms, giving an oxidation state of +8/3 for iron:

$$[(4 \text{ O atoms})(-2)] + [(3 \text{ Fe atoms})(+8/3)] = 0$$

Fractional oxidation states are allowed because oxidation states are a somewhat arbitrary way of keeping track of electrons. In fact, Fe_3O_4 can be viewed as having two Fe^{3+} ions and one Fe^{2+} ion per formula unit, giving a net positive charge of +8 per formula unit. Fe_3O_4 is a magnetic iron ore commonly called magnetite. In ancient times, magnetite was known as lodestone because it could be used to make primitive compasses that pointed toward Polaris (the North Star), which was called the "lodestar."

a. Initially, we assign oxidation states to the components of $\text{CH}_3\text{CO}_2\text{H}$ in the same way as any other compound. Hydrogen and oxygen have oxidation states of +1 and -2 (rules 4 and 5, respectively), resulting in a total charge for hydrogen and oxygen of

$$[(4 \text{ H atoms})(+1)] + [(2 \text{ O atoms})(-2)] = 0$$

So the oxidation state of carbon must also be zero (rule 6). This is, however, an *average* oxidation state for the two carbon atoms present. Because each carbon atom has a different set of atoms bonded to it, they are likely to have different oxidation states. To determine the oxidation states of the individual carbon atoms, we use the same rules as before but with the additional assumption that bonds between atoms of the same element do not affect the oxidation states of those atoms. The carbon atom of the methyl group ($-\text{CH}_3$) is bonded to three hydrogen atoms and one carbon atom. We know from rule 4 that hydrogen has an oxidation state of +1, and we have just said that the carbon-carbon bond can be ignored in calculating the oxidation state of the carbon atom. For the methyl group to be electrically neutral, its carbon atom must have an oxidation state of -3. Similarly, the carbon atom of the carboxylic acid group ($-\text{CO}_2\text{H}$) is bonded to one carbon atom and two oxygen atoms. Again ignoring the bonded carbon atom,

we assign oxidation states of -2 and $+1$ to the oxygen and hydrogen atoms, respectively, leading to a net charge of

$$[(2 \text{ O atoms})(-2)] + [(1 \text{ H atom})(+1)] = -3$$

To obtain an electrically neutral carboxylic acid group, the charge on this carbon must be $+3$. The oxidation states of the individual atoms in acetic acid are thus

$$\text{C} - 3 \text{ H} + 3 + 1 \text{ C} + 3 \text{ O} - 2 - 2 \text{ H} + 1$$

Thus the sum of the oxidation states of the two carbon atoms is indeed zero.

Exercise

Assign oxidation states to all atoms in each compound.

- a. barium fluoride (BaF_2)
- a. formaldehyde (CH_2O)
- b. potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$)
- c. cesium oxide (CsO_2)
- d. ethanol ($\text{CH}_3\text{CH}_2\text{OH}$)

Answer:

- a. Ba, $+2$; F, -1
- a. C, 0 ; H, $+1$; O, -2
- b. K, $+1$; Cr, $+6$; O, -2
- c. Cs, $+1$; O, $-\frac{1}{2}$
- d. C, -3 ; H, $+1$; C, -1 ; H, $+1$; O, -2 ; H, $+1$

Oxidants and Reductants

Compounds that are capable of accepting electrons, such as O_2 or F_2 , are called oxidants (or oxidizing agents) because they can oxidize other compounds. *In the process of accepting electrons, an oxidant is reduced.* Compounds that are capable of donating electrons, such as sodium metal or cyclohexane (C_6H_{12}), are called reductants (or reducing agents) because they can cause the reduction of another compound. *In the process of donating electrons, a reductant is oxidized.* These relationships are summarized in Equation 3.30:

Equation 3.30

oxidant + reductant $\rightarrow$ oxidation–reduction

$\text{O}_2(\text{g})$ gains e^- (is reduced) + $4\text{Na}(\text{s})$ loses e^- (is oxidized) $\rightarrow 2\text{Na}_2\text{O}(\text{s})$ redox reaction

Some oxidants have a greater ability than others to remove electrons from other compounds. Oxidants can range from very powerful, capable of oxidizing most compounds with which they come in contact, to rather weak. Both F_2 and Cl_2 are powerful oxidants: for example, F_2 will oxidize H_2O in a vigorous, potentially explosive reaction. In contrast, S_8 is a rather weak oxidant, and O_2 falls somewhere in between. Conversely, reductants vary in their tendency to donate electrons to other compounds. Reductants can also range from very powerful, capable of giving up electrons to almost anything, to weak. The alkali metals are powerful reductants, so they must be kept away from atmospheric oxygen to avoid a potentially hazardous redox reaction.

A combustion reaction, first introduced in Section 3.2 "Determining Empirical and Molecular Formulas", is an oxidation–reduction reaction in which the oxidant is O_2 . One example of a combustion reaction is the burning of a candle, shown in Figure 3.9 "An Example of a Combustion Reaction". Consider, for example, the combustion of cyclohexane, a typical hydrocarbon, in excess oxygen. The balanced chemical equation for the reaction, with the oxidation state shown for each atom, is as follows:

Equation 3.31

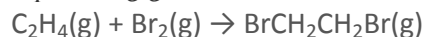


If we compare the oxidation state of each element in the products and the reactants, we see that hydrogen is the only element whose oxidation state does not change; it remains +1. Carbon, however, has an oxidation state of -2 in cyclohexane and $+4$ in CO_2 ; that is, each carbon atom changes its oxidation state by six electrons during the reaction. Oxygen has an oxidation state of 0 in the reactants, but it gains electrons to have an oxidation state of -2 in CO_2 and H_2O . Because carbon has been oxidized, cyclohexane is the reductant; because oxygen has been reduced, it is the oxidant. All combustion reactions are therefore oxidation–reduction reactions.

Condensation Reactions

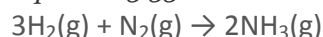
The reaction of bromine with ethylene to give 1,2-dibromoethane, which is used in agriculture to kill nematodes in soil, is as follows:

Equation 3.32



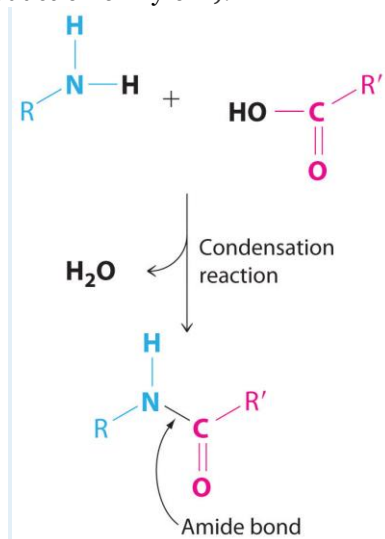
According to Table 3.1 "Basic Types of Chemical Reactions", this is a condensation reaction because it has the general form $A + B \rightarrow AB$. This reaction, however, can also be viewed as an oxidation–reduction reaction, in which electrons are transferred from carbon ($-2 \rightarrow -1$) to bromine ($0 \rightarrow -1$). Another example of a condensation reaction is the one used for the industrial synthesis of ammonia:

Equation 3.33



Although this reaction also has the general form of a condensation reaction, hydrogen has been oxidized ($0 \rightarrow +1$) and nitrogen has been reduced ($0 \rightarrow -3$), so it can also be classified as an oxidation–reduction reaction.

Not all condensation reactions are redox reactions. The reaction of an amine with a carboxylic acid, for example, is a variant of a condensation reaction ($A + B \rightarrow A'B' + C$): two large fragments condense to form a single molecule, and a much smaller molecule, such as H_2O , is eliminated. In this reaction, the $-\text{OH}$ from the carboxylic acid group and $-\text{H}$ from the amine group are eliminated as H_2O , and the reaction forms an *amide bond* (also called a *peptide bond*) that links the two fragments. Amide bonds are the essential structural unit linking the building blocks of proteins and many polymers together, as described in Chapter 12 "Solids". Nylon, for example, is produced from a condensation reaction (Figure 3.14 "The Production of Nylon").



Amide bonds. The reaction of an amine with a carboxylic acid proceeds by eliminating water and forms a new $\text{C}-\text{N}$ (amide) bond.

EXAMPLE 15

The following reactions have important industrial applications. Using Table 3.1 "Basic Types of Chemical Reactions", classify each reaction as an oxidation–reduction reaction, an acid–base reaction, an exchange reaction, a condensation reaction, or a cleavage reaction. For each redox reaction, identify the oxidant and reductant and specify which atoms are oxidized or reduced. (Don't forget that some reactions can be placed into more than one category.)

- a. $\text{C}_2\text{H}_4(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow \text{ClCH}_2\text{CH}_2\text{Cl}(\text{g})$
- b. $\text{AgNO}_3(\text{aq}) + \text{NaCl}(\text{aq}) \rightarrow \text{AgCl}(\text{s}) + \text{NaNO}_3(\text{aq})$
- c. $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
- d. $\text{Ca}_5(\text{PO}_4)_3(\text{OH})(\text{s}) + 7\text{H}_3\text{PO}_4(\text{aq}) + 4\text{H}_2\text{O}(\text{l}) \rightarrow 5\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}(\text{s})$
- e. $\text{Pb}(\text{s}) + \text{PbO}_2(\text{s}) + 2\text{H}_2\text{SO}_4(\text{aq}) \rightarrow 2\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l})$

Given: balanced chemical equation

Asked for: classification of chemical reaction

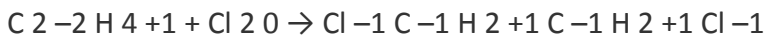
Strategy:

A Determine the general form of the equation by referring to Table 3.1 "Basic Types of Chemical Reactions" and then classify the reaction.

B For redox reactions, assign oxidation states to each atom present in the reactants and the products. If the oxidation state of one or more atoms changes, then the reaction is a redox reaction. If not, the reaction must be one of the other types of reaction listed in Table 3.1 "Basic Types of Chemical Reactions".

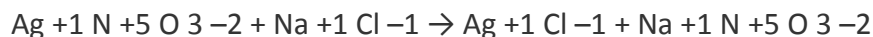
Solution:

- a. **A** This reaction is used to prepare 1,2-dichloroethane, one of the top 25 industrial chemicals in Figure 2.22 "Top 25 Chemicals Produced in the United States in 2002*". It has the general form $\text{A} + \text{B} \rightarrow \text{AB}$, which is typical of a condensation reaction. **B** Because reactions may fit into more than one category, we need to look at the oxidation states of the atoms:



The oxidation states show that chlorine is reduced from 0 to -1 and carbon is oxidized from -2 to -1 , so this is a redox reaction as well as a condensation reaction. Ethylene is the reductant, and chlorine is the oxidant.

- b. **A** This reaction is used to prepare silver chloride for making photographic film. The chemical equation has the general form $\text{AB} + \text{CD} \rightarrow \text{AD} + \text{CB}$, so it is classified as an exchange reaction. **B** The oxidation states of the atoms are as follows



There is no change in the oxidation states, so this is not a redox reaction.

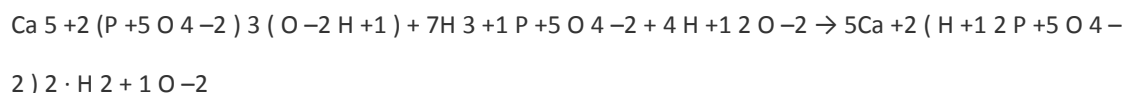
1. **A** This reaction is used to prepare lime (CaO) from limestone (CaCO₃) and has the general form AB → A + B. The chemical equation's general form indicates that it can be classified as a cleavage reaction, the reverse of a condensation reaction. **B** The oxidation states of the atoms are as follows:



Because the oxidation states of all the atoms are the same in the products and the reactant, this is *not* a redox reaction.

2. **A** This reaction is used to prepare "super triple phosphate" in fertilizer. One of the reactants is phosphoric acid, which transfers a proton (H⁺) to the phosphate and hydroxide ions of hydroxyapatite [Ca₅(PO₄)₃(OH)] to form H₂PO₄⁻ and H₂O, respectively. This is an acid–base reaction, in which H₃PO₄ is the acid (H⁺ donor) and Ca₅(PO₄)₃(OH) is the base (H⁺ acceptor).

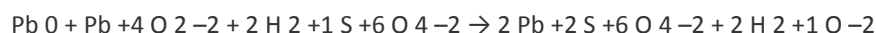
B To determine whether it is also a redox reaction, we assign oxidation states to the atoms:



Because there is no change in oxidation state, this is not a redox reaction.

3. **A** This reaction occurs in a conventional car battery every time the engine is started. An acid (H₂SO₄) is present and transfers protons to oxygen in PbO₂ to form water during the reaction. The reaction can therefore be described as an acid–base reaction.

B The oxidation states are as follows:



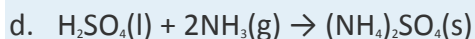
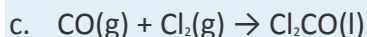
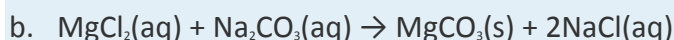
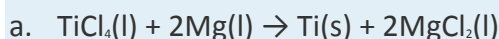
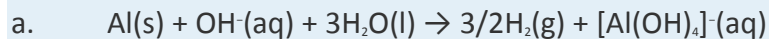
The oxidation state of lead changes from 0 in Pb and +4 in PbO₂ (both reactants) to +2 in PbSO₄.

This is also a redox reaction, in which elemental lead is the reductant, and PbO₂ is the oxidant.

Which description is correct? Both.

Exercise

Using Table 3.1 "Basic Types of Chemical Reactions", classify each reaction as an oxidation–reduction reaction, an acid–base reaction, an exchange reaction, a condensation reaction, or a cleavage reaction. For each redox reaction, identify the oxidant and the reductant and specify which atoms are oxidized or reduced.



Answer:

a. Redox reaction; reductant is Al, oxidant is H_2O ; Al is oxidized, H is reduced. This is the reaction that occurs when Drano is used to clear a clogged drain.

a. Redox reaction; reductant is Mg, oxidant is TiCl_4 ; Mg is oxidized, Ti is reduced.

b. Exchange reaction. This reaction is responsible for the scale that develops in coffee makers in areas that have hard water.

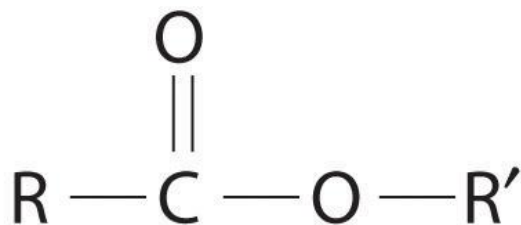
c. Both a condensation reaction and a redox reaction; reductant is CO, oxidant is Cl_2 ; C is oxidized, Cl is reduced. The product of this reaction is phosgene, a highly toxic gas used as a chemical weapon in World War I. Phosgene is now used to prepare polyurethanes, which are used in foams for bedding and furniture and in a variety of coatings.

d. Acid–base reaction.

Catalysts

Many chemical reactions, including some of those discussed previously, occur more rapidly in the presence of a catalyst, which is a substance that participates in a reaction and causes it to occur more rapidly but can be recovered unchanged at the end of a reaction and reused. Because catalysts are not involved in the stoichiometry of a reaction, they are usually shown above the arrow in a net chemical equation. Chemical processes in industry rely heavily on the use of catalysts, which are usually added to a reaction mixture in trace amounts, and most biological reactions do not take place without a biological catalyst or enzyme. Examples of catalyzed reactions in industry are the use of platinum in petroleum cracking and reforming, the reaction of SO_2 and O_2 in the presence of V_2O_5 to produce SO_3 in the industrial synthesis of sulfuric acid, and the use of sulfuric acid in the synthesis of compounds such as ethyl acetate

and procaine. Not only do catalysts greatly increase the rates of reactions, but in some cases such as in petroleum refining, they also control which products are formed. The acceleration of a reaction by a catalyst is called catalysis.



An ester

Catalysts may be classified as either homogeneous or heterogeneous. A homogeneous catalyst is uniformly dispersed throughout the reactant mixture to form a solution. Sulfuric acid, for example, is a homogeneous catalyst used in the synthesis of esters such as procaine (Example 13). An ester has a structure similar to that of a carboxylic acid, in which the hydrogen atom attached to oxygen has been replaced by an R group. They are responsible for the fragrances of many fruits, flowers, and perfumes. Other examples of homogeneous catalysts are the enzymes that allow our bodies to function. In contrast, a heterogeneous catalyst is in a different physical state than the reactants. For economic reasons, most industrial processes use heterogeneous catalysts in the form of solids that are added to solutions of the reactants. Because such catalysts often contain expensive precious metals such as platinum or palladium, it makes sense to formulate them as solids that can be easily separated from the liquid or gaseous reactant-product mixture and recovered. Examples of heterogeneous catalysts are the iron oxides used in the industrial synthesis of ammonia and the catalytic converters found in virtually all modern automobiles, which contain precious metals like palladium and rhodium. Catalysis will be discussed in more detail in Chapter 14 "Chemical Kinetics" when we discuss reaction rates, but you will encounter the term frequently throughout the text.

Summary

Chemical reactions may be classified as an **acid–base reaction**, an **exchange reaction**, a **condensation reaction** and its reverse, a **cleavage reaction**, and an **oxidation–reduction (or redox)** reaction. To keep track of electrons in chemical reactions, oxidation states are assigned to atoms in compounds. The **oxidation state** is the charge an atom would have if all its bonding electrons were transferred completely to the atom that has the greater attraction for electrons. In an **oxidation–**

reduction reaction, one atom must lose electrons and another must gain electrons. **Oxidation** is the loss of electrons, and an element whose oxidation state increases is said to be *oxidized*. **Reduction** is the gain of electrons, and an element whose oxidation state decreases is said to be *reduced*. **Oxidants** are compounds that are capable of accepting electrons from other compounds, so they are reduced during an oxidation–reduction reaction. In contrast, **reductants** are compounds that are capable of donating electrons to other compounds, so they are oxidized during an oxidation–reduction reaction.

A **combustion reaction** is a redox reaction in which the oxidant is $O_2(g)$. An *amide bond* is formed from the condensation reaction between a carboxylic acid and an amine; it is the essential structural unit of proteins and many polymers. A **catalyst** is a substance that increases the rate of a chemical reaction without undergoing a net chemical change itself. A biological catalyst is called an **enzyme**. **Catalysis** is an acceleration in the rate of a reaction caused by the presence of a substance that does not appear in the chemical equation. A **homogeneous catalyst** is uniformly dispersed in a solution of the reactants, whereas a **heterogeneous catalyst** is present as a different phase, usually a solid.

KEY TAKEAWAY

- Chemical reactions may be classified as acid–base, exchange, condensation, cleavage, and oxidation–reduction (redox).

CONCEPTUAL PROBLEMS

1. What is a combustion reaction? How can it be distinguished from an exchange reaction?
2. What two products are formed in the combustion of an organic compound containing only carbon, hydrogen, and oxygen? Is it possible to form only these two products from a reaction that is not a combustion reaction? Explain your answer.
3. What factors determine whether a reaction can be classified as a redox reaction?
4. Name three characteristics of a balanced redox reaction.
5. Does an oxidant accept electrons or donate them?
6. Does the oxidation state of a reductant become more positive or more negative during a redox reaction?
7. Nitrogen, hydrogen, and ammonia are known to have existed on primordial earth, yet mixtures of nitrogen and hydrogen do not usually react to give ammonia. What natural phenomenon would have enough energy to initiate a reaction between these two primordial gases?
8. Catalysts are not added to reactions in stoichiometric quantities. Why?

9. State whether each of the following uses a homogeneous catalyst or a heterogeneous catalyst.
- Platinum metal is used in the catalytic converter of an automobile.
 - Nitrogen is biologically converted to ammonia by an enzyme.
 - Carbon monoxide and hydrogen combine to form methane and water with a nickel catalyst.
 - A dissolved rhodium compound is used as a catalyst for the conversion of an alkene to an alkane.
10. State whether each of the following uses a homogeneous catalyst or a heterogeneous catalyst.
- Pellets of ZSM-5, an aluminum- and silicon-containing mineral, are used to catalyze the conversion of methanol to gasoline.
 - The conversion of glucose to a carboxylic acid occurs with catalysis by the enzyme glucose oxidase.
 - Metallic rhodium is used to the conversion of carbon monoxide and water to carbon dioxide and hydrogen.
11. Complete the following table to describe some key differences between homogeneous and heterogeneous catalysis.

	Homogeneous	Heterogeneous
number of phases		
ease of separation from product		
ease of recovery of catalyst		

12. To increase the rate of a reaction, a scientist decided to use a catalyst. Unexpectedly, the scientist discovered that the catalyst decreased the yield of the desired product, rather than increasing it. What might have happened?

ANSWER

11.

	Homogeneous	Heterogeneous
number of phases	single phase	at least two phases
ease of separation from product	difficult	easy
ease of recovery of catalyst	difficult	easy

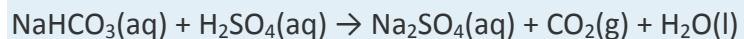
NUMERICAL PROBLEMS

Please be sure you are familiar with the topics discussed in *Essential Skills 2* (Section 3.7 "Essential Skills 2") before proceeding to the Numerical Problems.

- Classify each chemical reaction according to the types listed in Table 3.1 "Basic Types of Chemical Reactions".
 - $12\text{FeCl}_2(\text{s}) + 3\text{O}_2(\text{g}) \rightarrow 8\text{FeCl}_3(\text{s}) + 2\text{Fe}_2\text{O}_3(\text{s})$
 - $\text{CaCl}_2(\text{aq}) + \text{K}_2\text{SO}_4(\text{aq}) \rightarrow \text{CaSO}_4(\text{s}) + 2\text{KCl}(\text{aq})$
 - $\text{HCl}(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
 - $\text{Br}_2(\text{l}) + \text{C}_2\text{H}_4(\text{g}) \rightarrow \text{BrCH}_2\text{CH}_2\text{Br}(\text{l})$
- Classify each chemical reaction according to the types listed in Table 3.1 "Basic Types of Chemical Reactions".
 - $4\text{FeO}(\text{s}) + \text{O}_2(\text{g}) \rightarrow 2\text{Fe}_2\text{O}_3(\text{s})$
 - $\text{Ca}_3(\text{PO}_4)_2(\text{s}) + 3\text{H}_2\text{SO}_4(\text{aq}) \rightarrow 3\text{CaSO}_4(\text{s}) + 2\text{H}_3\text{PO}_4(\text{aq})$
 - $\text{HNO}_3(\text{aq}) + \text{KOH}(\text{aq}) \rightarrow \text{KNO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$
 - ethane(g) + oxygen(g) $\rightarrow$ carbon dioxide(g) + water(g)
- Assign oxidation states to the atoms in each compound or ion.
 - $(\text{NH}_4)_2\text{S}$
 - the phosphate ion
 - $[\text{AlF}_6]^{3-}$
 - CuS
 - HCO_3^-
 - NH_4^+
 - H_2SO_4
 - formic acid
 - n*-butanol
- Assign oxidation states to the atoms in each compound or ion.
 - ClO_2
 - HO_2^-
 - sodium bicarbonate
 - MnO_2

- e. PCl_5
- f. $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$
- g. N_2O_4
- h. butanoic acid
- i. methanol

5. Balance this chemical equation:



What type of reaction is this? Justify your answer.

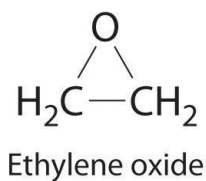
6. Assign oxidation states to the atoms in each compound.

- a. iron(III) nitrate
- b. Al_2O_3
- c. potassium sulfate
- d. Cr_2O_3
- e. sodium perchlorate
- f. Cu_2S
- g. hydrazine (N_2H_4)
- h. NO_2
- i. *n*-pentanol

7. Assign oxidation states to the atoms in each compound.

- a. calcium carbonate
- b. NaCl
- c. CO_2
- d. potassium dichromate
- e. KMnO_4
- f. ferric oxide
- g. $\text{Cu}(\text{OH})_2$
- h. Na_2SO_4
- i. *n*-hexanol

8. For each redox reaction, determine the identities of the oxidant, the reductant, the species oxidized, and the species reduced.
- $\text{H}_2(\text{g}) + \text{I}_2(\text{s}) \rightarrow 2\text{HI}(\text{g})$
 - $2\text{Na}(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{NaOH}(\text{aq}) + \text{H}_2(\text{g})$
 - $2\text{F}_2(\text{g}) + 2\text{NaOH}(\text{aq}) \rightarrow \text{OF}_2(\text{g}) + 2\text{NaF}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
9. For each redox reaction, determine the identities of the oxidant, the reductant, the species oxidized, and the species reduced.
- $2\text{Na}(\text{s}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{NaCl}(\text{s})$
 - $\text{SiCl}_4(\text{l}) + 2\text{Mg}(\text{s}) \rightarrow 2\text{MgCl}_2(\text{s}) + \text{Si}(\text{s})$
 - $2\text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$
10. Balance each chemical equation. Then identify the oxidant, the reductant, the species oxidized, and the species reduced. (Δ indicates that the reaction requires heating.)
- $\text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2(\text{g})$
 - the reaction of aluminum oxide, carbon, and chlorine gas at 900°C to produce aluminum chloride and carbon monoxide
 - $\text{HgO}(\text{s}) \rightarrow \Delta \text{Hg}(\text{l}) + \text{O}_2(\text{g})$
11. Balance each chemical equation. Then identify the oxidant, the reductant, the species oxidized, and the species reduced. (Δ indicates that the reaction requires heating.)
- the reaction of water and carbon at 800°C to produce hydrogen and carbon monoxide
 - $\text{Mn}(\text{s}) + \text{S}_8(\text{s}) + \text{CaO}(\text{s}) \rightarrow \text{CaS}(\text{s}) + \text{MnO}(\text{s})$
 - the reaction of ethylene and oxygen at elevated temperature in the presence of a silver catalyst to produce ethylene oxide



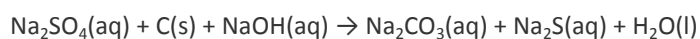
12.

- $\text{ZnS}(\text{s}) + \text{H}_2\text{SO}_4(\text{aq}) + \text{O}_2(\text{g}) \rightarrow \text{ZnSO}_4(\text{aq}) + \text{S}_8(\text{s}) + \text{H}_2\text{O}(\text{l})$

2. Silver is tarnished by hydrogen sulfide, an atmospheric contaminant, to form a thin layer of dark silver sulfide (Ag_2S) along with hydrogen gas.

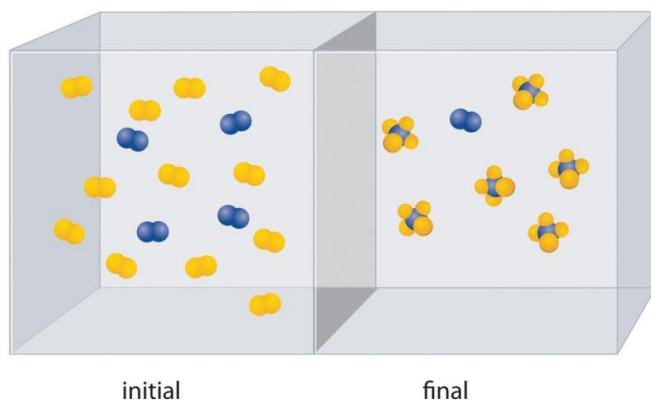
- Write a balanced chemical equation for this reaction.
- Which species has been oxidized and which has been reduced?
- Assuming 2.2 g of Ag has been converted to silver sulfide, construct a table showing the reaction in terms of the number of atoms in the reactants and products, the moles of reactants and products, the grams of reactants and products, and the molecules of reactants and products.

13. The following reaction is used in the paper and pulp industry:



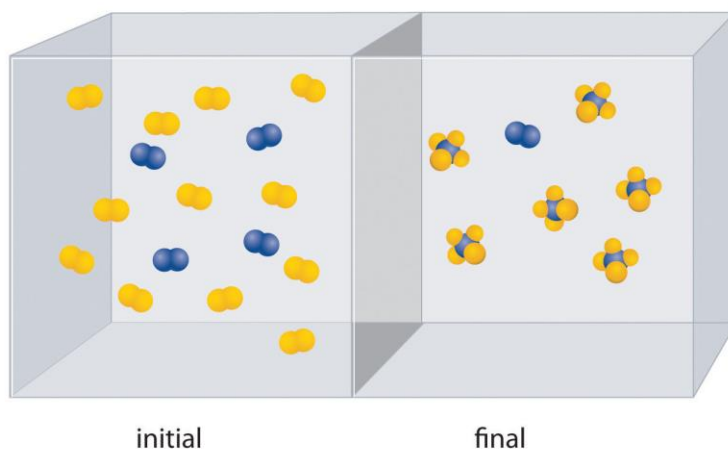
- Balance the chemical equation.
- Identify the oxidant and the reductant.
- How much carbon is needed to convert 2.8 kg of sodium sulfate to sodium sulfide?
- If the yield of the reaction were only 78%, how many kilograms of sodium carbonate would be produced from 2.80 kg of sodium sulfate?
- If 240 g of carbon and 2.80 kg of sodium sulfate were used in the reaction, what would be the limiting reactant (assuming an excess of sodium hydroxide)?

14. The reaction of A_2 (blue) with B_2 (yellow) is shown below. The initial reaction mixture is shown on the left and the mixture after the reaction has gone to completion is shown on the right.



- Write a balanced chemical equation for the reaction.
- Which is the limiting reactant in the initial reaction mixture?
- How many moles of the product AB_4 could you obtain from a mixture of 0.020 mol A_2 and 0.060 mol B_2 ?

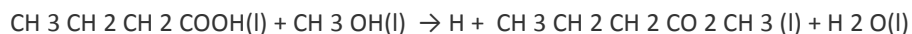
15. The reaction of X_4 (orange) with Y_2 (black) is shown below. The initial reaction mixture is shown on the left and the mixture after the reaction has gone to completion is shown on the right.



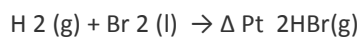
16.

- Write a balanced chemical equation for the reaction.
- Which is the limiting reactant in the initial reaction mixture?
- How many moles of the product XY_3 could you obtain from a mixture of 0.100 mol X_4 and 0.300 mol Y_2 ?

17. Methyl butyrate, an artificial apple flavor used in the food industry, is produced by the reaction of butanoic acid with methanol in the presence of an acid catalyst (H^+):



- Given 7.8 g of butanoic acid, how many grams of methyl butyrate would be synthesized, assuming 100% yield?
 - The reaction produced 5.5 g of methyl butyrate. What was the percent yield?
 - Is the catalyst used in this reaction heterogeneous or homogeneous?
18. In the presence of a platinum catalyst, hydrogen and bromine react at elevated temperatures ($300^\circ C$) to form hydrogen bromide (heat is indicated by Δ):



Given the following, calculate the mass of hydrogen bromide produced:

- 8.23×10^{22} molecules of H_2
- 6.1×10^3 mol of H_2
- 1.3×10^5 g of H_2
- Is the catalyst used in this reaction heterogeneous or homogeneous?

ANSWERS

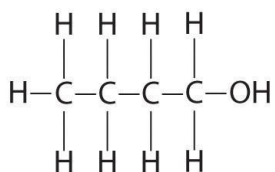
1.

- a. redox reaction
- b. exchange
- c. acid–base
- d. condensation

2.

3.

- a. S, -2; N, -3; H, +1
- b. P, +5; O, -2
- c. F, -1; Al, +3
- d. S, -2; Cu, +2
- e. H, +1; O, -2; C, +4
- f. H, +1; N, -3
- g. H, +1; O, -2; S, +6
- h. H, +1, O, -2; C, +2
- i. butanol:



1.

2.

- a. O, -2; H, +1

From left to right: C, -3-2-2-1

3.

- 4. $2\text{NaHCO}_3(\text{aq}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{Na}_2\text{SO}_4(\text{aq}) + 2\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$ acid–base reaction

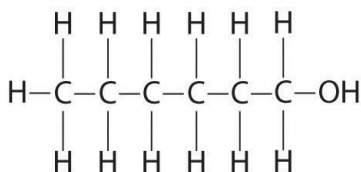
5.

6.

- a. Ca, +2; O, -2; C, +4

- b. Na, +1; Cl, -1
- c. O, -2; C, +4
- d. K, +1; O, -2; Cr, +6
- e. K, +1; O, -2; Mn, +7
- f. O, -2; Fe, +3
- g. O, -2; H, +1; Cu, +2
- h. O, -2; S, +6
- i.

Hexanol



O, -2; H, +1

From left to right: C: -3, -2, -2, -2, -2, -1

7.

8.

- a. Na is the reductant and is oxidized. Cl_2 is the oxidant and is reduced.
- b. Mg is the reductant and is oxidized. Si is the oxidant and is reduced.
- c. H_2O_2 is both the oxidant and reductant. One molecule is oxidized, and one molecule is reduced.

9.

10.

- a. $\text{H}_2\text{O}(\text{g}) + \text{C}(\text{s}) \rightarrow \Delta \text{H}_2(\text{g}) + \text{CO}(\text{g})$

C is the reductant and is oxidized. H_2O is the oxidant and is reduced.

- b. $8\text{Mn}(\text{s}) + \text{S}_8(\text{s}) + 8\text{CaO}(\text{s}) \rightarrow 8\text{CaS}(\text{s}) + 8\text{MnO}(\text{s})$

Mn is the reductant and is oxidized. The S_8 is the oxidant and is reduced.

- c. $2\text{C}_2\text{H}_4(\text{g}) + \text{O}_2(\text{g}) \rightarrow \Delta 2\text{C}_2\text{H}_4\text{O}(\text{g})$

Ethylene is the reductant and is oxidized. O_2 is the oxidant and is reduced.

- d. $8\text{ZnS}(\text{s}) + 8\text{H}_2\text{SO}_4(\text{aq}) + 4\text{O}_2(\text{g}) \rightarrow 8\text{ZnSO}_4(\text{aq}) + \text{S}_8(\text{s}) + 8\text{H}_2\text{O}(\text{l})$

Sulfide in ZnS is the reductant and is oxidized. O_2 is the oxidant and is reduced.

11.

12.

- a. $\text{Na}_2\text{SO}_4 + 2\text{C} + 4\text{NaOH} \rightarrow 2\text{Na}_2\text{CO}_3 + \text{Na}_2\text{S} + 2\text{H}_2\text{O}$
- b. The sulfate ion is the oxidant, and the reductant is carbon.
- c. 470 g
- d. 3300 g
- e. carbon

13.

14.

15.

16.

- a. 22.1 g
- b. $9.9 \times 10^5 \text{ g}$
- c. $1.0 \times 10^7 \text{ g}$
- d. heterogeneous

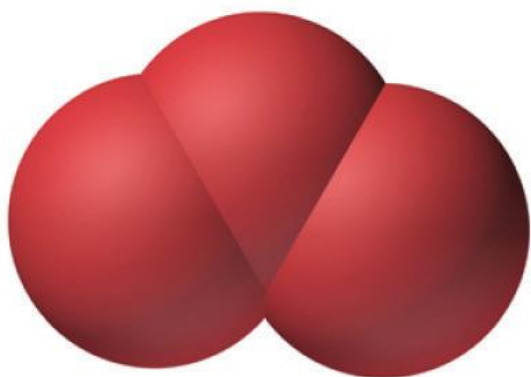
[1] Nonintegral oxidation states are encountered occasionally. They are usually due to the presence of two or more atoms of the same element with different oxidation states.

3.6 Chemical Reactions in the Atmosphere

LEARNING OBJECTIVE

1. To become familiar with the various reactions implicated in the destruction of Earth's ozone layer.

Section 3.5 "Classifying Chemical Reactions" described different classes of chemical reactions. Of the many different chemical reactions that occur in Earth's atmosphere, some are important and controversial because they affect our quality of life and health. The atmospheric reactions presented in this section provide examples of the various classes of reactions introduced in this chapter that are implicated in the destruction of Earth's protective ozone layer.



Ozone, O_3

Each year since the mid-1970s, scientists have noted a disappearance of approximately 70% of the ozone (O_3) layer above Antarctica during the Antarctic spring, creating what is commonly known as the “ozone hole.” Ozone is an unstable form of oxygen that consists of three oxygen atoms bonded together. In September 2009, the Antarctic ozone hole reached 24.1 million km^2 (9.3 million mi^2), about the size of North America. The largest area ever recorded was in the year 2000, when the hole measured 29.9 million km^2 and for the first time extended over a populated area—the city of Punta Arenas, Chile (population 154,000; Figure 3.15 “Satellite Photos of Earth Reveal the Sizes of the Antarctic Ozone Hole over Time”). A less extensive zone of depletion has been detected over the Arctic as well. Years of study from the ground, from the air, and from satellites in space have shown that chlorine from industrial chemicals used in spray cans, foam packaging, and refrigeration materials is largely responsible for the catalytic depletion of ozone through a series of condensation, cleavage, and oxidation–reduction reactions.

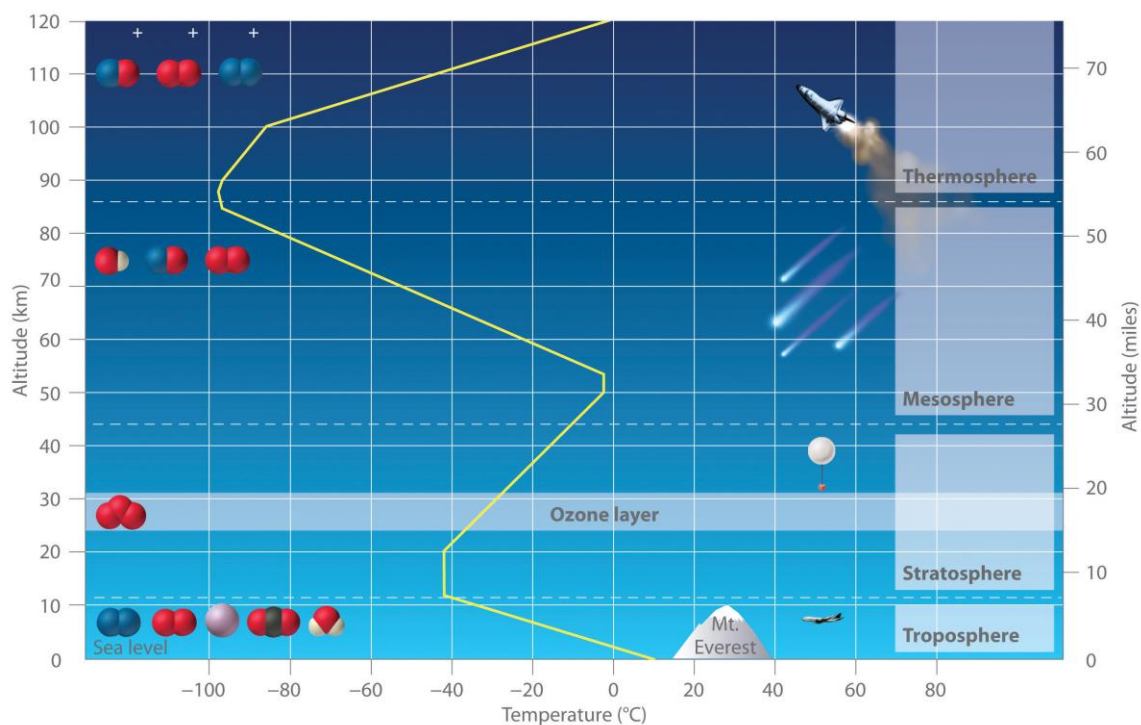
Earth’s Atmosphere and the Ozone Layer

Earth’s atmosphere at sea level is an approximately 80:20 solution of nitrogen and oxygen gases, with small amounts of carbon dioxide, water vapor, and the noble gases, and trace amounts of a variety of other compounds (Table 3.2 “The Composition of Earth’s Atmosphere at Sea Level”). A key feature of the atmosphere is that its composition, temperature, and pressure vary dramatically with altitude. Consequently, scientists have divided the atmosphere into distinct layers, which interact differently with the continuous flux of solar radiation from the top and the land and ocean masses at the bottom. Some of the characteristic features of the layers of the atmosphere are illustrated in Figure 3.16 “Variation of Temperature with Altitude in Earth’s Atmosphere”.

Table 3.2 The Composition of Earth's Atmosphere at Sea Level*

Gas	Formula	Volume (%)
nitrogen	N ₂	78.084
oxygen	O ₂	20.948
argon	Ar	0.934
carbon dioxide†	CO ₂	0.0314
neon	Ne	0.00182
helium	He	0.000524
krypton	Kr	0.000114
methane	CH ₄	0.0002
hydrogen	H ₂	0.00005
nitrous oxide	N ₂ O	0.00005
xenon	Xe	0.0000087
* In addition, air contains as much as 7% water vapor (H₂O), 0.0001% sulfur dioxide (SO₂), 0.00007% ozone (O₃), 0.000002% carbon monoxide (CO), and 0.000002% nitrogen dioxide (NO₂).		
† Carbon dioxide levels are highly variable; the typical range is 0.01–0.1%.		

Figure 3.16 *Variation of Temperature with Altitude in Earth's Atmosphere*



Note the important chemical species present in each layer. The yellow line indicates the temperature at various altitudes.

The troposphere is the lowest layer of the atmosphere, extending from Earth's surface to an altitude of about 11–13 km (7–8 mi). Above the troposphere lies the *stratosphere*, which extends from 13 km (8 mi) to about 44 km (27 mi). As shown in Figure 3.16 "Variation of Temperature with Altitude in Earth's Atmosphere", the temperature of the troposphere decreases steadily with increasing altitude. Because "hot air rises," this temperature gradient leads to continuous mixing of the upper and lower regions *within* the layer. The thermally induced turbulence in the troposphere produces fluctuations in temperature and precipitation that we collectively refer to as "weather." In contrast, mixing *between* the layers of the atmosphere occurs relatively slowly, so each layer has distinctive chemistry. We focus our attention on the stratosphere, which contains the highest concentration of ozone.

The sun's radiation is the major source of energy that initiates chemical reactions in the atmosphere. The sun emits many kinds of radiation, including visible light, which is radiation that the human eye can detect, and ultraviolet light, which is higher energy radiation that cannot be detected by the human eye. This higher energy ultraviolet light can cause a wide variety of chemical reactions that are harmful to

organisms. For example, ultraviolet light is used to sterilize items, and, as anyone who has ever suffered a severe sunburn knows, it can produce extensive tissue damage.

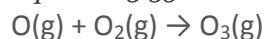
Light in the higher energy ultraviolet range is almost totally absorbed by oxygen molecules in the upper layers of the atmosphere, causing the O₂ molecules to dissociate into two oxygen atoms in a cleavage reaction:

Equation 3.34



In Equation 3.34, light is written above the arrow to indicate that light is required for the reaction to occur. The oxygen atoms produced in Equation 3.34 can undergo a condensation reaction with O₂ molecules to form ozone:

Equation 3.35



Ozone is responsible for the pungent smell we associate with lightning discharges and electric motors. It is also toxic and a significant air pollutant, particularly in cities.

In the stratosphere, the ozone produced via Equation 3.35 has a major beneficial effect. Ozone absorbs the less-energetic range of ultraviolet light, undergoing a cleavage reaction in the process to give O₂ and O:

Equation 3.36



The formation of ozone (Equation 3.35) and its decomposition (Equation 3.36) are normally in balance, resulting in essentially constant levels of about 10¹⁵ ozone molecules per liter in the stratosphere. This so-called ozone layer acts as a protective screen that absorbs ultraviolet light that would otherwise reach Earth's surface.

In 1974, F. Sherwood Rowland and Mario Molina published a paper claiming that commonly used chlorofluorocarbon (CFC) compounds were causing major damage to the ozone layer (Table 3.3 "Common CFCs and Related Compounds"). CFCs had been used as refrigerants and propellants in aerosol cans for many years, releasing millions of tons of CFC molecules into the atmosphere. Because CFCs are volatile compounds that do not readily undergo chemical reactions, they persist in the atmosphere long enough to be carried to the top of the troposphere, where they eventually enter the stratosphere. There they are exposed to intense ultraviolet light and undergo a cleavage reaction to produce a chlorine atom, which is shown for Freon-11:

Equation 3.37

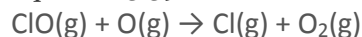


The resulting chlorine atoms act as a homogeneous catalyst in two redox reactions (Equation 3.38 and Equation 3.39):

Equation 3.38

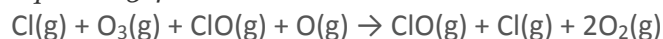


Equation 3.39



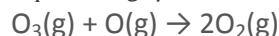
Adding the two reactions in Equation 3.38 and Equation 3.39 gives

Equation 3.40



Because chlorine and ClO (chlorine monoxide) appear on both sides of the equation, they can be canceled to give the following net reaction:

Equation 3.41



In the presence of chlorine atoms, one O_3 molecule and one oxygen atom react to give two O_2 molecules.

Although chlorine is necessary for the overall reaction to occur, it does not appear in the net equation. The chlorine atoms are a catalyst that increases the rate at which ozone is converted to oxygen.

Table 3.3 Common CFCs and Related Compounds

Name	Molecular Formula	Industrial Name
trichlorofluoromethane	CCl_3F	CFC-11 (Freon-11)
dichlorodifluoromethane	CCl_2F_2	CFC-12 (Freon-12)
chlorotrifluoromethane	CClF_3	CFC-13 (Freon-13)
bromotrifluoromethane	CBrF_3	Halon-1301*
bromochlorodifluoromethane	CBrClF_2	Halon-1211
*Halon-1301, compounds similar to CFCs that contain at least one bromine atom, are used as fire extinguishers in specific applications (e.g., the engine rooms of ships).		

Because the stratosphere is relatively isolated from the layers of the atmosphere above and below it, once chlorine-containing species enter the stratosphere, they remain there for long periods of time. Each chlorine atom produced from a CFC molecule can lead to the destruction of large numbers of ozone molecules, thereby decreasing the concentration of ozone in the stratosphere. Eventually, however, the

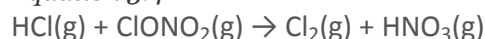
chlorine atom reacts with a water molecule to form hydrochloric acid, which is carried back into the troposphere and then washed out of the atmosphere in rainfall.

The Ozone Hole

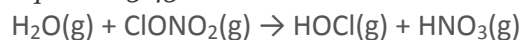
Massive ozone depletions were first observed in 1975 over the Antarctic and more recently over the Arctic. Although the reactions in Equation 3.38 and Equation 3.39 appear to account for most of the ozone destruction observed at low to middle latitudes, Equation 3.37 requires intense sunlight to generate chlorine atoms, and sunlight is in very short supply during the polar winters. At high latitudes (near the poles), therefore, a different set of reactions must be responsible for the depletion.

Recent research has shown that, in the absence of oxygen atoms, chlorine monoxide can react with stratospheric nitrogen dioxide in a redox reaction to form chlorine nitrate (ClONO_2). When chlorine nitrate is in the presence of trace amounts of HCl or adsorbed on ice particles in stratospheric clouds, additional redox reactions can occur in which chlorine nitrate produces Cl_2 or HOCl (hypochlorous acid):

Equation 3.42



Equation 3.43



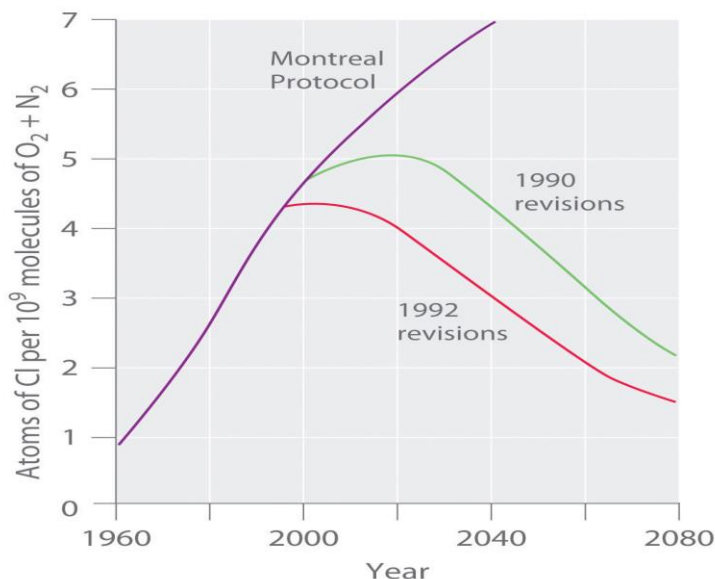
Both Cl_2 and HOCl undergo cleavage reactions by even weak sunlight to give reactive chlorine atoms.

When the sun finally rises after the long polar night, relatively large amounts of Cl_2 and HOCl are present and rapidly generate high levels of chlorine atoms. The reactions shown in Equation 3.38 and Equation 3.39 then cause ozone levels to fall dramatically.

Stratospheric ozone levels decreased about 2.5% from 1978 to 1988, which coincided with a fivefold increase in the widespread use of CFCs since the 1950s. If the trend were allowed to continue, the results could be catastrophic. Fortunately, many countries have banned the use of CFCs in aerosols. In 1987, representatives from 43 nations signed the Montreal Protocol, committing themselves to reducing CFC emissions by 50% by the year 2000. Later, representatives from a large number of countries, alarmed by data showing the rapid depletion of stratospheric chlorine, agreed to phase out CFCs completely by the early 21st century; the United States banned their use in 1995. The projected effects of these agreements on atmospheric chlorine levels are shown in Figure 3.17 "Projected Effects of International Agreements on Atmospheric Chlorine Levels". Because of the very slow rate at which CFCs are removed from the stratosphere, however, stratospheric chlorine levels will not fall to the level at which the Antarctic ozone

hole was first observed until about 2050. The scientific community recognized Molina and Rowland's work in 1995, when they shared the Nobel Prize in Chemistry.

Figure 3.17 *Projected Effects of International Agreements on Atmospheric Chlorine Levels*

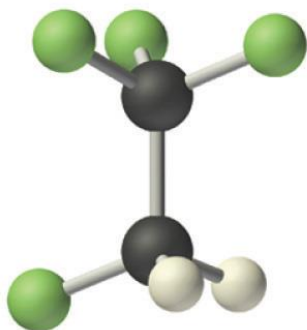


The graph plots atmospheric chlorine content in chlorine atoms per 10^9 molecules of O_2 plus N_2 from 1960 to 1990 (actual data) and 1990 to 2080 (estimated for various schemes for regulating CFC emissions).

Manufacturing companies are now under great political and economic pressure to find alternatives to the CFCs used in the air-conditioning units of cars, houses, and commercial buildings. One approach is to use *hydrochlorofluorocarbons (HCFCs)*, hydrocarbons in which only some of the hydrogen atoms are replaced by chlorine or fluorine, and *hydrofluorocarbons (HFCs)*, which do not contain chlorine (Table 3.4 "Selected HCFCs and HFCs"). The C–H bonds in HCFCs and HFCs act as “handles” that permit additional chemical reactions to occur. Consequently, these substances are degraded more rapidly, and most are washed out of the atmosphere before they can reach the stratosphere.

Table 3.4 Selected HCFCs and HFCs

Name	Molecular Formula	Industrial Name
chlorodifluoromethane	$CHClF_2$	HCFC-22 (freon-22)
1-chloro-1,1-difluoroethane	CH_3CClF_2	HCFC-141b
2,2-dichloro-1,1,1-trifluoroethane	$CHCl_2CF_3$	HCFC-123
1,1,1,2-tetrafluoroethane	CH_2FCF_3	HFC-134a



HFC-134a, CH_2FCF_3

HFCs are used as a replacement for CFCs. The molecular structure of HFC-134a is shown in this ball-and-stick model.

Nonetheless, the small fraction of HCFCs that reaches the stratosphere will deplete ozone levels just as CFCs do, so they are not the final answer. Indeed, the 1990 London amendment to the Montreal Protocol specifies that HCFCs must be phased out by 2040. Finding a suitable replacement for refrigerants is just one of the challenges facing chemists in the 21st century.

EXAMPLE 16

Nitric oxide (NO) may also be an important factor in the destruction of the ozone layer. One source of this compound is the combustion of hydrocarbons in jet engines. The fact that high-flying supersonic aircraft inject NO directly into the stratosphere was a major argument against the development of commercial supersonic transports. Do you agree with this decision? Why or why not?

Given: identity of compound

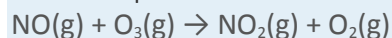
Asked for: assessment of likely role in ozone depletion

Strategy:

Predict what reactions are likely to occur between NO and ozone and then determine whether the reactions are likely to deplete ozone from the atmosphere.

Solution:

Both NO and NO_2 are known oxides of nitrogen. Thus NO is likely to react with ozone according to the chemical equation



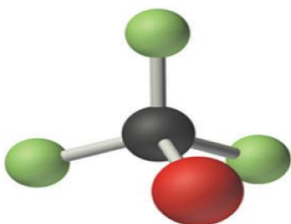
resulting in ozone depletion. If $\text{NO}_2\text{(g)}$ also reacts with atomic oxygen according to the equation

$$\text{NO}_2\text{(g)} + \text{O(g)} \rightarrow \text{NO(g)} + \text{O}_2\text{(g)}$$

then we would have a potential catalytic cycle for ozone destruction similar to that caused by chlorine atoms. Based on these reactions, the development of commercial supersonic transports is not recommended until the environmental impact has undergone additional testing. (Although these reactions have been observed, they do not appear to be a major factor in ozone destruction.)

Exercise

An industrial manufacturer proposed that halons such as CF_3Br could be used as replacements for CFC propellants. Do you think that this is a reasonable suggestion or is there a potential problem with such a use?



Halon-1301, CBrF_3

Answer: Because the compound CF_3Br contains carbon, fluorine, and a bromine atom that is chemically similar to chlorine, it is likely that it would also be a catalyst for ozone destruction. There is therefore a potential problem with its use.

Summary

Earth's atmosphere consists of discrete layers that do not mix readily with one another. The sun emits radiation with a wide range of energies, including **visible light**, which can be detected by the human eye, and **ultraviolet light**, which is more energetic than visible light and cannot be detected by the human eye. In the stratosphere, ultraviolet light reacts with O_2 molecules to form atomic oxygen. Atomic oxygen then reacts with an O_2 molecule to produce **ozone** (O_3). As a result of this reaction, the stratosphere contains an appreciable concentration of ozone molecules that constitutes the **ozone layer**. The absorption of ultraviolet light in the stratosphere protects Earth's surface from the sun's harmful effects. Volatile organic compounds that contain chlorine and fluorine, which are known as *chlorofluorocarbons* (CFCs), are capable of reaching the stratosphere, where they can react with ultraviolet light to generate chlorine atoms and other chlorine-containing species that catalyze the conversion of ozone to O_2 , thereby decreasing the amount of O_3 in the stratosphere. Replacing

chlorofluorocarbons with *hydrochlorofluorocarbons (HCFCs)* or *hydrofluorocarbons (HFCs)* is one strategy that has been developed to minimize further damage to Earth's ozone layer.

KEY TAKEAWAY

- The composition of Earth's atmosphere is vulnerable to degradation through reactions with common industrial chemicals.

CONCEPTUAL PROBLEMS

1. Carbon monoxide is a toxic gas that can be produced from the combustion of wood in wood-burning stoves when excess oxygen is not present. Write a balanced chemical equation showing how carbon monoxide is produced from carbon and suggest what might be done to prevent it from being a reaction product.
2. Explain why stratospheric ozone depletion has developed over the coldest part of Earth (the poles) and reaches a maximum at the beginning of the polar spring.
3. What type of reactions produce species that are believed to be responsible for catalytic depletion of ozone in the atmosphere?

NUMERICAL PROBLEM

Please be sure you are familiar with the topics discussed in Essential Skills 2 (Section 3.7 "Essential Skills 2") before proceeding to the Numerical Problems.

1. Sulfur dioxide and hydrogen sulfide are important atmospheric contaminants that have resulted in the deterioration of ancient objects. Sulfur dioxide combines with water to produce sulfurous acid, which then reacts with atmospheric oxygen to produce sulfuric acid. Sulfuric acid is known to attack many metals that were used by ancient cultures. Give the formulas for these four sulfur-containing species. What is the percentage of sulfur in each compound? What is the percentage of oxygen in each?

3.7 Essential Skills 2

TOPICS

- Proportions
- Percentages
- Unit Conversions

In Essential Skills 1 in Chapter 1 "Introduction to Chemistry", Section 1.9 "Essential Skills 1", we introduced you to some of the fundamental mathematical operations you need to successfully manipulate mathematical equations in

chemistry. Before proceeding to the problems in Chapter 3 "Chemical Reactions", you should become familiar with the additional skills described in this section on proportions, percentages, and unit conversions.

Proportions

We can solve many problems in general chemistry by using ratios, or proportions. For example, if the ratio of some quantity A to some quantity B is known, and the relationship between these quantities is known to be constant, then any change in A (from A_1 to A_2) produces a proportional change

in B (from B_1 to B_2) and vice versa. The relationship between A_1 , B_1 , A_2 , and B_2 can be written as follows:
 $A_1 B_1 = A_2 B_2 = \text{constant}$

To solve this equation for A_2 , we multiply both sides of the equality by B_2 , thus canceling B_2 from the denominator:

$$(B_2) A_1 B_1 = (B_2) A_2 B_2 B_2 A_1 B_1 = A_2$$

Similarly, we can solve for B_2 by multiplying both sides of the equality by $1/A_2$, thus canceling A_2 from the numerator:

$$(1/A_2) A_1 B_1 = (1/A_2) A_2 B_2 A_1 A_2 B_1 = 1 B_2$$

If the values of A_1 , A_2 , and B_1 are known, then we can solve the left side of the equation and invert the answer to obtain B_2 :

$$1 B_2 = \text{numerical value } B_2 = 1 \text{ numerical value}$$

If the value of A_1 , A_2 , or B_1 is unknown, however, we can solve for B_2 by inverting both sides of the equality:
 $B_2 = A_2 B_1 A_1$

When you manipulate equations, remember that *any operation carried out on one side of the equality must be carried out on the other*.

Skill Builder ES1 illustrates how to find the value of an unknown by using proportions.

SKILL BUILDER ES1

If 38.4 g of element A are needed to combine with 17.8 g of element B, then how many grams of element A are needed to combine with 52.3 g of element B?

Solution

We set up the proportions as follows:

$$A_1 = 38.4 \text{ g } B_1 = 17.8 \text{ g } A_2 = ? \text{ g } B_2 = 52.3 \text{ g } A_1 B_1 = A_2 B_2 \quad 38.4 \text{ g } 17.8 \text{ g} = A_2 52.3 \text{ g}$$

Multiplying both sides of the equation by 52.3 g gives

$$(38.4 \text{ g})(52.3 \text{ g}) 17.8 \text{ g} = A_2 (52.3 \text{ g}) (52.3 \text{ g}) \quad A_2 = 113 \text{ g}$$

Notice that grams cancel to leave us with an answer that is in the correct units. *Always check to make sure that your answer has the correct units.*

SKILL BUILDER ES2

Solve to find the indicated variable.

- $16.4 \text{ g} / 41.2 \text{ g} = x / 18.3 \text{ g}$
- $2.65 \text{ m} / 4.02 \text{ m} = 3.28 \text{ m} / y$
- $3.27 \times 10^{-3} \text{ g} / x = 5.0 \times 10^{-1} \text{ g} / 3.2 \text{ g}$
- Solve for V_1 : $P_1 P_2 = V_2 V_1$
- Solve for T_1 : $P_1 V_1 T_1 = P_2 V_2 T_2$

Solution

- Multiply both sides of the equality by 18.3 g to remove this measurement from the denominator:

$$(18.3 \text{ g}) (16.4 \text{ g} / 41.2 \text{ g}) = (18.3 \text{ g}) (x / 18.3 \text{ g}) \quad 7.28 \text{ g} = x$$

- Multiply both sides of the equality by $1/3.28 \text{ m}$, solve the left side of the equation, and then invert to solve for y :

$$(1/3.28 \text{ m}) (2.65 \text{ m} / 4.02 \text{ m}) = (1/3.28 \text{ m}) (3.28 \text{ m} / y) = 1/y \quad y = (4.02)(3.28)/2.65 = 4.98 \text{ m}$$

- Multiply both sides of the equality by $1/3.27 \times 10^{-3} \text{ g}$, solve the right side of the equation, and then invert to find x :

$$(1/3.27 \times 10^{-3} \text{ g}) (3.27 \times 10^{-3} \text{ g} / x) = (1/3.27 \times 10^{-3} \text{ g}) (5.0 \times 10^{-1} \text{ g} / 3.2 \text{ g}) = 1/x$$

$$x = (3.2 \text{ g})(3.27 \times 10^{-3} \text{ g}) / (5.0 \times 10^{-1} \text{ g}) = 2.1 \times 10^{-2} \text{ g}$$

- Multiply both sides of the equality by $1/V_2$, and then invert both sides to obtain V_1 :

$$(1/V_2) P_1 P_2 = (1/V_2) V_2 V_1 \quad P_2 V_2 P_1 = V_1$$

- Multiply both sides of the equality by $1/P_1 V_1$ and then invert both sides to obtain T_1 :

$$(1/P_1 V_1) P_1 V_1 T_1 = (1/P_1 V_1) P_2 V_2 T_2 \quad 1 T_1 = P_2 V_2 T_2 / P_1 V_1$$

$$T_1 = T_2 P_2 V_2 / P_1 V_1$$

Percentages

Because many measurements are reported as percentages, many chemical calculations require an understanding of how to manipulate such values. You may, for example, need to calculate the mass percentage of a substance, as described in Section 3.2 "Determining Empirical and Molecular Formulas", or determine the percentage of product obtained from a particular reaction mixture.

You can convert a percentage to decimal form by dividing the percentage by 100:

$$52.8\% = \frac{52.8}{100} = 0.528$$

Conversely, you can convert a decimal to a percentage by multiplying the decimal by 100:

$$0.356 \times 100 = 35.6\%$$

Suppose, for example, you want to determine the mass of substance A, one component of a sample with a mass of 27 mg, and you are told that the sample consists of 82% A. You begin by converting the

percentage to decimal form:

$$82\% = \frac{82}{100} = 0.82$$

The mass of A can then be calculated from the mass of the sample:

$$0.82 \times 27 \text{ mg} = 22 \text{ mg}$$

Skill Builder ES3 provides practice in converting and using percentages.

SKILL BUILDER ES3

Convert each number to a percentage or a decimal.

- a. 29.4%
- b. 0.390
- c. 101%
- d. 1.023

Solution

- a. $\frac{29.4}{100} = 0.294$
- b. $0.390 \times 100 = 39.0\%$
- c. $\frac{101}{100} = 1.01$
- d. $1.023 \times 100 = 102.3\%$

SKILL BUILDER ES4

Use percentages to answer the following questions, being sure to use the correct number of significant figures (see Essential Skills 1 in Chapter 1 "Introduction to Chemistry", Section 1.9 "Essential Skills 1"). Express your answer in scientific notation where appropriate.

- What is the mass of hydrogen in 52.83 g of a compound that is 11.2% hydrogen?
- What is the percentage of carbon in 28.4 g of a compound that contains 13.79 g of that element?
- A compound that is 4.08% oxygen contains 194 mg of that element. What is the mass of the compound?

Solution

- $52.83 \text{ g} \times 11.2 \div 100 = 52.83 \text{ g} \times 0.112 = 5.92 \text{ g}$
- $13.79 \text{ g carbon} \div 28.4 \text{ g} \times 100 = 48.6 \% \text{ carbon}$
- This problem can be solved by using a proportion:
 $4.08\% \text{ oxygen} \quad 100\% \text{ compound} = 194 \text{ mg} \times \text{mg} \times = 4.75 \times 10^3 \text{ mg (or } 4.75 \text{ g)}$

Unit Conversions

As you learned in Essential Skills 1 in Chapter 1 "Introduction to Chemistry", Section 1.9 "Essential Skills 1", all measurements must be expressed in the correct units to have any meaning. This sometimes requires converting between different units (Table 1.7 "SI Base Units"). Conversions are carried out using conversion factors, which are ratios constructed from the relationships between different units or measurements. The relationship between milligrams and grams, for example, can be expressed as either 1 g/1000 mg or 1000 mg/1 g. When making unit conversions, use arithmetic steps accompanied by unit cancellation.

Suppose you have measured a mass in milligrams but need to report the measurement in kilograms. In problems that involve SI units, you can use the definitions of the prefixes given in Table 1.6 "Approximate Elemental Composition of a Typical 70 kg Human" to get the necessary conversion factors. For example, you can convert milligrams to grams and then convert grams to kilograms:
 milligrams → grams → kilograms
 $1000 \text{ mg} \rightarrow 1 \text{ g} \quad 1000 \text{ g} \rightarrow 1 \text{ kilogram}$

If you have measured 928 mg of a substance, you can convert that value to kilograms as follows:
 $928 \text{ mg} \times 1 \text{ g} \div 1000 \text{ mg} = 0.928 \text{ g} \quad 0.928 \text{ g} \times 1 \text{ kg} \div 1000 \text{ g} = 0.000928 \text{ kg} = 9.28 \times 10^{-4} \text{ kg}$

In each arithmetic step, the units cancel as if they were algebraic variables, leaving us with an answer in kilograms. In the conversion to grams, we begin with milligrams in the numerator. Milligrams must therefore appear in the denominator of the conversion factor to produce an answer in grams. The

individual steps may be connected as follows:

$$928 \text{ mg} \times 1 \text{ g} \div 1000 \text{ mg} \times 1 \text{ kg} \div 1000 \text{ g} = 928 \text{ kg} \div 10^6 = 928 \times 10^{-6} \text{ kg} = 9.28 \times 10^{-4} \text{ kg}$$

Skill Builder ES5 provides practice converting between units.

SKILL BUILDER ES5

Use the information in Table 1.8 "Prefixes Used with SI Units" to convert each measurement. Be sure that your answers contain the correct number of significant figures and are expressed in scientific notation where appropriate.

- a. 59.2 cm to decimeters
- b. 3.7×10^5 mg to kilograms
- c. 270 mL to cubic decimeters
- d. 2.04×10^3 g to tons
- e. 9.024×10^{10} s to years

Solution

- a. $59.2 \text{ cm} \times \frac{1 \text{ m}}{100 \text{ cm}} = 0.592 \text{ m}$
- b. $3.7 \times 10^5 \text{ mg} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 3.7 \times 10^{-1} \text{ kg}$
- c. $270 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.270 \text{ L}$
 $0.270 \text{ L} \times \frac{1 \text{ dm}^3}{1 \text{ L}} = 0.270 \text{ dm}^3$
- d. $2.04 \times 10^3 \text{ g} \times \frac{1 \text{ lb}}{453.6 \text{ g}} \times \frac{1 \text{ tn}}{2000 \text{ lb}} = 0.00225 \text{ tn} = 2.25 \times 10^{-3} \text{ tn}$
- e. $9.024 \times 10^{10} \text{ s} \times \frac{1 \text{ min}}{60 \text{ s}} \times \frac{1 \text{ h}}{60 \text{ min}} \times \frac{1 \text{ d}}{24 \text{ h}} \times \frac{1 \text{ yr}}{365 \text{ d}} = 2.86 \times 10^3 \text{ yr}$

3.8 End-of-Chapter Material

APPLICATION PROBLEMS

Please be sure you are familiar with the topics discussed in Essential Skills 2 (Section 3.7 "Essential Skills 2") before proceeding to the Application Problems. Problems marked with a ♦ involve multiple concepts.

1. Hydrogen sulfide is a noxious and toxic gas produced from decaying organic matter that contains sulfur. A lethal concentration in rats corresponds to an inhaled dose of 715 molecules per million molecules of air. How many molecules does this correspond to per mole of air? How many moles of hydrogen sulfide does this correspond to per mole of air?

2. Bromine, sometimes produced from brines (salt lakes) and ocean water, can be used for bleaching fibers and silks. How many moles of bromine atoms are found in 8.0 g of molecular bromine (Br_2)?
3. Paris yellow is a lead compound that is used as a pigment; it contains 16.09% chromium, 19.80% oxygen, and 64.11% lead. What is the empirical formula of Paris yellow?
4. A particular chromium compound used for dyeing and waterproofing fabrics has the elemental composition 18.36% chromium, 13.81% potassium, 45.19% oxygen, and 22.64% sulfur. What is the empirical formula of this compound?
5. Compounds with aluminum and silicon are commonly found in the clay fractions of soils derived from volcanic ash. One of these compounds is *vermiculite*, which is formed in reactions caused by exposure to weather. Vermiculite has the following formula: $\text{Ca}_{0.7}[\text{Si}_{6.6}\text{Al}_{1.4}]\text{Al}_4\text{O}_{20}(\text{OH})_4$. (The content of calcium, silicon, and aluminum are not shown as integers because the relative amounts of these elements vary from sample to sample.) What is the mass percent of each element in this sample of vermiculite?
6. ♦ Pheromones are chemical signals secreted by a member of one species to evoke a response in another member of the same species. One honeybee pheromone is an organic compound known as an alarm pheromone, which smells like bananas. It induces an aggressive attack by other honeybees, causing swarms of angry bees to attack the same aggressor. The composition of this alarm pheromone is 64.58% carbon, 10.84% hydrogen, and 24.58% oxygen by mass, and its molecular mass is 130.2 amu.
 - a. Calculate the empirical formula of this pheromone.
 - b. Determine its molecular formula.
 - c. Assuming a honeybee secretes 1.00×10^{-11} g of pure pheromone, how many molecules of pheromone are secreted?
7. Amoxicillin is a prescription drug used to treat a wide variety of bacterial infections, including infections of the middle ear and the upper and lower respiratory tracts. It destroys the cell walls of bacteria, which causes them to die. The elemental composition of amoxicillin is 52.59% carbon, 5.24% hydrogen, 11.50% nitrogen, 21.89% oxygen, and 8.77% sulfur by mass. What is its empirical formula?
8. Monosodium glutamate (MSG; molar mass = 169 g/mol), is used as a flavor enhancer in food preparation. It is known to cause headaches and chest pains in some individuals, the so-called Chinese food syndrome. Its composition was found to be 35.51% carbon, 4.77% hydrogen, 8.28% nitrogen, and 13.59% sodium by mass. If the “missing” mass is oxygen, what is the empirical formula of MSG?

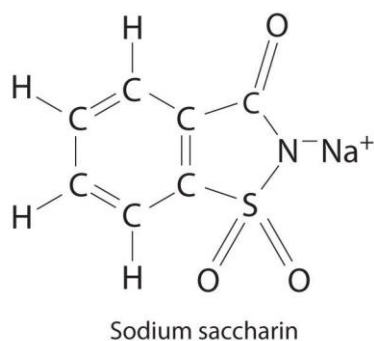
9. Ritalin is a mild central nervous system stimulant that is prescribed to treat attention deficit disorders and narcolepsy (an uncontrollable desire to sleep). Its chemical name is methylphenidate hydrochloride, and its empirical formula is $C_{14}H_{20}ClNO_2$. If you sent a sample of this compound to a commercial laboratory for elemental analysis, what results would you expect for the mass percentages of carbon, hydrogen, and nitrogen?
10. Fructose, a sugar found in fruit, contains only carbon, oxygen, and hydrogen. It is used in ice cream to prevent a sandy texture. Complete combustion of 32.4 mg of fructose in oxygen produced 47.6 mg of CO_2 and 19.4 mg of H_2O . What is the empirical formula of fructose?
11. Coniine, the primary toxin in hemlock, contains only carbon, nitrogen, and hydrogen. When ingested, it causes paralysis and eventual death. Complete combustion of 28.7 mg of coniine produced 79.4 mg of CO_2 and 34.4 mg of H_2O . What is the empirical formula of the coniine?
12. Copper and tin alloys (bronzes) with a high arsenic content were presumably used by Bronze Age metallurgists because bronze produced from arsenic-rich ores had superior casting and working properties.

The compositions of some representative bronzes of this type are as follows:

Origin	% Composition	
	Cu	As
Dead Sea	87.0	12.0
Central America	90.7	3.8

13. If ancient metallurgists had used the mineral As_2S_3 as their source of arsenic, how much As_2S_3 would have been required to process 100 g of cuprite (Cu_2O) bronzes with these compositions?
14. ♦ The phrase *mad as a hatter* refers to mental disorders caused by exposure to mercury(II) nitrate in the felt hat manufacturing trade during the 18th and 19th centuries. An even greater danger to humans, however, arises from alkyl derivatives of mercury.
 - a. Give the empirical formula of mercury(II) nitrate.
 - b. One alkyl derivative, dimethylmercury, is a highly toxic compound that can cause mercury poisoning in humans. How many molecules are contained in a 5.0 g sample of dimethylmercury?
 - c. What is the percentage of mercury in the sample?

15. Magnesium carbonate, aluminum hydroxide, and sodium bicarbonate are commonly used as antacids. Give the empirical formulas and determine the molar masses of these compounds. Based on their formulas, suggest another compound that might be an effective antacid.
16. ♦ Nickel(II) acetate, lead(II) phosphate, zinc nitrate, and beryllium oxide have all been reported to induce cancers in experimental animals.
- Give the empirical formulas for these compounds.
 - Calculate their formula masses.
 - Based on the location of cadmium in the periodic table, would you predict that cadmium chloride might also induce cancer?
17. ♦ Methane, the major component of natural gas, is found in the atmospheres of Jupiter, Saturn, Uranus, and Neptune.
- What is the structure of methane?
 - Calculate the molecular mass of methane.
 - Calculate the mass percentage of both elements present in methane.
18. Sodium saccharin, which is approximately 500 times sweeter than sucrose, is frequently used as a sugar substitute. What are the percentages of carbon, oxygen, and sulfur in this artificial sweetener?



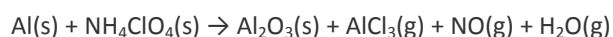
18. Lactic acid, found in sour milk, dill pickles, and sauerkraut, has the functional groups of both an alcohol and a carboxylic acid. The empirical formula for this compound is CH_2O , and its molar mass is 90 g/mol. If this compound were sent to a laboratory for elemental analysis, what results would you expect for carbon, hydrogen, and oxygen content?
19. The compound 2-nonenal is a cockroach repellent that is found in cucumbers, watermelon, and carrots. Determine its molecular mass.



2-Nonenal

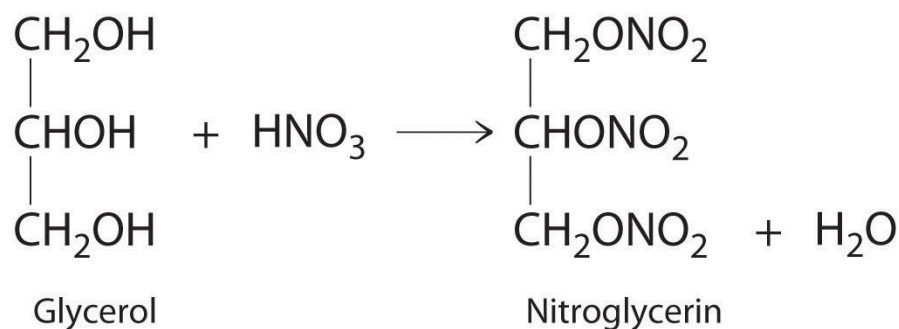
20. You have obtained a 720 mg sample of what you believe to be pure fructose, although it is possible that the sample has been contaminated with formaldehyde. Fructose and formaldehyde both have the empirical formula CH_2O . Could you use the results from combustion analysis to determine whether your sample is pure?

21. ♦ The booster rockets in the space shuttles used a mixture of aluminum metal and ammonium perchlorate for fuel. Upon ignition, this mixture can react according to the chemical equation



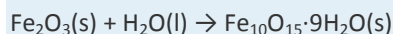
22. Balance the equation and construct a table showing how to interpret this information in terms of the following:

- numbers of individual atoms, molecules, and ions
 - moles of reactants and products
 - grams of reactants and products
 - numbers of molecules of reactants and products given 1 mol of aluminum metal
2. ♦ One of the byproducts of the manufacturing of soap is glycerol. In 1847, it was discovered that the reaction of glycerol with nitric acid produced nitroglycerin according to the following unbalanced chemical equation:



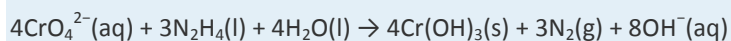
- Nitroglycerine is both an explosive liquid and a blood vessel dilator that is used to treat a heart condition known as angina.
 - Balance the chemical equation and determine how many grams of nitroglycerine would be produced from 15.00 g of glycerol.

- b. If 9.00 g of nitric acid had been used in the reaction, which would be the limiting reactant?
 - c. What is the theoretical yield in grams of nitroglycerin?
 - d. If 9.3 g of nitroglycerin was produced from 9.0 g of nitric acid, what would be the percent yield?
 - e. Given the data in part d, how would you rate the success of this reaction according to the criteria mentioned in this chapter?
 - f. Derive a general expression for the theoretical yield of nitroglycerin in terms of x grams of glycerol.
2. ♦ A significant weathering reaction in geochemistry is hydration–dehydration. An example is the transformation of hematite (Fe_2O_3) to ferrihydrite ($\text{Fe}_{10}\text{O}_{15}\cdot 9\text{H}_2\text{O}$) as the relative humidity of the soil approaches 100%:



This reaction occurs during advanced stages of the weathering process.

- a. Balance the chemical equation.
 - b. Is this a redox reaction? Explain your answer.
 - c. If 1 tn of hematite rock weathered in this manner, how many kilograms of ferrihydrite would be formed?
3. ♦ Hydrazine (N_2H_4) is used not only as a rocket fuel but also in industry to remove toxic chromates from waste water according to the following chemical equation:



Identify the species that is oxidized and the species that is reduced. What mass of water is needed for the complete reaction of 15.0 kg of hydrazine? Write a general equation for the mass of chromium(III) hydroxide $[\text{Cr}(\text{OH})_3]$ produced from x grams of hydrazine.

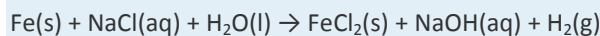
4. ♦ *Corrosion* is a term for the deterioration of metals through chemical reaction with their environment. A particularly difficult problem for the archaeological chemist is the formation of CuCl , an unstable compound that is formed by the corrosion of copper and its alloys. Although copper and bronze objects can survive burial for centuries without significant deterioration, exposure to air can cause cuprous chloride to react with atmospheric oxygen to form Cu_2O and cupric chloride. The cupric chloride then reacts with the free metal to produce cuprous chloride. Continued reaction of oxygen and water with cuprous chloride causes “bronze disease,” which consists of spots of a pale green, powdery deposit of $[\text{CuCl}_2\cdot 3\text{Cu}(\text{OH})_2\cdot \text{H}_2\text{O}]$ on the surface of the object that continues to grow. Using this series of reactions described, complete and balance the following equations, which together result in bronze disease:

Equation 1: $\text{___} + \text{O}_2 \rightarrow \text{___} + \text{___}$

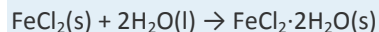
Equation 2: $\text{___} + \text{Cu} \rightarrow \text{___}$

Equation 3: $\text{___} + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$ bronze disease + CuCl_2

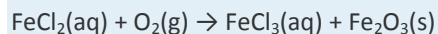
- a. Which species are the oxidants and the reductants in each equation?
- b. If 8.0% by mass of a 350.0 kg copper statue consisted of CuCl_2 , and the statue succumbed to bronze disease, how many pounds of the powdery green hydrate would be formed?
- c. What factors could affect the rate of deterioration of a recently excavated bronze artifact?
5. ♦ Iron submerged in seawater will react with dissolved oxygen, but when an iron object, such as a ship, sinks into the seabed where there is little or no free oxygen, the iron remains fresh until it is brought to the surface. Even in the seabed, however, iron can react with salt water according to the following unbalanced chemical equation:



The ferrous chloride and water then form hydrated ferrous chloride according to the following equation:

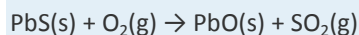


When the submerged iron object is removed from the seabed, the ferrous chloride dihydrate reacts with atmospheric moisture to form a solution that seeps outward, producing a characteristic “sweat” that may continue to emerge for many years. Oxygen from the air oxidizes the solution to ferric resulting in the formation of what is commonly referred to as rust (ferric oxide):



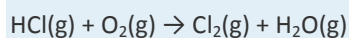
The rust layer will continue to grow until arrested.

- a. Balance each chemical equation.
- b. Given a 10.0 tn ship of which 2.60% is now rust, how many kilograms of iron were converted to FeCl_2 , assuming that the ship was pure iron?
- c. What mass of rust in grams would result?
- d. What is the overall change in the oxidation state of iron for this process?
- e. In the first equation given, what species has been reduced? What species has been oxidized?
6. ♦ The glass industry uses lead oxide in the production of fine crystal glass, such as crystal goblets. Lead oxide can be formed by the following reaction:



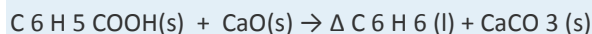
Balance the equation and determine what has been oxidized and what has been reduced. How many grams of sulfur dioxide would be produced from 4.0×10^3 g of lead sulfide? Discuss some potential environmental hazards that stem from this reaction.

7. ♦ The Deacon process is one way to recover Cl_2 on-site in industrial plants where the chlorination of hydrocarbons produces HCl. The reaction uses oxygen to oxidize HCl to chlorine, as shown.



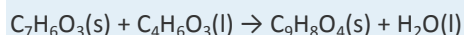
The reaction is frequently carried out in the presence of NO as a catalyst.

- Balance the chemical equation.
 - Which compound is the oxidant, and which is the reductant?
 - If 26 kg of HCl was produced during a chlorination reaction, how many kilograms of water would result from the Deacon process?
8. In 1834, Eilhardt Mitscherlich of the University of Berlin synthesized benzene (C_6H_6) by heating benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$) with calcium oxide according to this balanced chemical equation:



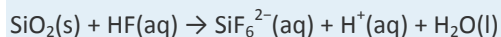
(Heating is indicated by the symbol Δ .) How much benzene would you expect from the reaction of 16.9 g of benzoic acid and 18.4 g of calcium oxide? Which is the limiting reactant? How many grams of benzene would you expect to obtain from this reaction, assuming a 73% yield?

9. Aspirin ($\text{C}_9\text{H}_8\text{O}_4$) is synthesized by the reaction of salicylic acid ($\text{C}_7\text{H}_6\text{O}_3$) with acetic anhydride ($\text{C}_4\text{H}_6\text{O}_3$) according to the following equation:



Balance the equation and find the limiting reactant given 10.0 g of acetic anhydride and 8.0 g of salicylic acid. How many grams of aspirin would you expect from this reaction, assuming an 83% yield?

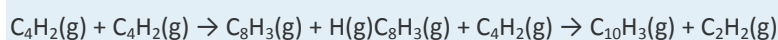
10. ♦ Hydrofluoric acid etches glass because it dissolves silicon dioxide, as represented in the following chemical equation:



- Balance the equation.
- How many grams of silicon dioxide will react with 5.6 g of HF?
- How many grams of HF are needed to remove 80% of the silicon dioxide from a 4.0 kg piece of glass?

(Assume that the glass is pure silicon dioxide.)

11. ♦ Lead sulfide and hydrogen peroxide react to form lead sulfate and water. This reaction is used to clean oil paintings that have blackened due to the reaction of the lead-based paints with atmospheric hydrogen sulfide.
- Write the balanced chemical equation for the oxidation of lead sulfide by hydrogen peroxide.
 - What mass of hydrogen peroxide would be needed to remove 3.4 g of lead sulfide?
 - If the painting had originally been covered with 5.4 g of lead sulfide and you had 3.0 g of hydrogen peroxide, what percent of the lead sulfide could be removed?
12. ♦ It has been suggested that diacetylene (C_4H_2 , $HC\equiv C-C\equiv CH$) may be the ozone of the outer planets. As the largest hydrocarbon yet identified in planetary atmospheres, diacetylene shields planetary surfaces from ultraviolet radiation and is itself reactive when exposed to light. One reaction of diacetylene is an important route for the formation of higher hydrocarbons, as shown in the following chemical equations:



Consider the second reaction.

- Given 18.4 mol of C_8H_3 and 1000 g of C_4H_2 , which is the limiting reactant?
 - Given 2.8×10^{24} molecules of C_8H_3 and 250 g of C_4H_2 , which is the limiting reactant?
 - Given 385 g of C_8H_3 and 200 g of C_4H_2 , which is in excess? How many grams of excess reactant would remain?
 - Suggest why this reaction might be of interest to scientists.
13. ♦ Glucose ($C_6H_{12}O_6$) can be converted to ethanol and carbon dioxide using certain enzymes. As alcohol concentrations are increased, however, catalytic activity is inhibited, and alcohol production ceases.
- Write a balanced chemical equation for the conversion of glucose to ethanol and carbon dioxide.
 - Given 12.6 g of glucose, how many grams of ethanol would be produced, assuming complete conversion?
 - If 4.3 g of ethanol had been produced, what would be the percent yield for this reaction?
 - Is a heterogeneous catalyst or a homogeneous catalyst used in this reaction?
 - You have been asked to find a way to increase the rate of this reaction given stoichiometric quantities of each reactant. How would you do this?
14. Early spacecraft developed by the National Aeronautics and Space Administration for its manned missions used capsules that had a pure oxygen atmosphere. This practice was stopped when a spark from an electrical short in the wiring inside the capsule of the Apollo 1 spacecraft ignited its contents. The resulting explosion

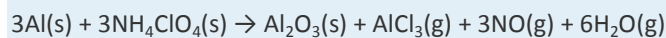
and fire killed the three astronauts on board within minutes. What chemical steps could have been taken to prevent this disaster?

ANSWERS

1. 4.31×10^{20} molecules, 7.15×10^{-4}
- 2.
3. PbCrO_4
- 4.
5. To two decimal places, the percentages are: H: 0.54%; O: 51.39%; Al: 19.50%; Si: 24.81%; Ca: 3.75%
- 6.
7. $\text{C}_{16}\text{H}_{19}\text{O}_5\text{N}_3\text{S}$
- 8.
- 9.
- 10.
- 11.
- 12.
13.
 - a. $\text{Hg}(\text{NO}_3)_2$
 - b. 1.3×10^{22} molecules
 - c. 86.96% mercury by mass.
- 14.
15.
 - a. $\text{Ni}(\text{O}_2\text{CCH}_3)_2$; $\text{Pb}_3(\text{PO}_4)_2$; $\text{Zn}(\text{NO}_3)_2$; BeO
 - b. To four significant figures, the values are: $\text{Ni}(\text{O}_2\text{CCH}_3)_2$, 176.8 amu; $\text{Pb}_3(\text{PO}_4)_2$, 811.5 amu; $\text{Zn}(\text{NO}_3)_2$, 189.4 amu; BeO, 25.01 amu.
 - c. Yes.
- 16.
17. C, 40.98%; O, 23.39%; S, 15.63%
- 18.
19. 140.22 amu

20.

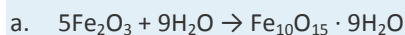
21.



	3Al	3NH ₄ ClO ₄	Al ₂ O ₃
a.	3 atoms	30 atoms, 6 ions	5 atoms
b.	3 mol	3 mol	1 mol
c.	81 g	352 g	102 g
d.	6×10^{23}	6×10^{23}	2×10^{23}
	AlCl ₃	3NO	6H ₂ O
a.	4 atoms, 1 molecule	6 atoms, 3 molecules	18 atoms, 6 molecules
b.	1 mol	3 mol	6 mol
c.	133 g	90 g	108 g
d.	2×10^{23}	6×10^{23}	1.2×10^{22}

22.

23.

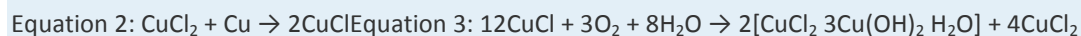
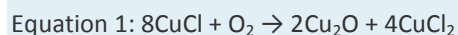


b. No.

c. 1090 kg

24.

25.

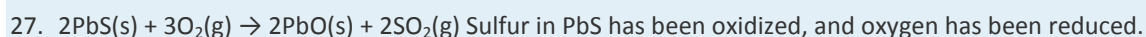


a. Equation 1: Oxygen is the oxidant, and CuCl is the reductant. Equation 2: Copper is the reductant, and copper(II) chloride is the oxidant. Equation 3: Copper(I) chloride is the reductant, and oxygen is the oxidant.

b. 46 pounds

c. temperature, humidity, and wind (to bring more O₂ into contact with the statue)

26.



1.1×10^3 g SO₂ is produced. Lead is a toxic metal. Sulfur dioxide reacts with water to make acid rain.

28.

29. 10.8 g benzene; limiting reactant is benzoic acid; 7.9 g of benzene
- 30.
- 31.
- a. $\text{SiO}_2 + 6\text{HF} \rightarrow \text{SiF}_6^{2-} + 2\text{H}^+ + 2\text{H}_2\text{O}$
- b. 2.8 g
- c. 6400 g HF
- 32.
- 33.
- a. C_8H_3
- b. C_8H_3
- c. C_4H_2 ; 6.0 g
- d. Complex molecules are essential for life. Reactions that help block UV may have implications regarding life on other planets.
- 34.
35. The disaster occurred because organic compounds are highly flammable in a pure oxygen atmosphere. Using a mixture of 20% O_2 and an inert gas such as N_2 or He would have prevented the disaster.

Chapter 4

Reactions in Aqueous Solution

In Chapter 3 "Chemical Reactions", we described chemical reactions in general and introduced some techniques that are used to characterize them quantitatively. For the sake of simplicity, we discussed situations in which the reactants and the products of a given reaction were the only chemical species present. In reality, however, virtually every chemical reaction that takes place within and around us, such as the oxidation of foods to generate energy or the treatment of an upset stomach with an antacid tablet, occur *in solution*. In fact, many reactions must be carried out in solution and do not take place at all if the solid reactants are simply mixed.

The reaction of mercury(II) acetate with sodium iodide. When colorless aqueous solutions of each reactant are mixed, they produce a red precipitate, mercury(II) iodide, which is the result of an exchange reaction.

As you learned in Chapter 1 "Introduction to Chemistry", a solution is a homogeneous mixture in which substances present in lesser amounts, called solutes, are dispersed uniformly throughout the substance in the greater amount, the solvent. An aqueous solution is a solution in which the solvent is water, whereas in a *nonaqueous solution*, the solvent is a substance other than water. Familiar examples of nonaqueous solvents are ethyl acetate, used in nail polish removers, and turpentine, used to clean paint brushes. In this chapter, we focus on reactions that occur in aqueous solution.

There are many reasons for carrying out reactions in solution. For a chemical reaction to occur, individual atoms, molecules, or ions must collide, and collisions between two solids, which are not dispersed at the atomic, molecular, or ionic level, do not occur at a significant rate. In addition, when the amount of a substance required for a reaction is so small that it cannot be weighed accurately, using a solution of that substance, in which the solute is dispersed in a much larger mass of solvent, enables chemists to measure its quantity with great precision. Chemists can also more effectively control the amount of heat consumed or produced in a reaction when the reaction occurs in solution, and sometimes the nature of the reaction itself can be controlled by the choice of solvent.

This chapter introduces techniques for preparing and analyzing aqueous solutions, for balancing equations that describe reactions in solution, and for solving problems using solution stoichiometry. By the time you complete this chapter, you will know enough about aqueous solutions to explain what causes acid rain, why acid rain is harmful, and how a Breathalyzer measures alcohol levels. You will also understand the chemistry of photographic development, be able to explain why rhubarb leaves are toxic, and learn about a possible chemical reason for the decline and fall of the Roman Empire.

4.1 Aqueous Solutions

LEARNING OBJECTIVE

1. To understand how and why solutions form.

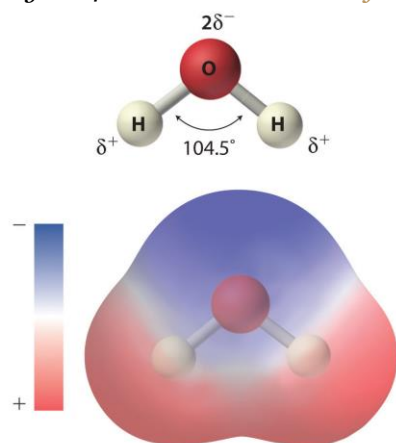
The solvent in aqueous solutions is water, which makes up about 70% of the mass of the human body and is essential for life. Many of the chemical reactions that keep us alive depend on the interaction of water molecules with dissolved compounds. Moreover, as we will discuss in Chapter 5 "Energy Changes in Chemical Reactions", the presence of large amounts of water on Earth's surface helps maintain its surface temperature in a range suitable for life. In this section,

we describe some of the interactions of water with various substances and introduce you to the characteristics of aqueous solutions.

Polar Substances

As shown in Figure 4.1 "The Polar Nature of Water", the individual water molecule consists of two hydrogen atoms bonded to an oxygen atom in a bent (V-shaped) structure. As is typical of group 16 elements, the oxygen atom in each O–H covalent bond attracts electrons more strongly than the hydrogen atom does. (For more information on periodic table groups and covalent bonding, see Chapter 2 "Molecules, Ions, and Chemical Formulas" and Chapter 7 "The Periodic Table and Periodic Trends".) Consequently, the oxygen and hydrogen nuclei do not equally share electrons. Instead, hydrogen atoms are electron poor compared with a neutral hydrogen atom and have a partial positive charge, which is indicated by δ^+ . The oxygen atom, in contrast, is more electron rich than a neutral oxygen atom, so it has a partial negative charge. This charge must be twice as large as the partial positive charge on each hydrogen for the molecule to have a net charge of zero. Thus its charge is indicated by $2\delta^-$. This unequal distribution of charge creates a polar bond, in which one portion of the molecule carries a partial negative charge, while the other portion carries a partial positive charge (Figure 4.1 "The Polar Nature of Water"). Because of the arrangement of polar bonds in a water molecule, water is described as a polar substance.

Figure 4.1 *The Polar Nature of Water*

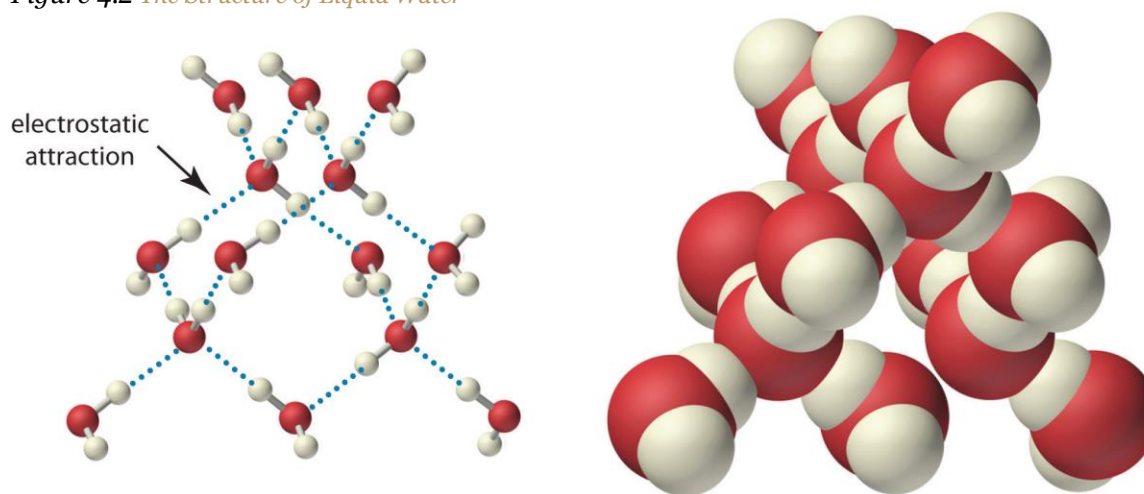


Each water molecule consists of two hydrogen atoms bonded to an oxygen atom in a bent (V-shaped) structure. Because the oxygen atom attracts electrons more strongly than the hydrogen atoms do, the oxygen atom is partially negatively charged ($2\delta^-$; blue) and the hydrogen atoms are partially positively charged (δ^+ ; red). For the molecule

to have a net charge of zero, the partial negative charge on oxygen must be twice as large as the partial positive charge on each hydrogen.

Because of the asymmetric charge distribution in the water molecule, adjacent water molecules are held together by attractive electrostatic ($\delta^+ \dots \delta^-$) interactions between the partially negatively charged oxygen atom of one molecule and the partially positively charged hydrogen atoms of adjacent molecules (Figure 4.2 "The Structure of Liquid Water"). Energy is needed to overcome these electrostatic attractions. In fact, without them, water would evaporate at a much lower temperature, and neither Earth's oceans nor we would exist!

Figure 4.2 The Structure of Liquid Water



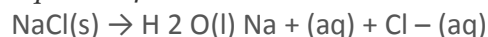
Two views of a water molecule are shown: (a) a ball-and-stick structure and (b) a space-filling model. Water molecules are held together by electrostatic attractions (dotted lines) between the partially negatively charged oxygen atom of one molecule and the partially positively charged hydrogen atoms on adjacent molecules. As a result, the water molecules in liquid water form transient networks with structures similar to that shown. Because the interactions between water molecules are continually breaking and reforming, liquid water does not have a single fixed structure.

As you learned in Section 2.1 "Chemical Compounds", ionic compounds such as sodium chloride (NaCl) are also held together by electrostatic interactions—in this case, between oppositely charged ions in the highly ordered solid, where each ion is surrounded by ions of the opposite charge in a fixed arrangement. In contrast to an ionic solid, the structure of liquid water is not completely ordered because the interactions between molecules in a liquid are constantly breaking and reforming.

The unequal charge distribution in polar liquids such as water makes them good solvents for ionic compounds. When an ionic solid dissolves in water, the ions *dissociate*. That is, the partially negatively charged oxygen atoms of the H_2O

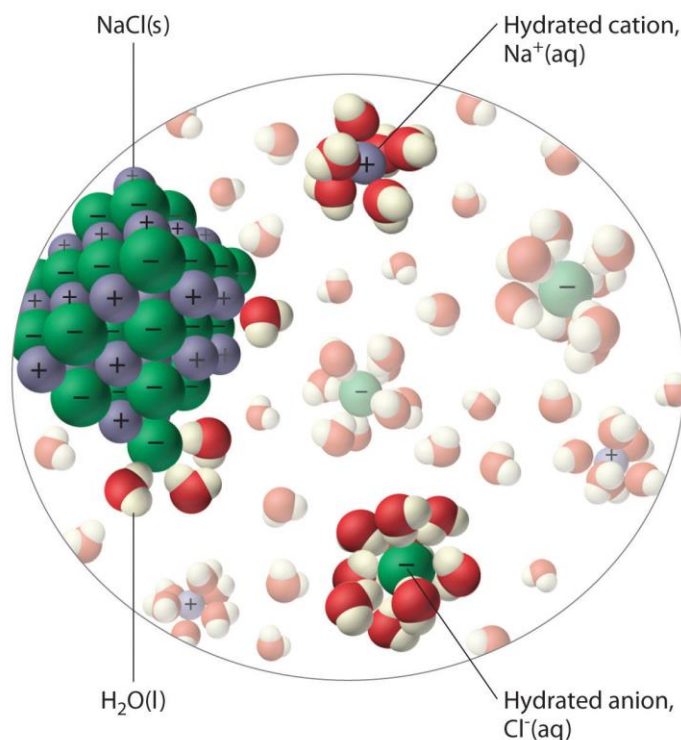
molecules surround the cations (Na^+ in the case of NaCl), and the partially positively charged hydrogen atoms in H_2O surround the anions (Cl^- ; Figure 4.3 "The Dissolution of Sodium Chloride in Water"). Individual cations and anions that are each surrounded by their own shell of water molecules are called hydrated ions. We can describe the dissolution of NaCl in water as

Equation 4.1



where (aq) indicates that Na^+ and Cl^- are hydrated ions.

Figure 4.3 The Dissolution of Sodium Chloride in Water



An ionic solid such as sodium chloride dissolves in water because of the electrostatic attraction between the cations (Na^+) and the partially negatively charged oxygen atoms of water molecules, and between the anions (Cl^-) and the partially positively charged hydrogen atoms of water.

Note the Pattern

Polar liquids are good solvents for ionic compounds.

Electrolytes

When electricity, in the form of an *electrical potential*, is applied to a solution, ions in solution migrate toward the oppositely charged rod or plate to complete an electrical circuit, whereas neutral molecules in solution do not (Figure 4.4 "The Effect of Ions on the Electrical Conductivity of Water"). Thus solutions

that contain ions conduct electricity, while solutions that contain only neutral molecules do not. Electrical current will flow through the circuit shown in Figure 4.4 "The Effect of Ions on the Electrical Conductivity of Water" and the bulb will glow *only* if ions are present. The lower the concentration of ions in solution, the weaker the current and the dimmer the glow. Pure water, for example, contains only very low concentrations of ions, so it is a poor electrical conductor.

Note the Pattern

Solutions that contain ions conduct electricity.

Figure 4.4 *The Effect of Ions on the Electrical Conductivity of Water*



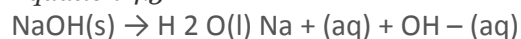
An electrical current will flow and light the bulb only if the solution contains ions. (a) Pure water or an aqueous solution of a nonelectrolyte allows almost no current to flow, and the bulb does not light. (b) A weak electrolyte produces a few ions, allowing some current to flow and the bulb to glow dimly. (c) A strong electrolyte produces many ions, allowing more current to flow and the bulb to shine brightly.

An electrolyte is any compound that can form ions when it dissolves in water. When strong electrolytes dissolve, the constituent ions dissociate completely due to strong electrostatic interactions with the solvent, producing aqueous solutions that conduct electricity very well (Figure 4.4 "The Effect of Ions on the Electrical Conductivity of Water"). Examples include ionic compounds such as barium chloride (BaCl_2) and sodium hydroxide (NaOH), which are both strong electrolytes and dissociate as follows:

Equation 4.2



Equation 4.3



The single arrows from reactant to products in Equation 4.2 and Equation 4.3 indicate that dissociation is complete.

When weak electrolytes dissolve, they produce relatively few ions in solution. This does *not* mean that the compounds do not dissolve readily in water; many weak electrolytes contain polar bonds and are therefore very soluble in a polar solvent such as water. They do not completely dissociate to form ions, however, because of their weaker electrostatic interactions with the solvent. Because very few of the dissolved particles are ions, aqueous solutions of weak electrolytes do not conduct electricity as well as solutions of strong electrolytes. One such compound is acetic acid ($\text{CH}_3\text{CO}_2\text{H}$), which contains the $-\text{CO}_2\text{H}$ unit. Although it is soluble in water, it is a weak acid and therefore also a weak electrolyte. Similarly, ammonia (NH_3) is a weak base and therefore a weak electrolyte. The behavior of weak acids and weak bases will be described in more detail when we discuss acid–base reactions in Section 4.6 "Acid–Base Reactions".

Nonelectrolytes that dissolve in water do so as neutral molecules and thus have essentially no effect on conductivity. Examples of nonelectrolytes that are very soluble in water but that are essentially nonconductive are ethanol, ethylene glycol, glucose, and sucrose, all of which contain the $-\text{OH}$ group that is characteristic of alcohols. In Chapter 8 "Ionic versus Covalent Bonding", we will discuss why alcohols and carboxylic acids behave differently in aqueous solution; for now, however, you can simply look for the presence of the $-\text{OH}$ and $-\text{CO}_2\text{H}$ groups when trying to predict whether a substance is a strong electrolyte, a weak electrolyte, or a nonelectrolyte. In addition to alcohols, two other classes of organic compounds that are nonelectrolytes are aldehydes and ketones, whose general structures are shown here. The distinctions between soluble and insoluble substances and between strong, weak, and nonelectrolytes are illustrated in Figure 4.5 "The Difference between Soluble and Insoluble Compounds (a) and Strong, Weak, and Nonelectrolytes (b)".

Note the Pattern

Ionic substances and carboxylic acids are electrolytes; alcohols, aldehydes, and ketones are nonelectrolytes.

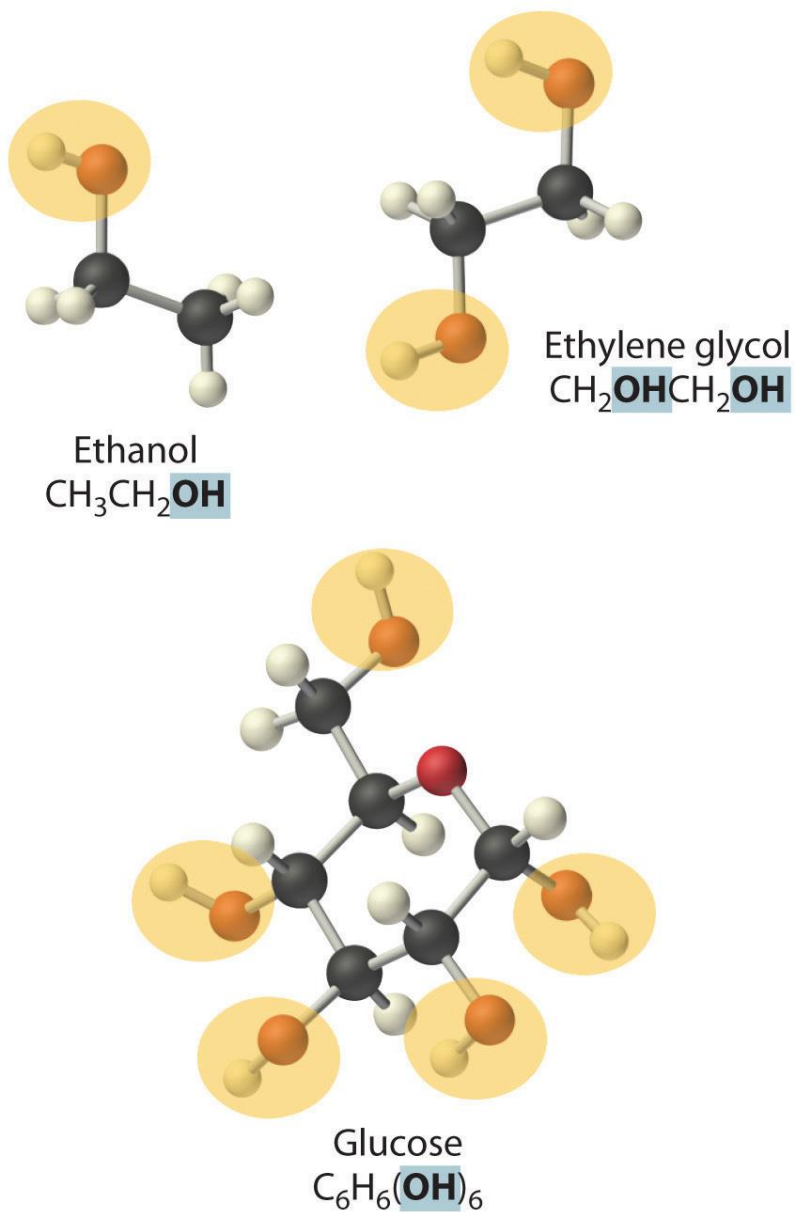
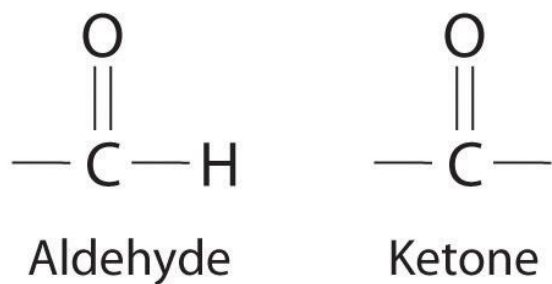
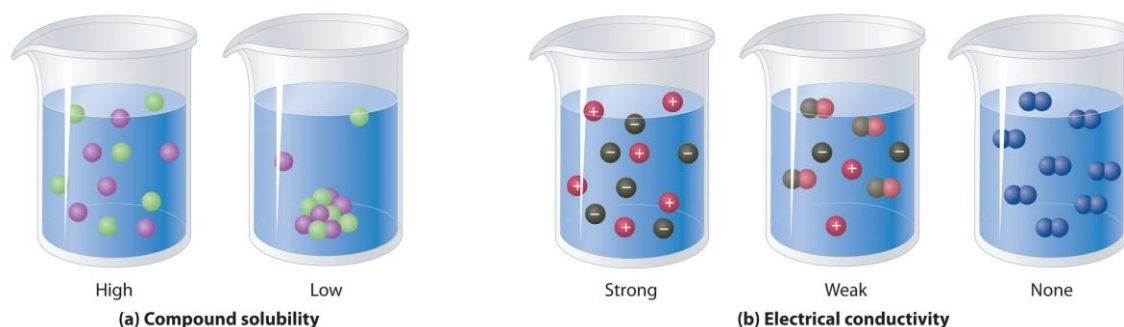


Figure 4.5 The Difference between Soluble and Insoluble Compounds (a) and Strong, Weak, and Nonelectrolytes (b)



General structure of an aldehyde and a ketone. Notice that both contain the $\text{C}=\text{O}$ group.

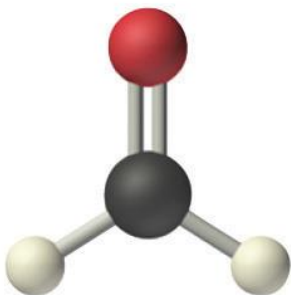


When a soluble compound dissolves, its constituent atoms, molecules, or ions disperse throughout the solvent. In contrast, the constituents of an insoluble compound remain associated with one another in the solid. A soluble compound is a strong electrolyte if it dissociates completely into ions, a weak electrolyte if it dissociates only slightly into ions, and a nonelectrolyte if it dissolves to produce only neutral molecules.

EXAMPLE 1

1. Predict whether each compound is a strong electrolyte, a weak electrolyte, or a nonelectrolyte in water.

a. formaldehyde



Formaldehyde,
 CH_2O

b. cesium chloride

Given: compound

Asked for: relative ability to form ions in water

Strategy:

A Classify the compound as ionic or covalent.

B If the compound is ionic and dissolves, it is a strong electrolyte that will dissociate in water completely to produce a solution that conducts electricity well. If the compound is covalent and organic, determine whether it contains the carboxylic acid group. If the compound contains this group, it is a weak electrolyte. If not, it is a nonelectrolyte.

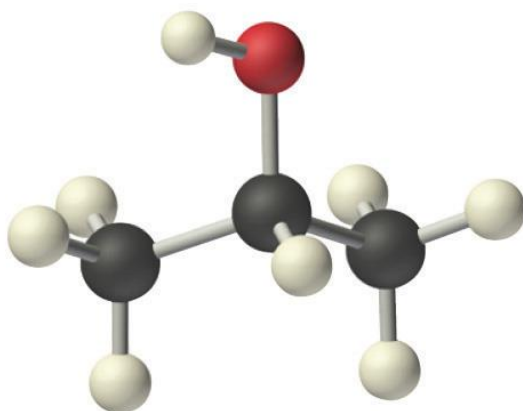
Solution:

- a. **A** Formaldehyde is an organic compound, so it is covalent. **B** It contains an aldehyde group, not a carboxylic acid group, so it should be a nonelectrolyte.
- b. **A** Cesium chloride (CsCl) is an ionic compound that consists of Cs^+ and Cl^- ions. **B** Like virtually all other ionic compounds that are soluble in water, cesium chloride will dissociate completely into $\text{Cs}^+(\text{aq})$ and $\text{Cl}^-(\text{aq})$ ions. Hence it should be a strong electrolyte.

Exercise

Predict whether each compound is a strong electrolyte, a weak electrolyte, or a nonelectrolyte in water.

- a. $(\text{CH}_3)_2\text{CHOH}$ (2-propanol)



2-Propanol (isopropyl alcohol),
 $(\text{CH}_3)_2\text{CHOH}$

- b. ammonium sulfate

Answer:

- a. nonelectrolyte
- a. strong electrolyte

Summary

Most chemical reactions are carried out in *solutions*, which are homogeneous mixtures of two or more substances. In a solution, a *solute* (the substance present in the lesser amount) is dispersed in a *solvent* (the substance present in the greater amount). *Aqueous solutions* contain water as the solvent, whereas *nonaqueous solutions* have solvents other than water.

Polar substances, such as water, contain asymmetric arrangements of **polar bonds**, in which electrons are shared unequally between bonded atoms. Polar substances and ionic compounds tend to be most soluble in water because they interact favorably with its structure. In aqueous solution, dissolved ions become **hydrated**; that is, a shell of water molecules surrounds them.

Substances that dissolve in water can be categorized according to whether the resulting aqueous solutions conduct electricity. **Strong electrolytes** dissociate completely into ions to produce solutions that conduct electricity well. **Weak electrolytes** produce a relatively small number of ions, resulting in solutions that conduct electricity poorly. **Nonelectrolytes** dissolve as uncharged molecules and have no effect on the electrical conductivity of water.

KEY TAKEAWAY

- Aqueous solutions can be classified as polar or nonpolar depending on how well they conduct electricity.

CONCEPTUAL PROBLEMS

1. What are the advantages to carrying out a reaction in solution rather than simply mixing the pure reactants?
2. What types of compounds dissolve in polar solvents?
3. Describe the charge distribution in liquid water. How does this distribution affect its physical properties?
4. Must a molecule have an asymmetric charge distribution to be polar? Explain your answer.
5. Why are many ionic substances soluble in water?
6. Explain the phrase *like dissolves like*.
7. What kinds of covalent compounds are soluble in water?
8. Why do most aromatic hydrocarbons have only limited solubility in water? Would you expect their solubility to be higher, lower, or the same in ethanol compared with water? Why?
9. Predict whether each compound will dissolve in water and explain why.
 - a. toluene
 - b. acetic acid
 - c. sodium acetate

- d. butanol
 - e. pentanoic acid
10. Predict whether each compound will dissolve in water and explain why.
- a. ammonium chloride
 - b. 2-propanol
 - c. heptane
 - d. potassium dichromate
 - e. 2-octanol
11. Given water and toluene, predict which is the better solvent for each compound and explain your reasoning.
- a. sodium cyanide
 - b. benzene
 - c. acetic acid
 - d. sodium ethoxide ($\text{CH}_3\text{CH}_2\text{ONa}$)
12. Of water and toluene, predict which is the better solvent for each compound and explain your reasoning.
- a. *t*-butanol
 - b. calcium chloride
 - c. sucrose
 - d. cyclohexene
13. Compound A is divided into three equal samples. The first sample does not dissolve in water, the second sample dissolves only slightly in ethanol, and the third sample dissolves completely in toluene. What does this suggest about the polarity of A?
14. You are given a mixture of three solid compounds—A, B, and C—and are told that A is a polar compound, B is slightly polar, and C is nonpolar. Suggest a method for separating these three compounds.
15. A laboratory technician is given a sample that contains only sodium chloride, sucrose, and cyclodecanone (a ketone). You must tell the technician how to separate these three compounds from the mixture. What would you suggest?
16. Many over-the-counter drugs are sold as ethanol/water solutions rather than as purely aqueous solutions. Give a plausible reason for this practice.
17. What distinguishes a weak electrolyte from a strong electrolyte?

18. Which organic groups result in aqueous solutions that conduct electricity?
19. It is considered highly dangerous to splash barefoot in puddles during a lightning storm. Why?
20. Which solution(s) would you expect to conduct electricity well? Explain your reasoning.
- an aqueous solution of sodium chloride
 - a solution of ethanol in water
 - a solution of calcium chloride in water
 - a solution of sucrose in water
21. Which solution(s) would you expect to conduct electricity well? Explain your reasoning.
- an aqueous solution of acetic acid
 - an aqueous solution of potassium hydroxide
 - a solution of ethylene glycol in water
 - a solution of ammonium chloride in water
22. Which of the following is a strong electrolyte, a weak electrolyte, or a nonelectrolyte in an aqueous solution?
Explain your reasoning.
- potassium hydroxide
 - ammonia
 - calcium chloride
 - butanoic acid
23. Which of the following is a strong electrolyte, a weak electrolyte, or a nonelectrolyte in an aqueous solution?
Explain your reasoning.
- magnesium hydroxide
 - butanol
 - ammonium bromide
 - pentanoic acid
24. Which of the following is a strong electrolyte, a weak electrolyte, or a nonelectrolyte in aqueous solution?
Explain your reasoning.
- H_2SO_4
 - diethylamine
 - 2-propanol

- d. ammonium chloride
- e. propanoic acid

ANSWERS

- 1.
- 2.
- 3.
- 4.
5. Ionic compounds such as NaCl are held together by electrostatic interactions between oppositely charged ions in the highly ordered solid. When an ionic compound dissolves in water, the partially negatively charged oxygen atoms of the H₂O molecules surround the cations, and the partially positively charged hydrogen atoms in H₂O surround the anions. The favorable electrostatic interactions between water and the ions compensate for the loss of the electrostatic interactions between ions in the solid.
- 6.
- 7.
- 8.
9.
 - a. Because toluene is an aromatic hydrocarbon that lacks polar groups, it is unlikely to form a homogenous solution in water.
 - b. Acetic acid contains a carboxylic acid group attached to a small alkyl group (a methyl group). Consequently, the polar characteristics of the carboxylic acid group will be dominant, and acetic acid will form a homogenous solution with water.
 - c. Because most sodium salts are soluble, sodium acetate should form a homogenous solution with water.
 - d. Like all alcohols, butanol contains an –OH group that can interact well with water. The alkyl group is rather large, consisting of a 4-carbon chain. In this case, the nonpolar character of the alkyl group is likely to be as important as the polar character of the –OH, decreasing the likelihood that butanol will form a homogeneous solution with water.
 - e. Like acetic acid, pentanoic acid is a carboxylic acid. Unlike acetic acid, however, the alkyl group is rather large, consisting of a 4-carbon chain as in butanol. As with butanol, the nonpolar character of the alkyl group is likely to be as important as the polar character of the carboxylic acid group, making it unlikely that pentanoic

acid will form a homogeneous solution with water. (In fact, the solubility of both butanol and pentanoic acid in water is quite low, only about 3 g per 100 g water at 25°C.)

10.

11.

12.

13.

14.

15.

16.

17. An *electrolyte* is any compound that can form ions when it dissolves in water. When a strong electrolyte dissolves in water, it dissociates completely to give the constituent ions. In contrast, when a weak electrolyte dissolves in water, it produces relatively few ions in solution.

4.2 Solution Concentrations

LEARNING OBJECTIVE

1. To describe the concentrations of solutions quantitatively.

All of us have a qualitative idea of what is meant by *concentration*. Anyone who has made instant coffee or lemonade knows that too much powder gives a strongly flavored, highly concentrated drink, whereas too little results in a dilute solution that may be hard to distinguish from water. In chemistry, the *concentration* of a solution describes the quantity of a solute that is contained in a particular quantity of solvent or solution. Knowing the concentration of solutes is important in controlling the stoichiometry of reactants for reactions that occur in solution. Chemists use many different ways to define concentrations, some of which are described in this section.

Molarity

The most common unit of concentration is *molarity*, which is also the most useful for calculations involving the stoichiometry of reactions in solution. The molarity (M) of a solution is the number of moles of solute present in exactly 1 L of solution. Molarity is also the number of millimoles of solute present in exactly 1 mL of solution:

Equation 4.4

molarity = moles of solute / liters of solution = mmol of solute / milliliters of solution

The units of molarity are therefore moles per liter of solution (mol/L), abbreviated as M. An aqueous solution that contains 1 mol (342 g) of sucrose in enough water to give a final volume of 1.00 L has a sucrose concentration of 1.00 mol/L or 1.00 M. In chemical notation, square brackets around the name or formula of the solute represent the concentration of a solute. So $[\text{sucrose}] = 1.00 \text{ M}$

is read as “the concentration of sucrose is 1.00 molar.” The relationships between volume, molarity, and moles may be expressed as either

Equation 4.5

$$V \text{ L } M \text{ mol/L} = L \text{ (mol L)} = \text{moles}$$

or

Equation 4.6

$$V \text{ mL } M \text{ mmol/mL} = \text{mL (mmol mL)} = \text{mmoles}$$

Example 2 illustrates the use of Equation 4.5 and Equation 4.6.

EXAMPLE 2

Calculate the number of moles of sodium hydroxide (NaOH) in 2.50 L of 0.100 M NaOH.

Given: identity of solute and volume and molarity of solution

Asked for: amount of solute in moles

Strategy:

Use either Equation 4.5 or Equation 4.6, depending on the units given in the problem.

Solution:

Because we are given the volume of the solution in liters and are asked for the number of moles of substance, Equation 4.5 is more useful:

$$\text{moles NaOH} = V \text{ L } M \text{ mol/L} = (2.50 \text{ L}) (0.100 \text{ mol/L}) = 0.250 \text{ mol NaOH}$$

Exercise

Calculate the number of millimoles of alanine, a biologically important molecule, in 27.2 mL of 1.53 M alanine.

Answer: 41.6 mmol

Concentrations are often reported on a mass-to-mass (m/m) basis or on a mass-to-volume (m/v) basis, particularly in clinical laboratories and engineering applications. A concentration expressed on an m/m basis is equal to the number of grams of solute per gram of solution; a concentration on an m/v basis is

the number of grams of solute per milliliter of solution. Each measurement can be expressed as a percentage by multiplying the ratio by 100; the result is reported as percent m/m or percent m/v. The concentrations of very dilute solutions are often expressed in *parts per million (ppm)*, which is grams of solute per 10^6 g of solution, or in *parts per billion (ppb)*, which is grams of solute per 10^9 g of solution. For aqueous solutions at 20°C, 1 ppm corresponds to 1 µg per milliliter, and 1 ppb corresponds to 1 ng per milliliter. These concentrations and their units are summarized in Table 4.1 "Common Units of Concentration".

Table 4.1 Common Units of Concentration

Concentration	Units
m/m	g of solute/g of solution
m/v	g of solute/mL of solution
ppm	g of solute/ 10^6 g of solution
	µg/mL
ppb	g of solute/ 10^9 g of solution
	ng/mL

The Preparation of Solutions

To prepare a solution that contains a specified concentration of a substance, it is necessary to dissolve the desired number of moles of solute in enough solvent to give the desired final volume of solution. Figure 4.6 "Preparation of a Solution of Known Concentration Using a Solid Solute" illustrates this procedure for a solution of cobalt(II) chloride dihydrate in ethanol. Note that the volume of the *solvent* is not specified. Because the solute occupies space in the solution, the volume of the solvent needed is almost always *less* than the desired volume of solution. For example, if the desired volume were 1.00 L, it would be incorrect to add 1.00 L of water to 342 g of sucrose because that would produce more than 1.00 L of solution. As shown in Figure 4.7 "Preparation of 250 mL of a Solution of (NH", for some substances this effect can be significant, especially for concentrated solutions.

Figure 4.6 Preparation of a Solution of Known Concentration Using a Solid Solute

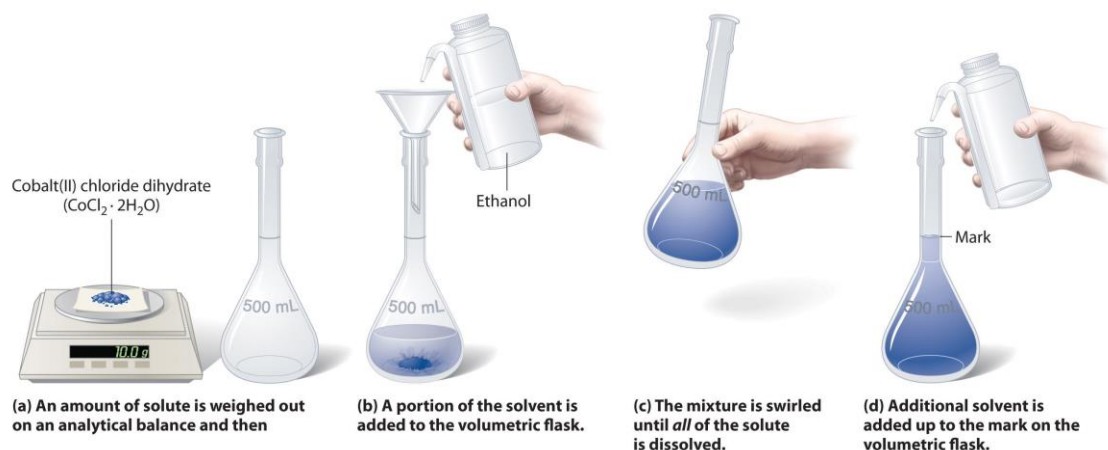
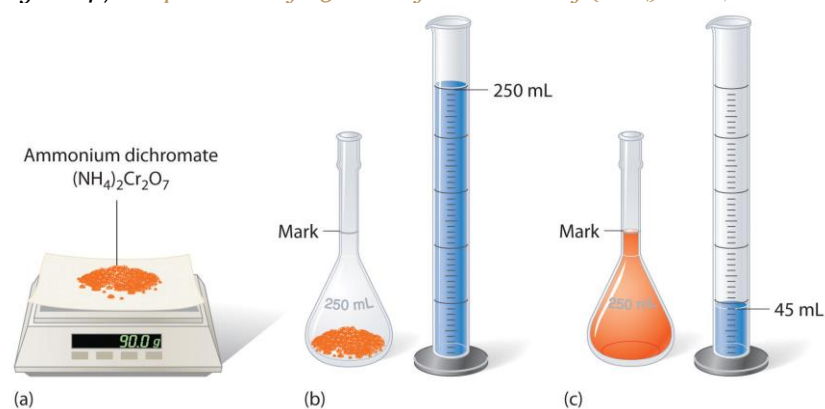


Figure 4.7 Preparation of 250 mL of a Solution of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ in Water



The solute occupies space in the solution, so less than 250 mL of water are needed to make 250 mL of solution.

EXAMPLE 3

The solution in Figure 4.6 "Preparation of a Solution of Known Concentration Using a Solid

Solute" contains 10.0 g of cobalt(II) chloride dihydrate, $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$, in enough ethanol to make exactly 500 mL of solution. What is the molar concentration of $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$?

Given: mass of solute and volume of solution

Asked for: concentration (M)

Strategy:

To find the number of moles of $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$, divide the mass of the compound by its molar mass. Calculate the molarity of the solution by dividing the number of moles of solute by the volume of the solution in liters.

Solution:

The molar mass of $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ is 165.87 g/mol. Therefore,

$$\text{moles } \text{CoCl}_2 \cdot 2\text{H}_2\text{O} = \left(\frac{10.0 \text{ g}}{165.87 \text{ g/mol}} \right) = 0.0603 \text{ mol}$$

The volume of the solution in liters is
 $\text{volume} = 500 \text{ mL} \left(\frac{1 \text{ L}}{1000 \text{ mL}} \right) = 0.500 \text{ L}$

Molarity is the number of moles of solute per liter of solution, so the molarity of the solution is
 $\text{molarity} = \frac{0.0603 \text{ mol}}{0.500 \text{ L}} = 0.121 \text{ M} = \text{CoCl}_2 \cdot 2 \text{H}_2\text{O}$

Exercise

The solution shown in Figure 4.7 "Preparation of 250 mL of a Solution of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ " contains 90.0 g of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ in enough water to give a final volume of exactly 250 mL. What is the molar concentration of ammonium dichromate?

Answer: $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 = 1.43 \text{ M}$

To prepare a particular volume of a solution that contains a specified concentration of a solute, we first need to calculate the number of moles of solute in the desired volume of solution using the relationship shown in Equation 4.5. We then convert the number of moles of solute to the corresponding mass of solute needed. This procedure is illustrated in Example 4.

EXAMPLE 4

The so-called D5W solution used for the intravenous replacement of body fluids contains 0.310 M glucose. (D5W is an approximately 5% solution of dextrose [the medical name for glucose] in water.) Calculate the mass of glucose necessary to prepare a 500 mL pouch of D5W. Glucose has a molar mass of 180.16 g/mol.

Given: molarity, volume, and molar mass of solute

Asked for: mass of solute

Strategy:

A Calculate the number of moles of glucose contained in the specified volume of solution by multiplying the volume of the solution by its molarity.

B Obtain the mass of glucose needed by multiplying the number of moles of the compound by its molar mass.

Solution:

A We must first calculate the number of moles of glucose contained in 500 mL of a 0.310 M solution:
 $V \text{ L} \times M \text{ mol/L} = \text{moles}$
 $500 \text{ mL} \left(\frac{1 \text{ L}}{1000 \text{ mL}} \right) \left(0.310 \text{ mol glucose} \right) = 0.155 \text{ mol glucose}$

B We then convert the number of moles of glucose to the required mass of glucose:
 $\text{mass of glucose} = 0.155 \text{ mol glucose} \left(180.16 \text{ g glucose} \right) = 27.9 \text{ g glucose}$

Exercise

Another solution commonly used for intravenous injections is normal saline, a 0.16 M solution of sodium chloride in water. Calculate the mass of sodium chloride needed to prepare 250 mL of normal saline solution.

Answer: 2.3 g NaCl

A solution of a desired concentration can also be prepared by diluting a small volume of a more concentrated solution with additional solvent. A stock solution, which is a commercially prepared solution of known concentration, is often used for this purpose. Diluting a stock solution is preferred because the alternative method, weighing out tiny amounts of solute, is difficult to carry out with a high degree of accuracy. Dilution is also used to prepare solutions from substances that are sold as concentrated aqueous solutions, such as strong acids.

The procedure for preparing a solution of known concentration from a stock solution is shown in **Figure 4.8**

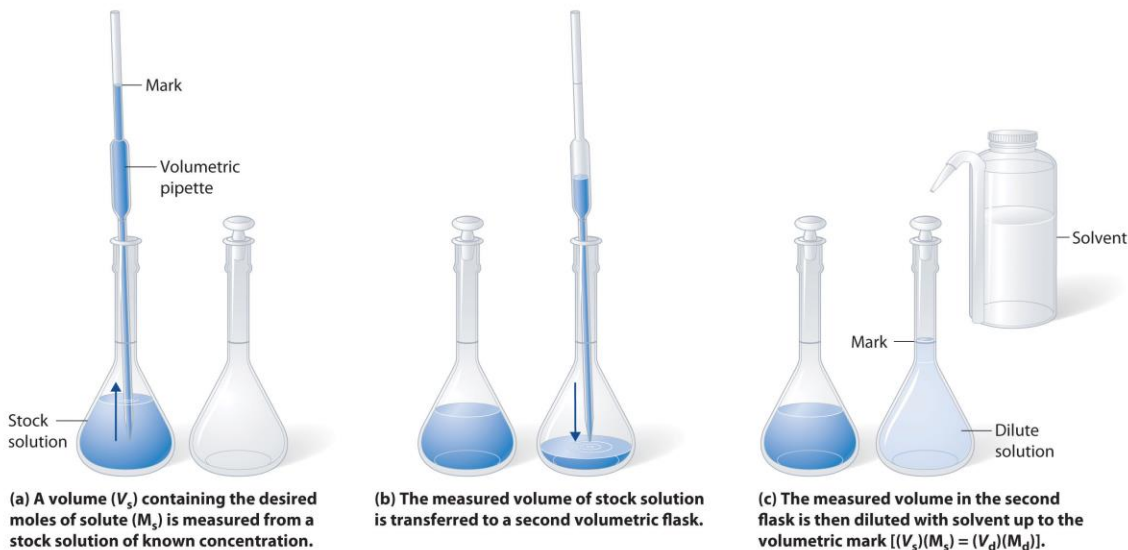
"Preparation of a Solution of Known Concentration by Diluting a Stock Solution". It requires calculating the number of moles of solute desired in the final volume of the more dilute solution and then calculating the volume of the stock solution that contains this amount of solute. Remember that diluting a given quantity of stock solution with solvent does *not* change the number of moles of solute present. The relationship between the volume and concentration of the stock solution and the volume and concentration of the desired diluted solution is therefore

Equation 4.7

$$(V_s)(M_s) = \text{moles of solute} = (V_d)(M_d)$$

where the subscripts *s* and *d* indicate the stock and dilute solutions, respectively. Example 5 demonstrates the calculations involved in diluting a concentrated stock solution.

Figure 4.8 *Preparation of a Solution of Known Concentration by Diluting a Stock Solution*



(a) A volume (V_s) containing the desired moles of solute (M_s) is measured from a stock solution of known concentration. (b) The measured volume of stock solution is transferred to a second volumetric flask. (c) The measured volume in the second flask is then diluted with solvent up to the volumetric mark [$(V_s)(M_s) = (V_d)(M_d)$].

EXAMPLE 5

What volume of a 3.00 M glucose stock solution is necessary to prepare 2500 mL of the D5W solution in Example 4?

Given: volume and molarity of dilute solution

Asked for: volume of stock solution

Strategy:

A Calculate the number of moles of glucose contained in the indicated volume of dilute solution by multiplying the volume of the solution by its molarity.

B To determine the volume of stock solution needed, divide the number of moles of glucose by the molarity of the stock solution.

Solution:

A The D5W solution in Example 4 was 0.310 M glucose. We begin by using Equation 4.7 to calculate the number of moles of glucose contained in 2500 mL of the solution:

$$\text{moles glucose} = 2500 \text{ mL} \left(\frac{1 \text{ L}}{1000 \text{ mL}} \right) (0.310 \text{ mol glucose } 1 \text{ L}) = 0.775 \text{ mol glucose}$$

B We must now determine the volume of the 3.00 M stock solution that contains this amount of glucose:

$$\text{volume of stock soln} = 0.775 \text{ mol glucose} \left(\frac{1 \text{ L}}{3.00 \text{ mol glucose}} \right) = 0.258 \text{ L or } 258 \text{ mL}$$

In determining the volume of stock solution that was needed, we had to divide the desired number of moles of glucose by the concentration of the stock solution to obtain the appropriate units. Also, the number of moles of solute in 258 mL of the stock solution is the same as the number of moles in 2500 mL of the more dilute solution; *only the amount of solvent has changed*. The answer we obtained makes sense: diluting the stock solution about tenfold increases its volume by about a factor of 10 (258 mL → 2500 mL). Consequently, the concentration of the solute must decrease by about a factor of 10, as it does (3.00 M → 0.310 M).

We could also have solved this problem in a single step by solving Equation 4.7 for V_s and substituting the appropriate values:

$$V_s = (V_d)(M_d) / M_s = (2.500 \text{ L})(0.310 \text{ M}) / 3.00 \text{ M} = 0.258 \text{ L}$$

As we have noted, there is often more than one correct way to solve a problem.

Exercise

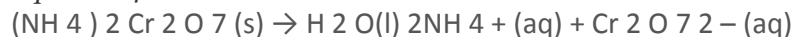
What volume of a 5.0 M NaCl stock solution is necessary to prepare 500 mL of normal saline solution (0.16 M NaCl)?

Answer: 16 mL

Ion Concentrations in Solution

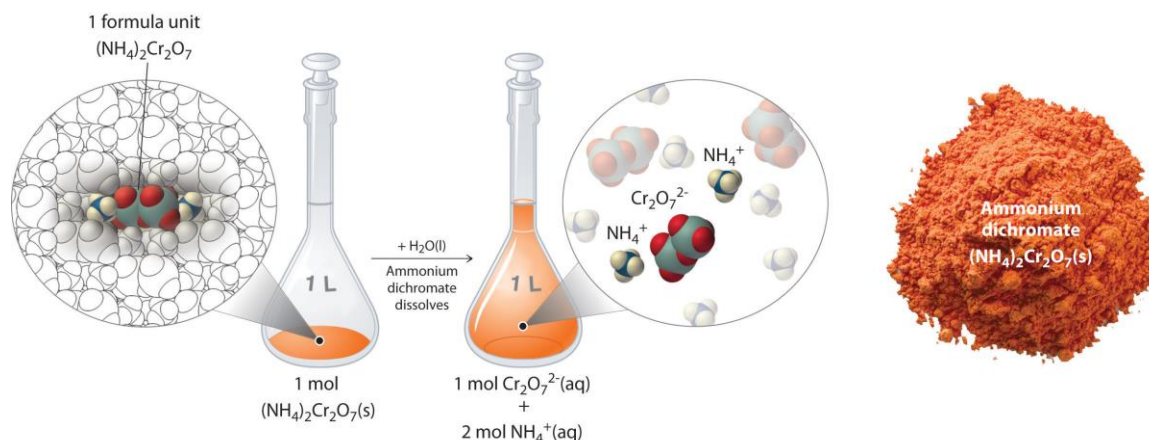
In Example 3, you calculated that the concentration of a solution containing 90.00 g of ammonium dichromate in a final volume of 250 mL is 1.43 M. Let's consider in more detail exactly what that means. Ammonium dichromate is an ionic compound that contains two NH_4^+ ions and one $\text{Cr}_2\text{O}_7^{2-}$ ion per formula unit. Like other ionic compounds, it is a strong electrolyte that dissociates in aqueous solution to give hydrated NH_4^+ and $\text{Cr}_2\text{O}_7^{2-}$ ions:

Equation 4.8



Thus 1 mol of ammonium dichromate formula units dissolves in water to produce 1 mol of $\text{Cr}_2\text{O}_7^{2-}$ anions and 2 mol of NH_4^+ cations (see Figure 4.9 "Dissolution of 1 mol of an Ionic Compound").

Figure 4.9 Dissolution of 1 mol of an Ionic Compound



In this case, dissolving 1 mol of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ produces a solution that contains 1 mol of $\text{Cr}_2\text{O}_7^{2-}$ ions and 2 mol of NH_4^+ ions. (Water molecules are omitted from a molecular view of the solution for clarity.)

When we carry out a chemical reaction using a solution of a salt such as ammonium dichromate, we need to know the concentration of each ion present in the solution. If a solution contains 1.43 M $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$, then the concentration of $\text{Cr}_2\text{O}_7^{2-}$ must also be 1.43 M because there is one $\text{Cr}_2\text{O}_7^{2-}$ ion per formula unit. However, there are two NH_4^+ ions per formula unit, so the concentration of NH_4^+ ions is $2 \times 1.43 \text{ M} = 2.86 \text{ M}$. Because each formula unit of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ produces *three* ions when dissolved in water ($2\text{NH}_4^+ + 1\text{Cr}_2\text{O}_7^{2-}$), the *total* concentration of ions in the solution is $3 \times 1.43 \text{ M} = 4.29 \text{ M}$.

EXAMPLE 6

What are the concentrations of all species derived from the solutes in these aqueous solutions?

- a. 0.21 M NaOH
- a. 3.7 M $(\text{CH}_3)\text{CHOH}$
- b. 0.032 M $\text{In}(\text{NO}_3)_3$

Given: molarity

Asked for: concentrations

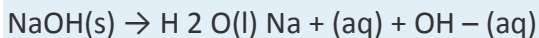
Strategy:

A Classify each compound as either a strong electrolyte or a nonelectrolyte.

B If the compound is a nonelectrolyte, its concentration is the same as the molarity of the solution. If the compound is a strong electrolyte, determine the number of each ion contained in one formula unit. Find the concentration of each species by multiplying the number of each ion by the molarity of the solution.

Solution:

a. Sodium hydroxide is an ionic compound that is a strong electrolyte (and a strong base) in aqueous solution:

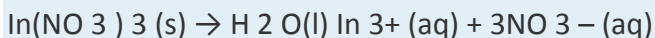


B Because each formula unit of NaOH produces one Na^+ ion and one OH^- ion, the concentration of each ion is the same as the concentration of NaOH: $[\text{Na}^+] = 0.21 \text{ M}$ and $[\text{OH}^-] = 0.21 \text{ M}$.

b. **A** The formula $(\text{CH}_3)_2\text{CHOH}$ represents 2-propanol (isopropyl alcohol) and contains the $-\text{OH}$ group, so it is an alcohol. Recall from Section 4.1 "Aqueous Solutions" that alcohols are covalent compounds that dissolve in water to give solutions of neutral molecules. Thus alcohols are nonelectrolytes.

B The only solute species in solution is therefore $(\text{CH}_3)_2\text{CHOH}$ molecules, so $[(\text{CH}_3)_2\text{CHOH}] = 3.7 \text{ M}$.

c. **A** Indium nitrate is an ionic compound that contains In^{3+} ions and NO_3^- ions, so we expect it to behave like a strong electrolyte in aqueous solution:



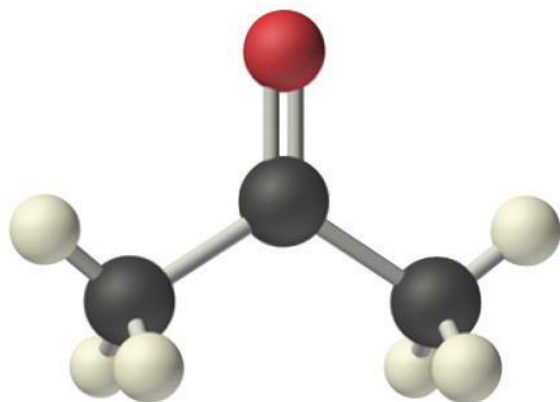
B One formula unit of $\text{In}(\text{NO}_3)_3$ produces one In^{3+} ion and three NO_3^- ions, so a 0.032 M

$\text{In}(\text{NO}_3)_3$ solution contains 0.032 M In^{3+} and $3 \times 0.032 \text{ M} = 0.096 \text{ M}$ NO_3^- —that is, $[\text{In}^{3+}] = 0.032 \text{ M}$ and $[\text{NO}_3^-] = 0.096 \text{ M}$.

Exercise

What are the concentrations of all species derived from the solutes in these aqueous solutions?

- $0.0012 \text{ M Ba}(\text{OH})_2$
- $0.17 \text{ M Na}_2\text{SO}_4$
- $0.50 \text{ M } (\text{CH}_3)_2\text{CO}$, commonly known as acetone



Acetone
(CH₃)₂CO

Answer:

- a. [Ba²⁺] = 0.0012 M; [OH⁻] = 0.0024 M
- b. [Na⁺] = 0.34 M; [SO₄²⁻] = 0.17 M
- c. [(CH₃)₂CO] = 0.50 M

KEY EQUATIONS

definition of molarity

Equation 4.4: $\text{molarity} = \frac{\text{moles of solute}}{\text{liters of solution}} = \frac{\text{mmoles of solute}}{\text{milliliters of solution}}$

relationship among volume, molarity, and moles

Equation 4.5: $V \text{ L} \times M \text{ mol/L} = L \text{ (mol/L)} = \text{moles}$

relationship between volume and concentration of stock and dilute solutions

Equation 4.7: $(V_s)(M_s) = \text{moles of solute} = (V_d)(M_d)$

Summary

The **concentration** of a substance is the quantity of solute present in a given quantity of solution.

Concentrations are usually expressed as **molarity**, the number of moles of solute in 1 L of solution.

Solutions of known concentration can be prepared either by dissolving a known mass of solute in a solvent and diluting to a desired final volume or by diluting the appropriate volume of a more concentrated solution (a **stock solution**) to the desired final volume.

KEY TAKEAWAY

- Solution concentrations are typically expressed as molarity and can be prepared by dissolving a known mass of solute in a solvent or diluting a stock solution.

CONCEPTUAL PROBLEMS

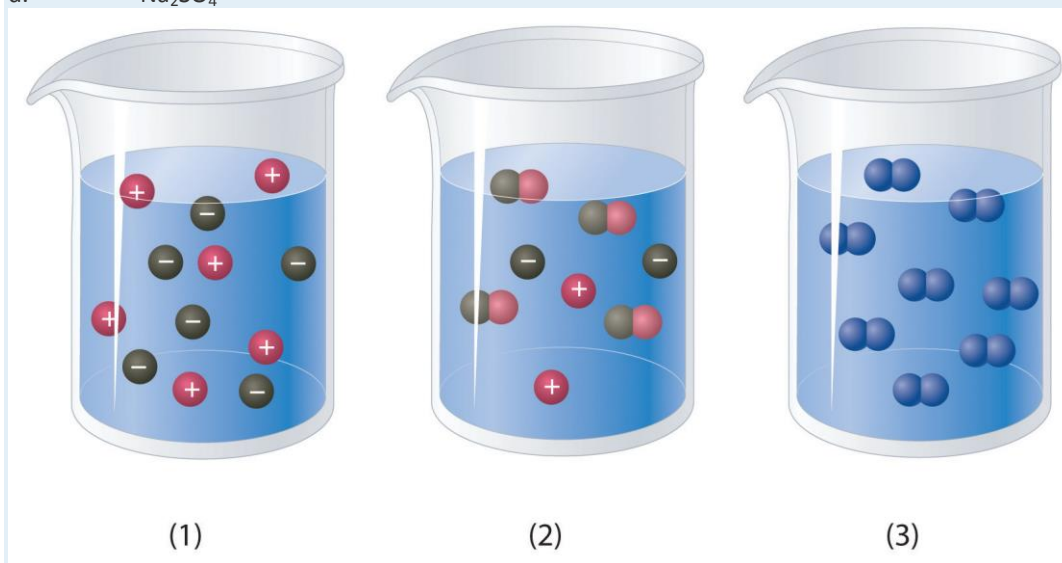
1. Which of the representations best corresponds to a 1 M aqueous solution of each compound? Justify your answers.

a. NH_3

b. HF

c. $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$

d. Na_2SO_4



2. Which of the representations shown in Problem 1 best corresponds to a 1 M aqueous solution of each compound? Justify your answers.

a. $\text{CH}_3\text{CO}_2\text{H}$

b. NaCl

c. Na_2S

d. Na_3PO_4

e. acetaldehyde

3. Would you expect a 1.0 M solution of CaCl_2 to be a better conductor of electricity than a 1.0 M solution of NaCl ? Why or why not?

4. An alternative way to define the concentration of a solution is *molality*, abbreviated *m*. Molality is defined as the number of moles of solute in 1 kg of *solvent*. How is this different from molarity? Would you expect a 1 M solution of sucrose to be more or less concentrated than a 1 *m* solution of sucrose? Explain your answer.

5. What are the advantages of using solutions for quantitative calculations?

ANSWER

5. If the amount of a substance required for a reaction is too small to be weighed accurately, the use of a solution of the substance, in which the solute is dispersed in a much larger mass of solvent, allows chemists to measure the quantity of the substance more accurately.

NUMERICAL PROBLEMS

1. Calculate the number of grams of solute in 1.000 L of each solution.

- a. 0.2593 M NaBrO₃
- b. 1.592 M KNO₃
- c. 1.559 M acetic acid
- d. 0.943 M potassium iodate

2. Calculate the number of grams of solute in 1.000 L of each solution.

- a. 0.1065 M BaI₂
- b. 1.135 M Na₂SO₄
- c. 1.428 M NH₄Br
- d. 0.889 M sodium acetate

3. If all solutions contain the same solute, which solution contains the greater mass of solute?

- a. 1.40 L of a 0.334 M solution or 1.10 L of a 0.420 M solution
- b. 25.0 mL of a 0.134 M solution or 10.0 mL of a 0.295 M solution
- c. 250 mL of a 0.489 M solution or 150 mL of a 0.769 M solution

4. Complete the following table for 500 mL of solution.

Compound	Mass (g)	Moles	Concentration (M)
calcium sulfate	4.86		
acetic acid		3.62	
hydrogen iodide dihydrate			1.273
barium bromide	3.92		
glucose			0.983

Compound	Mass (g)	Moles	Concentration (M)
sodium acetate		2.42	

5. What is the concentration of each species present in the following aqueous solutions?
 - a. 0.489 mol of NiSO_4 in 600 mL of solution
 - b. 1.045 mol of magnesium bromide in 500 mL of solution
 - c. 0.146 mol of glucose in 800 mL of solution
 - d. 0.479 mol of CeCl_3 in 700 mL of solution
6. What is the concentration of each species present in the following aqueous solutions?
 - a. 0.324 mol of K_2MoO_4 in 250 mL of solution
 - b. 0.528 mol of potassium formate in 300 mL of solution
 - c. 0.477 mol of KClO_3 in 900 mL of solution
 - d. 0.378 mol of potassium iodide in 750 mL of solution
7. What is the molar concentration of each solution?
 - a. 8.7 g of calcium bromide in 250 mL of solution
 - b. 9.8 g of lithium sulfate in 300 mL of solution
 - c. 12.4 g of sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) in 750 mL of solution
 - d. 14.2 g of iron(III) nitrate hexahydrate in 300 mL of solution
8. What is the molar concentration of each solution?
 - a. 12.8 g of sodium hydrogen sulfate in 400 mL of solution
 - b. 7.5 g of potassium hydrogen phosphate in 250 mL of solution
 - c. 11.4 g of barium chloride in 350 mL of solution
 - d. 4.3 g of tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$) in 250 mL of solution
9. Give the concentration of each reactant in the following equations, assuming 20.0 g of each and a solution volume of 250 mL for each reactant.
 - a. $\text{BaCl}_2(\text{aq}) + \text{Na}_2\text{SO}_4(\text{aq}) \rightarrow$
 - b. $\text{Ca}(\text{OH})_2(\text{aq}) + \text{H}_3\text{PO}_4(\text{aq}) \rightarrow$
 - c. $\text{Al}(\text{NO}_3)_3(\text{aq}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow$
 - d. $\text{Pb}(\text{NO}_3)_2(\text{aq}) + \text{CuSO}_4(\text{aq}) \rightarrow$
 - e. $\text{Al}(\text{CH}_3\text{CO}_2)_3(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow$

10. An experiment required 200.0 mL of a 0.330 M solution of Na_2CrO_4 . A stock solution of Na_2CrO_4 containing 20.0% solute by mass with a density of 1.19 g/cm^3 was used to prepare this solution. Describe how to prepare 200.0 mL of a 0.330 M solution of Na_2CrO_4 using the stock solution.
11. Calcium hypochlorite $[\text{Ca}(\text{OCl})_2]$ is an effective disinfectant for clothing and bedding. If a solution has a $\text{Ca}(\text{OCl})_2$ concentration of 3.4 g per 100 mL of solution, what is the molarity of hypochlorite?
12. Phenol ($\text{C}_6\text{H}_5\text{OH}$) is often used as an antiseptic in mouthwashes and throat lozenges. If a mouthwash has a phenol concentration of 1.5 g per 100 mL of solution, what is the molarity of phenol?
13. If a tablet containing 100 mg of caffeine ($\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$) is dissolved in water to give 10.0 oz of solution, what is the molar concentration of caffeine in the solution?
14. A certain drug label carries instructions to add 10.0 mL of sterile water, stating that each milliliter of the resulting solution will contain 0.500 g of medication. If a patient has a prescribed dose of 900.0 mg, how many milliliters of the solution should be administered?

ANSWERS

11. 0.48 M ClO^-
13. $1.74 \times 10^{-3} \text{ M caffeine}$

4.3 Stoichiometry of Reactions in Solution

LEARNING OBJECTIVES

1. To balance equations that describe reactions in solution.
2. To solve quantitative problems involving the stoichiometry of reactions in solution.

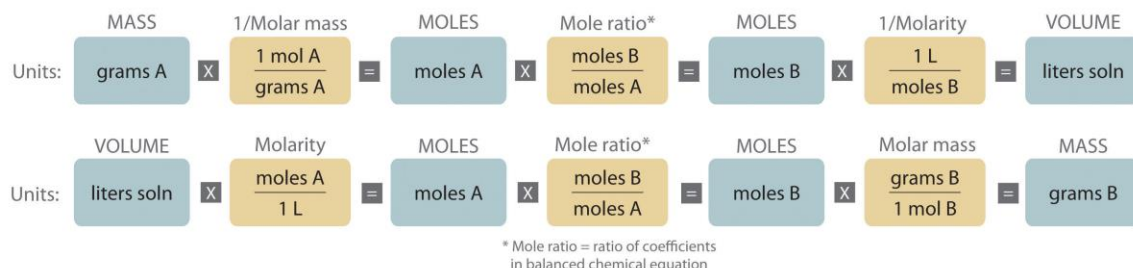
Quantitative calculations involving reactions in solution are carried out in the same manner as we discussed in Chapter 3 "Chemical Reactions". Instead of *masses*, however, we use *volumes* of solutions of known concentration to determine the number of moles of reactants. Whether we are dealing with volumes of solutions of reactants or masses of reactants, the coefficients in the balanced chemical equation tell us the number of moles of each reactant needed and the number of moles of each product that can be produced.

Calculating Moles from Volume

An expanded version of the flowchart for stoichiometric calculations illustrated in Figure 3.5 "Steps for Obtaining an Empirical Formula from Combustion Analysis" is shown in Figure 4.10 "An Expanded Flowchart for Stoichiometric Calculations". We can use the balanced chemical equation for the reaction

and *either* the masses of solid reactants and products *or* the volumes of solutions of reactants and products to determine the amounts of other species, as illustrated in Example 7, Example 8, and Example 9.

Figure 4.10 An Expanded Flowchart for Stoichiometric Calculations



Either the masses or the volumes of solutions of reactants and products can be used to determine the amounts of other species in a balanced chemical equation.

Note the Pattern

The balanced chemical equation for a reaction and either the masses of solid reactants and products or the volumes of solutions of reactants and products can be used in stoichiometric calculations.

EXAMPLE 7

Gold is extracted from its ores by treatment with an aqueous cyanide solution, which causes a reaction that forms the soluble $[\text{Au}(\text{CN})_2]^-$ ion. Gold is then recovered by reduction with metallic zinc according to the following equation:



What mass of gold would you expect to recover from 400.0 L of a $3.30 \times 10^{-4} \text{ M}$ solution of $[\text{Au}(\text{CN})_2]^-$?

Given: chemical equation and molarity and volume of reactant

Asked for: mass of product

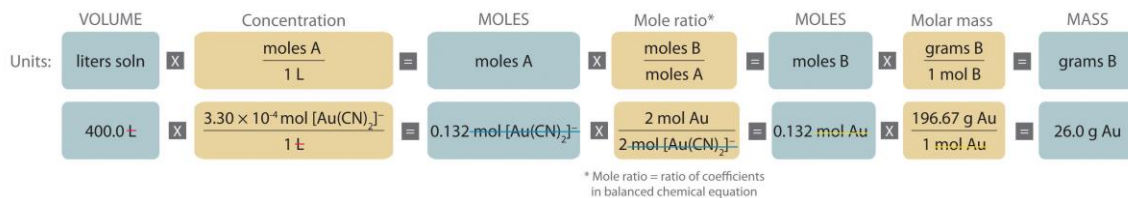
Strategy:

A Check the chemical equation to make sure it is balanced as written; balance if necessary. Then calculate the number of moles of $[\text{Au}(\text{CN})_2]^-$ present by multiplying the volume of the solution by its concentration.

B From the balanced chemical equation, use a mole ratio to calculate the number of moles of gold that can be obtained from the reaction. To calculate the mass of gold recovered, multiply the number of moles of gold by its molar mass.

Solution:

A The equation is balanced as written, so we can proceed to the stoichiometric calculation. We can adapt Figure 4.10 "An Expanded Flowchart for Stoichiometric Calculations" for this particular problem as follows:



As indicated in the strategy, we start by calculating the number of moles of $[\text{Au}(\text{CN})_2]^-$ present in the solution from the volume and concentration of the $[\text{Au}(\text{CN})_2]^-$ solution:

$$\text{moles } [\text{Au}(\text{CN})_2]^- = V \text{ L} M \text{ mol/L} = 400.0 \text{ L} (3.30 \times 10^{-4} \text{ mol } [\text{Au}(\text{CN})_2]^- / 1 \text{ L}) = 0.132 \text{ mol } [\text{Au}(\text{CN})_2]^-$$

B Because the coefficients of gold and the $[\text{Au}(\text{CN})_2]^-$ ion are the same in the balanced chemical equation, if we assume that Zn(s) is present in excess, the number of moles of gold produced is the same as the number of moles of $[\text{Au}(\text{CN})_2]^-$ we started with (i.e., 0.132 mol of Au). The problem asks for the mass of gold that can be obtained, so we need to convert the number of moles of gold to the corresponding mass using the molar mass of gold:

$$\text{mass of Au} = (\text{moles Au})(\text{molar mass Au}) = 0.132 \text{ mol Au} (196.67 \text{ g Au} / 1 \text{ mol Au}) = 26.0 \text{ g Au}$$

At a 2011 market price of over \$1400 per troy ounce (31.10 g), this amount of gold is worth \$1170.
 $26.0 \text{ g Au} \times 1 \text{ troy oz} / 31.10 \text{ g} \times \$1400 / 1 \text{ troy oz Au} = \$1170$

Exercise

What mass of solid lanthanum(III) oxalate nonahydrate $[\text{La}_2(\text{C}_2\text{O}_4)_3 \cdot 9\text{H}_2\text{O}]$ can be obtained from 650 mL of a 0.0170 M aqueous solution of LaCl_3 by adding a stoichiometric amount of sodium oxalate?

Answer: 3.89 g

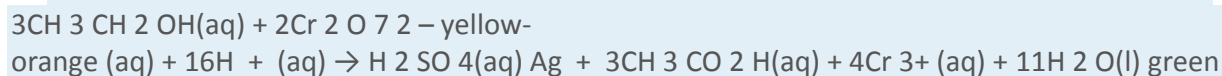
Limiting Reactants in Solutions

The concept of limiting reactants applies to reactions that are carried out in solution as well as to reactions that involve pure substances. If all the reactants but one are present in excess, then the amount of the limiting reactant may be calculated as illustrated in Example 8.

EXAMPLE 8

Because the consumption of alcoholic beverages adversely affects the performance of tasks that require skill and judgment, in most countries it is illegal to drive while under the influence of alcohol. In almost all

US states, a blood alcohol level of 0.08% by volume is considered legally drunk. Higher levels cause acute intoxication (0.20%), unconsciousness (about 0.30%), and even death (about 0.50%). The Breathalyzer is a portable device that measures the ethanol concentration in a person's breath, which is directly proportional to the blood alcohol level. The reaction used in the Breathalyzer is the oxidation of ethanol by the dichromate ion:



When a measured volume (52.5 mL) of a suspect's breath is bubbled through a solution of excess potassium dichromate in dilute sulfuric acid, the ethanol is rapidly absorbed and oxidized to acetic acid by the dichromate ions. In the process, the chromium atoms in some of the $\text{Cr}_2\text{O}_7^{2-}$ ions are reduced from Cr^{6+} to Cr^{3+} . In the presence of Ag^+ ions that act as a catalyst, the reaction is complete in less than a minute. Because the $\text{Cr}_2\text{O}_7^{2-}$ ion (the reactant) is yellow-orange and the Cr^{3+} ion (the product) forms a green solution, the amount of ethanol in the person's breath (the limiting reactant) can be determined quite accurately by comparing the color of the final solution with the colors of standard solutions prepared with known amounts of ethanol.

A typical Breathalyzer ampul contains 3.0 mL of a 0.25 mg/mL solution of $\text{K}_2\text{Cr}_2\text{O}_7$ in 50% H_2SO_4 as well as a fixed concentration of AgNO_3 (typically 0.25 mg/mL is used for this purpose). How many grams of ethanol must be present in 52.5 mL of a person's breath to convert all the Cr^{6+} to Cr^{3+} ?

Given: volume and concentration of one reactant

Asked for: mass of other reactant needed for complete reaction

Strategy:

A Calculate the number of moles of $\text{Cr}_2\text{O}_7^{2-}$ ion in 1 mL of the Breathalyzer solution by dividing the mass of $\text{K}_2\text{Cr}_2\text{O}_7$ by its molar mass.

B Find the total number of moles of $\text{Cr}_2\text{O}_7^{2-}$ ion in the Breathalyzer ampul by multiplying the number of moles contained in 1 mL by the total volume of the Breathalyzer solution (3.0 mL).

C Use the mole ratios from the balanced chemical equation to calculate the number of moles of $\text{C}_2\text{H}_5\text{OH}$ needed to react completely with the number of moles of $\text{Cr}_2\text{O}_7^{2-}$ ions present. Then find the mass of $\text{C}_2\text{H}_5\text{OH}$ needed by multiplying the number of moles of $\text{C}_2\text{H}_5\text{OH}$ by its molar mass.

Solution:

A In any stoichiometry problem, the first step is always to calculate the number of moles of each reactant present. In

this case, we are given the mass of $K_2Cr_2O_7$ in 1 mL of solution, which we can use to calculate the number of moles of

$K_2Cr_2O_7$ contained in 1 mL:

$$\text{moles } K_2Cr_2O_7 \text{ in } 1 \text{ mL} = (0.25 \text{ mg } K_2Cr_2O_7) \left(\frac{1 \text{ g}}{1000 \text{ mg}} \right) \left(\frac{1 \text{ mol}}{294.18 \text{ g } K_2Cr_2O_7} \right) = 8.5 \times 10^{-7} \text{ moles}$$

B Because 1 mol of $K_2Cr_2O_7$ produces 1 mol of $Cr_2O_7^{2-}$ when it dissolves, each milliliter of solution contains

$$8.5 \times 10^{-7} \text{ mol of } Cr_2O_7^{2-}. \text{ The total number of moles of } Cr_2O_7^{2-} \text{ in a 3.0 mL Breathalyzer ampul is thus}$$

$$\text{moles } Cr_2O_7^{2-} = (8.5 \times 10^{-7} \text{ mol } Cr_2O_7^{2-} \text{ mL}^{-1}) (3.0 \text{ mL}) = 2.6 \times 10^{-6} \text{ mol } Cr_2O_7^{2-}$$

C The balanced chemical equation tells us that 3 mol of C_2H_5OH is needed to consume 2 mol of $Cr_2O_7^{2-}$ ion, so the total

number of moles of C_2H_5OH required for complete reaction is

$$\text{moles of } C_2H_5OH = (2.6 \times 10^{-6} \text{ mol } Cr_2O_7^{2-}) \left(\frac{3 \text{ mol } C_2H_5OH}{2 \text{ mol } Cr_2O_7^{2-}} \right) = 3.9 \times 10^{-6} \text{ mol } C_2H_5OH$$

As indicated in the strategy, this number can be converted to the mass of C_2H_5OH using its molar mass:

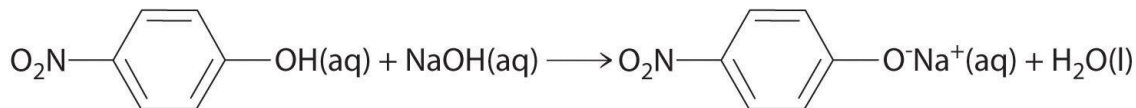
$$\text{mass } C_2H_5OH = (3.9 \times 10^{-6} \text{ mol } C_2H_5OH) (46.07 \text{ g/mol } C_2H_5OH) = 1.8 \times 10^{-4} \text{ g } C_2H_5OH$$

Thus $1.8 \times 10^{-4} \text{ g}$ or 0.18 mg of C_2H_5OH must be present. Experimentally, it is found that this value corresponds to a

blood alcohol level of 0.7%, which is usually fatal.

Exercise

The compound *para*-nitrophenol (molar mass = 139 g/mol) reacts with sodium hydroxide in aqueous solution to generate a yellow anion via the reaction



***para*-Nitrophenol**

Yellow

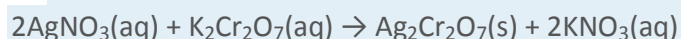
Because the amount of *para*-nitrophenol is easily estimated from the intensity of the yellow color that results when excess NaOH is added, reactions that produce *para*-nitrophenol are commonly used to measure the activity of enzymes, the catalysts in biological systems. What volume of 0.105 M NaOH must be added to 50.0 mL of a solution containing $7.20 \times 10^{-4} \text{ g}$ of *para*-nitrophenol to ensure that formation of the yellow anion is complete?

Answer: $4.93 \times 10^{-5} \text{ L}$ or 49.3 μL

In Example 7 and Example 8, the identity of the limiting reactant has been apparent: $[\text{Au}(\text{CN})_2]^-$, LaCl_3 , ethanol, and *para*-nitrophenol. When the limiting reactant is not apparent, we can determine which reactant is limiting by comparing the molar amounts of the reactants with their coefficients in the balanced chemical equation, just as we did in Chapter 3 "Chemical Reactions", Section 3.4 "Mass Relationships in Chemical Equations". The only difference is that now we use the volumes and concentrations of solutions of reactants rather than the masses of reactants to calculate the number of moles of reactants, as illustrated in Example 9.

EXAMPLE 9

When aqueous solutions of silver nitrate and potassium dichromate are mixed, an exchange reaction occurs, and silver dichromate is obtained as a red solid. The overall chemical equation for the reaction is as follows:



What mass of $\text{Ag}_2\text{Cr}_2\text{O}_7$ is formed when 500 mL of 0.17 M $\text{K}_2\text{Cr}_2\text{O}_7$ are mixed with 250 mL of 0.57 M AgNO_3 ?

Given: balanced chemical equation and volume and concentration of each reactant

Asked for: mass of product

Strategy:

A Calculate the number of moles of each reactant by multiplying the volume of each solution by its molarity.

B Determine which reactant is limiting by dividing the number of moles of each reactant by its stoichiometric coefficient in the balanced chemical equation.

C Use mole ratios to calculate the number of moles of product that can be formed from the limiting reactant. Multiply the number of moles of the product by its molar mass to obtain the corresponding mass of product.

Solution:

A The balanced chemical equation tells us that 2 mol of $\text{AgNO}_3(\text{aq})$ reacts with 1 mol of $\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$ to form 1 mol of $\text{Ag}_2\text{Cr}_2\text{O}_7(\text{s})$ (Figure 4.11 "What Happens at the Molecular Level When Solutions of AgNO_3 "). The first step is to calculate the number of moles of each reactant in the specified volumes:

moles $\text{K}_2\text{Cr}_2\text{O}_7 = 500 \text{ mL} \left(\frac{1 \text{ L}}{1000 \text{ mL}} \right) (0.17 \text{ mol } \text{K}_2\text{Cr}_2\text{O}_7 / \text{L}) = 0.085 \text{ mol } \text{K}_2\text{Cr}_2\text{O}_7$
 moles $\text{AgNO}_3 = 250 \text{ mL} \left(\frac{1 \text{ L}}{1000 \text{ mL}} \right) (0.57 \text{ mol } \text{AgNO}_3 / \text{L}) = 0.14 \text{ mol } \text{AgNO}_3$

B Now we can determine which reactant is limiting by dividing the number of moles of each reactant by its stoichiometric coefficient:

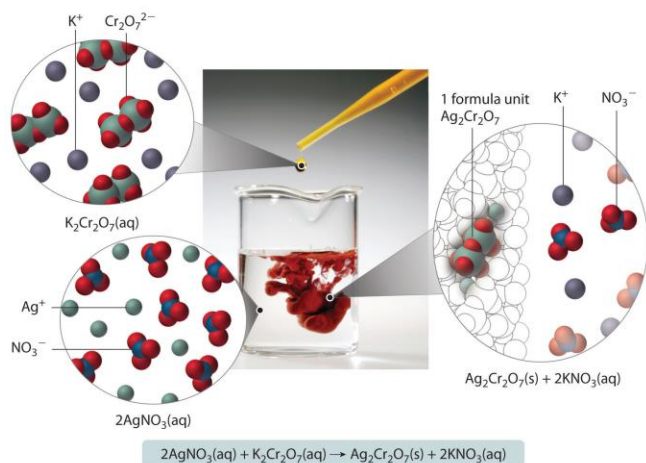
$$K_2Cr_2O_7 : 0.085 \text{ mol } 1 \text{ mol} = 0.085 \text{ AgNO}_3 : 0.14 \text{ mol } 2 \text{ mol} = 0.070$$

Because $0.070 < 0.085$, we know that $AgNO_3$ is the limiting reactant.

Each mole of $Ag_2Cr_2O_7$ formed requires 2 mol of the limiting reactant ($AgNO_3$), so we can obtain only $0.14/2 = 0.070$ mol of $Ag_2Cr_2O_7$. Finally, we convert the number of moles of $Ag_2Cr_2O_7$ to the corresponding mass:

$$\text{mass of } Ag_2Cr_2O_7 = 0.070 \text{ mol } (431.72 \text{ g } 1 \text{ mol}) = 30 \text{ g } Ag_2Cr_2O_7$$

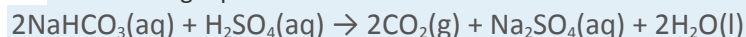
Figure 4.11 *What Happens at the Molecular Level When Solutions of $AgNO_3$ and $K_2Cr_2O_7$ Are Mixed*



The Ag^+ and $Cr_2O_7^{2-}$ ions form a red precipitate of solid $Ag_2Cr_2O_7$, while the K^+ and NO_3^- ions remain in solution. (Water molecules are omitted from molecular views of the solutions for clarity.)

Exercise

Aqueous solutions of sodium bicarbonate and sulfuric acid react to produce carbon dioxide according to the following equation:



If 13.0 mL of 3.0 M H_2SO_4 are added to 732 mL of 0.112 M $NaHCO_3$, what mass of CO_2 is produced?

Answer: 3.4 g

Summary

Quantitative calculations that involve the stoichiometry of reactions in solution use volumes of solutions of known concentration instead of masses of reactants or products. The coefficients in the balanced chemical equation tell how many moles of reactants are needed and how many moles of product can be produced.

KEY TAKEAWAY

- Either the masses or the volumes of solutions of reactants and products can be used to determine the amounts of other species in the balanced chemical equation.

CONCEPTUAL PROBLEMS

1. What information is required to determine the mass of solute in a solution if you know the molar concentration of the solution?
2. Is it possible for one reactant to be limiting in a reaction that does not go to completion?

NUMERICAL PROBLEMS

1. Refer to the Breathalyzer test described in Example 8. How much ethanol must be present in 89.5 mL of a person's breath to consume all the potassium dichromate in a Breathalyzer ampul containing 3.0 mL of a 0.40 mg/mL solution of potassium dichromate?
2. Phosphoric acid and magnesium hydroxide react to produce magnesium phosphate and water. If 45.00 mL of 1.50 M phosphoric acid are used in the reaction, how many grams of magnesium hydroxide are needed for the reaction to go to completion?
3. Barium chloride and sodium sulfate react to produce sodium chloride and barium sulfate. If 50.00 mL of 2.55 M barium chloride are used in the reaction, how many grams of sodium sulfate are needed for the reaction to go to completion?
4. How many grams of sodium phosphate are obtained in solution from the reaction of 75.00 mL of 2.80 M sodium carbonate with a stoichiometric amount of phosphoric acid? A second product is water; what is the third product? How many grams of the third product are obtained?
5. How many grams of ammonium bromide are produced from the reaction of 50.00 mL of 2.08 M iron(II) bromide with a stoichiometric amount of ammonium sulfide? What is the second product? How many grams of the second product are produced?
6. Lead(II) nitrate and hydroiodic acid react to produce lead(II) iodide and nitric acid. If 3.25 g of lead(II) iodide were obtained by adding excess HI to 150.0 mL of lead(II) nitrate, what was the molarity of the lead(II) nitrate solution?
7. Silver nitrate and sodium chloride react to produce sodium nitrate and silver chloride. If 2.60 g of AgCl was obtained by adding excess NaCl to 100 mL of AgNO₃, what was the molarity of the silver nitrate solution?

4.4 Ionic Equations

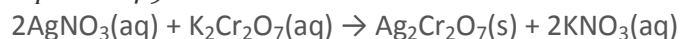
LEARNING OBJECTIVE

1. To understand what information is obtained by each type of ionic equation.

The chemical equations discussed in Chapter 3 "Chemical Reactions" showed the identities of the reactants and the products and gave the stoichiometries of the reactions, but they told us very little about what was occurring in solution. In contrast, equations that show only the hydrated species focus our attention on the chemistry that is taking place and allow us to see similarities between reactions that might not otherwise be apparent.

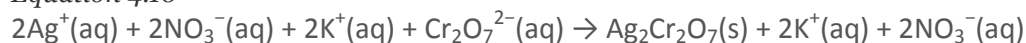
Let's consider the reaction of silver nitrate with potassium dichromate. As you learned in Example 9, when aqueous solutions of silver nitrate and potassium dichromate are mixed, silver dichromate forms as a red solid. The overall chemical equation for the reaction shows each reactant and product as undissociated, electrically neutral compounds:

Equation 4.9



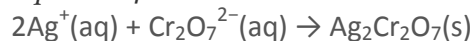
Although Equation 4.9 gives the identity of the reactants and the products, it does not show the identities of the actual species in solution. Because ionic substances such as AgNO_3 and $\text{K}_2\text{Cr}_2\text{O}_7$ are strong electrolytes, they dissociate completely in aqueous solution to form ions. In contrast, because $\text{Ag}_2\text{Cr}_2\text{O}_7$ is not very soluble, it separates from the solution as a solid. To find out what is actually occurring in solution, it is more informative to write the reaction as a complete ionic equation, showing which ions and molecules are hydrated and which are present in other forms and phases:

Equation 4.10



Note that $\text{K}^+(\text{aq})$ and $\text{NO}_3^-(\text{aq})$ ions are present on both sides of the equation, and their coefficients are the same on both sides. These ions are called spectator ions because they do not participate in the actual reaction. Canceling the spectator ions gives the net ionic equation, which shows only those species that participate in the chemical reaction:

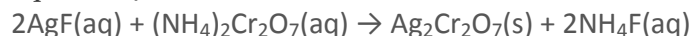
Equation 4.11



Both mass and charge must be conserved in chemical reactions because the numbers of electrons and protons do not change. For charge to be conserved, the sum of the charges of the ions multiplied by their coefficients must be the same on both sides of the equation. In Equation 4.11, the charge on the left side is $2(+1) + 1(-2) = 0$, which is the same as the charge of a neutral $\text{Ag}_2\text{Cr}_2\text{O}_7$ formula unit.

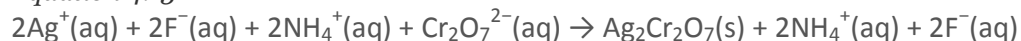
By eliminating the spectator ions, we can focus on the chemistry that takes place in a solution. For example, the overall chemical equation for the reaction between silver fluoride and ammonium dichromate is as follows:

Equation 4.12



The complete ionic equation for this reaction is as follows:

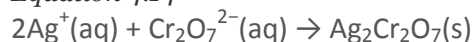
Equation 4.13



Because two $\text{NH}_4^+(\text{aq})$ and two $\text{F}^-(\text{aq})$ ions appear on both sides of Equation 4.13, they are spectator ions.

They can therefore be canceled to give the net ionic equation (Equation 4.14), which is identical to Equation 4.11:

Equation 4.14



If we look at net ionic equations, it becomes apparent that many different combinations of reactants can result in the same net chemical reaction. For example, we can predict that silver fluoride could be replaced by silver nitrate in the preceding reaction without affecting the outcome of the reaction.

EXAMPLE 10

Write the overall chemical equation, the complete ionic equation, and the net ionic equation for the reaction of aqueous barium nitrate with aqueous sodium phosphate to give solid barium phosphate and a solution of sodium nitrate.

Given: reactants and products

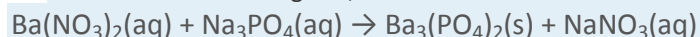
Asked for: overall, complete ionic, and net ionic equations

Strategy:

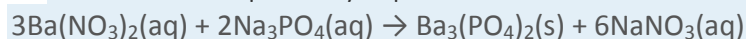
Write and balance the overall chemical equation. Write all the soluble reactants and products in their dissociated form to give the complete ionic equation; then cancel species that appear on both sides of the complete ionic equation to give the net ionic equation.

Solution:

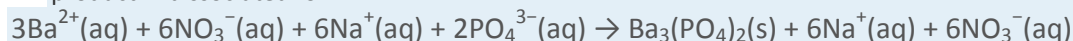
From the information given, we can write the unbalanced chemical equation for the reaction:



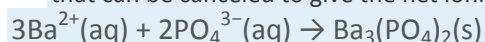
Because the product is $\text{Ba}_3(\text{PO}_4)_2$, which contains three Ba^{2+} ions and two PO_4^{3-} ions per formula unit, we can balance the equation by inspection:



This is the overall balanced chemical equation for the reaction, showing the reactants and products in their undissociated form. To obtain the complete ionic equation, we write each soluble reactant and product in dissociated form:



The six $\text{NO}_3^{-}(\text{aq})$ ions and the six $\text{Na}^{+}(\text{aq})$ ions that appear on both sides of the equation are spectator ions that can be canceled to give the net ionic equation:



Exercise

Write the overall chemical equation, the complete ionic equation, and the net ionic equation for the reaction of aqueous silver fluoride with aqueous sodium phosphate to give solid silver phosphate and a solution of sodium fluoride.

Answer:

overall chemical equation: $3\text{AgF}(\text{aq}) + \text{Na}_3\text{PO}_4(\text{aq}) \rightarrow \text{Ag}_3\text{PO}_4(\text{s}) + 3\text{NaF}(\text{aq})$

complete ionic equation: $3\text{Ag}^{+}(\text{aq}) + 3\text{F}^{-}(\text{aq}) + 3\text{Na}^{+}(\text{aq}) + \text{PO}_4^{3-}(\text{aq}) \rightarrow \text{Ag}_3\text{PO}_4(\text{s}) + 3\text{Na}^{+}(\text{aq}) + 3\text{F}^{-}(\text{aq})$

net ionic equation: $3\text{Ag}^{+}(\text{aq}) + \text{PO}_4^{3-}(\text{aq}) \rightarrow \text{Ag}_3\text{PO}_4(\text{s})$

So far, we have always indicated whether a reaction will occur when solutions are mixed and, if so, what products will form. As you advance in chemistry, however, you will need to predict the results of mixing solutions of compounds, anticipate what kind of reaction (if any) will occur, and predict the identities of the products. Students tend to think that this means they are supposed to “just know” what will happen when two substances are mixed. Nothing could be further from the truth: an infinite number of chemical reactions is possible, and neither you nor anyone else could possibly memorize them all. Instead, you must begin by identifying the various reactions that *could* occur and then assessing which is the most probable (or least improbable) outcome.

The most important step in analyzing an unknown reaction is to *write down all the species—whether molecules or dissociated ions—that are actually present in the solution* (not forgetting the solvent itself) so that you can assess which species are most likely to react with one another. The easiest way to make

that kind of prediction is to attempt to place the reaction into one of several familiar classifications, refinements of the five general kinds of reactions introduced in Chapter 3 "Chemical Reactions" (acid–base, exchange, condensation, cleavage, and oxidation–reduction reactions). In the sections that follow, we discuss three of the most important kinds of reactions that occur in aqueous solutions: precipitation reactions (also known as exchange reactions), acid–base reactions, and oxidation–reduction reactions.

Summary

The chemical equation for a reaction in solution can be written in three ways. The **overall chemical equation** shows all the substances present in their undissociated forms; the **complete ionic equation** shows all the substances present in the form in which they actually exist in solution; and the **net ionic equation** is derived from the complete ionic equation by omitting all **spectator ions**, ions that occur on both sides of the equation with the same coefficients. Net ionic equations demonstrate that many different combinations of reactants can give the same net chemical reaction.

KEY TAKEAWAY

- A complete ionic equation consists of the net ionic equation and spectator ions.

CONCEPTUAL PROBLEM

1. What information can be obtained from a complete ionic equation that cannot be obtained from the overall chemical equation?

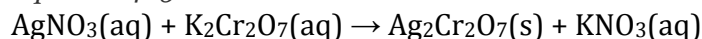
4.5 Precipitation Reactions

LEARNING OBJECTIVE

1. To identify a precipitation reaction and predict solubilities.

A precipitation reaction is a reaction that yields an insoluble product—a precipitate—when two solutions are mixed. In Section 4.4 "Ionic Equations", we described a precipitation reaction in which a colorless solution of silver nitrate was mixed with a yellow-orange solution of potassium dichromate to give a reddish precipitate of silver dichromate:

Equation 4.15



This equation has the general form of an exchange reaction:

Equation 4.16



Thus precipitation reactions are a subclass of exchange reactions that occur between ionic compounds when one of the products is insoluble. Because both components of each compound change partners, such reactions are sometimes called *double-displacement reactions*. Two important uses of precipitation reactions are to isolate metals that have been extracted from their ores and to recover precious metals for recycling.

Note the Pattern

Precipitation reactions are a subclass of exchange reactions.

Predicting Solubilities

Table 4.2 "Guidelines for Predicting the Solubility of Ionic Compounds in Water" gives guidelines for predicting the solubility of a wide variety of ionic compounds. To determine whether a precipitation reaction will occur, we identify each species in the solution and then refer to Table 4.2 "Guidelines for Predicting the Solubility of Ionic Compounds in Water" to see which, if any, combination(s) of cation and anion are likely to produce an insoluble salt. In doing so, it is important to recognize that *soluble* and *insoluble* are relative terms that span a wide range of actual solubilities. We will discuss solubilities in more detail in Chapter 17 "Solubility and Complexation Equilibria", where you will learn that very small amounts of the constituent ions remain in solution even after precipitation of an "insoluble" salt. For our purposes, however, we will assume that precipitation of an insoluble salt is complete.

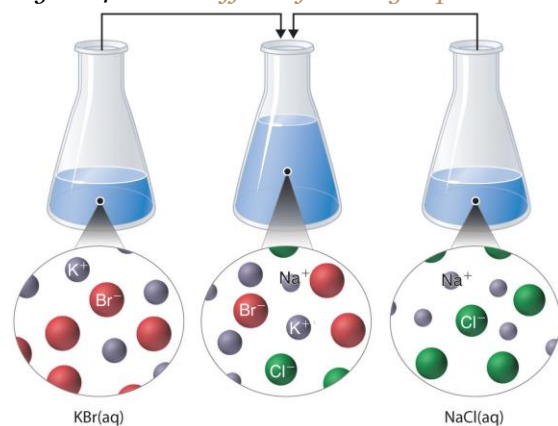
Table 4.2 Guidelines for Predicting the Solubility of Ionic Compounds in Water

	Soluble		Exceptions
Rule 1	most salts that contain an alkali metal (Li ⁺ , Na ⁺ , K ⁺ , Rb ⁺ , and Cs ⁺) and ammonium (NH ₄ ⁺)		
Rule 2	most salts that contain the nitrate (NO ₃ ⁻) anion		
Rule 3	most salts of anions derived from monocarboxylic acids (e.g., CH ₃ CO ₂ ⁻)	but not	silver acetate and salts of long-chain carboxylates
Rule 4	most chloride, bromide, and iodide salts	but not	salts of metal ions located on the lower right side of the periodic table (e.g., Cu ⁺ , Ag ⁺ , Pb ²⁺ , and Hg ₂ ²⁺).
	Insoluble		Exceptions
Rule 5	most salts that contain the hydroxide (OH ⁻) and sulfide (S ²⁻) anions	but not	salts of the alkali metals (group 1), the heavier alkaline earths (Ca ²⁺ , Sr ²⁺ , and Ba ²⁺ in group 2), and the NH ₄ ⁺ ion.

Rule 6	most carbonate (CO_3^{2-}) and phosphate (PO_4^{3-}) salts	but not	salts of the alkali metals or the NH_4^+ ion.
Rule 7	most sulfate (SO_4^{2-}) salts that contain main group cations with a charge $\geq +2$	but not	salts of +1 cations, Mg^{2+} , and dipositive transition metal cations (e.g., Ni^{2+})

Just as important as predicting the product of a reaction is knowing when a chemical reaction will *not* occur. Simply mixing solutions of two different chemical substances does *not* guarantee that a reaction will take place. For example, if 500 mL of a 1.0 M aqueous NaCl solution is mixed with 500 mL of a 1.0 M aqueous KBr solution, the final solution has a volume of 1.00 L and contains 0.50 M $\text{Na}^+(\text{aq})$, 0.50 M $\text{Cl}^-(\text{aq})$, 0.50 M $\text{K}^+(\text{aq})$, and 0.50 M $\text{Br}^-(\text{aq})$. As you will see in the following sections, none of these species reacts with any of the others. When these solutions are mixed, the only effect is to dilute each solution with the other (Figure 4.12 "The Effect of Mixing Aqueous KBr and NaCl Solutions").

Figure 4.12 *The Effect of Mixing Aqueous KBr and NaCl Solutions*



Because no net reaction occurs, the only effect is to dilute each solution with the other. (Water molecules are omitted from molecular views of the solutions for clarity.)

EXAMPLE 11

Using the information in Table 4.2 "Guidelines for Predicting the Solubility of Ionic Compounds in Water", predict what will happen in each case involving strong electrolytes. Write the net ionic equation for any reaction that occurs.

- Aqueous solutions of barium chloride and lithium sulfate are mixed.
- Aqueous solutions of rubidium hydroxide and cobalt(II) chloride are mixed.
- Aqueous solutions of strontium bromide and aluminum nitrate are mixed.

d. Solid lead(II) acetate is added to an aqueous solution of ammonium iodide.

Given: reactants

Asked for: reaction and net ionic equation

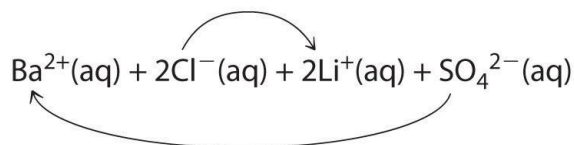
Strategy:

A Identify the ions present in solution and write the products of each possible exchange reaction.

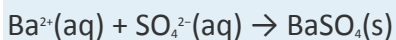
B Refer to Table 4.2 "Guidelines for Predicting the Solubility of Ionic Compounds in Water" to determine which, if any, of the products is insoluble and will therefore form a precipitate. If a precipitate forms, write the net ionic equation for the reaction.

Solution:

a. **A** Because barium chloride and lithium sulfate are strong electrolytes, each dissociates completely in water to give a solution that contains the constituent anions and cations. Mixing the two solutions *initially* gives an aqueous solution that contains Ba^{2+} , Cl^- , Li^+ , and SO_4^{2-} ions. The only possible exchange reaction is to form LiCl and BaSO_4 :



B We now need to decide whether either of these products is insoluble. Table 4.2 "Guidelines for Predicting the Solubility of Ionic Compounds in Water" shows that LiCl is soluble in water (rules 1 and 4), but BaSO_4 is not soluble in water (rule 5). Thus BaSO_4 will precipitate according to the net ionic equation

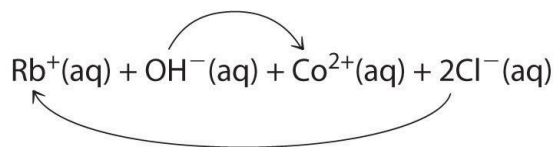


Although soluble barium salts are toxic, BaSO_4 is so insoluble that it can be used to diagnose stomach and intestinal problems without being absorbed into tissues. An outline of the digestive organs appears on x-rays of patients who have been given a "barium milkshake" or a "barium enema"—a suspension of very fine BaSO_4 particles in water.

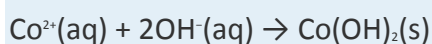
to x-rays.

b. **A** Rubidium hydroxide and cobalt(II) chloride are strong electrolytes, so when aqueous solutions of these compounds are mixed, the resulting solution initially contains Rb^+ , OH^- , Co^{2+} , and

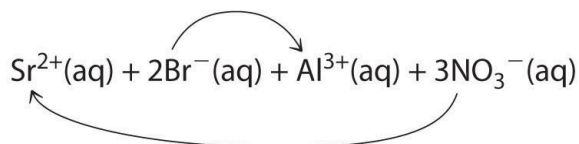
Cl^- ions. The possible products of an exchange reaction are rubidium chloride and cobalt(II) hydroxide):



B According to Table 4.2 "Guidelines for Predicting the Solubility of Ionic Compounds in Water", RbCl is soluble (rules 1 and 4), but $\text{Co}(\text{OH})_2$ is not soluble (rule 5). Hence $\text{Co}(\text{OH})_2$ will precipitate according to the following net ionic equation:

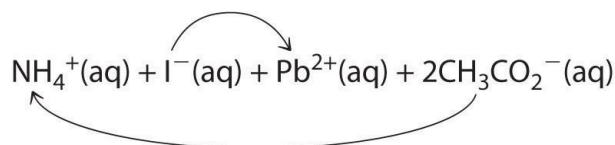


c. **A** When aqueous solutions of strontium bromide and aluminum nitrate are mixed, we initially obtain a solution that contains Sr^{2+} , Br^- , Al^{3+} , and NO_3^- ions. The two possible products from an exchange reaction are aluminum bromide and strontium nitrate:

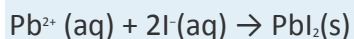


B According to Table 4.2 "Guidelines for Predicting the Solubility of Ionic Compounds in Water", both AlBr_3 (rule 4) and $\text{Sr}(\text{NO}_3)_2$ (rule 2) are soluble. Thus no net reaction will occur.

d. **A** According to Table 4.2 "Guidelines for Predicting the Solubility of Ionic Compounds in Water", lead acetate is soluble (rule 3). Thus solid lead acetate dissolves in water to give Pb^{2+} and CH_3CO_2^- ions. Because the solution also contains NH_4^+ and I^- ions, the possible products of an exchange reaction are ammonium acetate and lead(II) iodide:



B According to Table 4.2 "Guidelines for Predicting the Solubility of Ionic Compounds in Water", ammonium acetate is soluble (rules 1 and 3), but PbI_2 is insoluble (rule 4). Thus $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ will dissolve, and PbI_2 will precipitate. The net ionic equation is as follows:

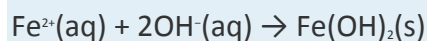


Exercise

Using the information in Table 4.2 "Guidelines for Predicting the Solubility of Ionic Compounds in Water", predict what will happen in each case involving strong electrolytes. Write the net ionic equation for any reaction that occurs.

- An aqueous solution of strontium hydroxide is added to an aqueous solution of iron(II) chloride.
- Solid potassium phosphate is added to an aqueous solution of mercury(II) perchlorate.
- Solid sodium fluoride is added to an aqueous solution of ammonium formate.
- Aqueous solutions of calcium bromide and cesium carbonate are mixed.

Answer:



- $2\text{PO}_4^{3-}(\text{aq}) + 3\text{Hg}_2^{2+}(\text{aq}) \rightarrow \text{Hg}_3(\text{PO}_4)_2(\text{s})$
- NaF(s) dissolves; no net reaction
- $\text{Ca}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightarrow \text{CaCO}_3(\text{s})$

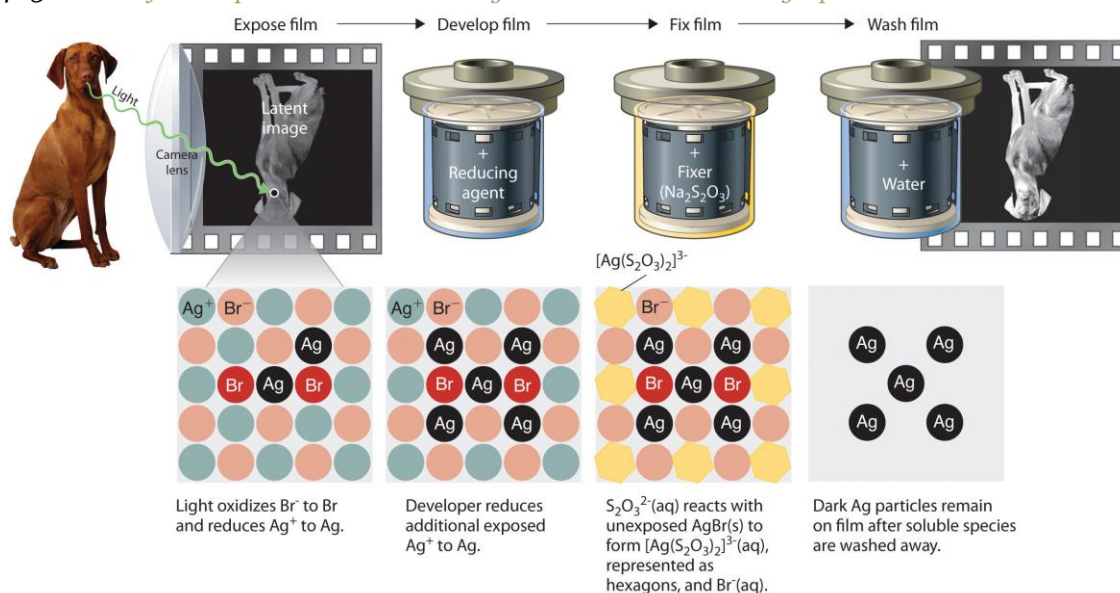
d. Precipitation Reactions in Photography

e. Precipitation reactions can be used to recover silver from solutions used to develop conventional photographic film. Although largely supplanted by digital photography, conventional methods are often used for artistic purposes. Silver bromide is an off-white solid that turns black when exposed to light, which is due to the formation of small particles of silver metal. Black-and-white photography uses this reaction to capture images in shades of gray, with the darkest areas of the film corresponding to the areas that received the most light. The first step in film processing is to enhance the black/white contrast by using a developer to increase the amount of black. The developer is a reductant: because silver atoms catalyze the reduction reaction, grains of silver bromide that have already been partially reduced by exposure to light react with the reductant much more rapidly than unexposed grains.

After the film is developed, any unexposed silver bromide must be removed by a process called "fixing"; otherwise, the entire film would turn black with additional exposure to light. Although silver bromide is insoluble in water, it is soluble in a dilute solution of sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$; *photographer's hypo*) because of the formation of $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$ ions. Thus washing the film with thiosulfate solution dissolves unexposed silver bromide and leaves a

pattern of metallic silver granules that constitutes the negative. This procedure is summarized in Figure 4.13 "Outline of the Steps Involved in Producing a Black-and-White Photograph". The negative image is then projected onto paper coated with silver halides, and the developing and fixing processes are repeated to give a positive image. (Color photography works in much the same way, with a combination of silver halides and organic dyes superimposed in layers.) "Instant photo" operations can generate more than a hundred gallons of dilute silver waste solution per day. Recovery of silver from thiosulfate fixing solutions involves first removing the thiosulfate by oxidation and then precipitating Ag^+ ions with excess chloride ions.

Figure 4.13 Outline of the Steps Involved in Producing a Black-and-White Photograph



EXAMPLE 12

A silver recovery unit can process 1500 L of photographic silver waste solution per day. Adding excess solid sodium chloride to a 500 mL sample of the waste (after removing the thiosulfate as described previously) gives a white precipitate that, after filtration and drying, consists of 3.73 g of AgCl . What mass of NaCl must be added to the 1500 L of silver waste to ensure that all the Ag^+ ions precipitate?

Given: volume of solution of one reactant and mass of product from a sample of reactant solution

Asked for: mass of second reactant needed for complete reaction

Strategy:

A Write the net ionic equation for the reaction. Calculate the number of moles of AgCl obtained from the 500 mL sample and then determine the concentration of Ag^+ in the sample by dividing the number of moles of AgCl formed by the volume of solution.

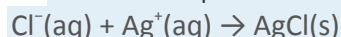
B Determine the total number of moles of Ag^+ in the 1500 L solution by multiplying the Ag^+ concentration by the total volume.

C Use mole ratios to calculate the number of moles of chloride needed to react with Ag^+ . Obtain the mass of NaCl by multiplying the number of moles of NaCl needed by its molar mass.

Solution:

We can use the data provided to determine the concentration of Ag^+ ions in the waste, from which the number of moles of Ag^+ in the entire waste solution can be calculated. From the net ionic equation, we can determine how many moles of Cl^- are needed, which in turn will give us the mass of NaCl necessary.

A The first step is to write the net ionic equation for the reaction:



We know that 500 mL of solution produced 3.73 g of AgCl. We can convert this value to the number of moles of AgCl as follows:

$$\text{moles AgCl} = \frac{\text{grams AgCl}}{\text{molar mass AgCl}} = \frac{3.73 \text{ g AgCl}}{143.32 \text{ g AgCl/mol}} = 0.0260 \text{ mol AgCl}$$

Therefore, the 500 mL sample of the solution contained 0.0260 mol of Ag^+ . The Ag^+ concentration is determined as follows:

$$[\text{Ag}^+] = \frac{\text{moles Ag}}{\text{liters soln}} = \frac{0.0260 \text{ mol AgCl}}{0.500 \text{ L}} = 0.0520 \text{ M}$$

B The total number of moles of Ag^+ present in 1500 L of solution is as follows:

$$\text{moles Ag}^+ = 1500 \text{ L} (0.0520 \text{ mol/L}) = 78.1 \text{ mol Ag}^+$$

C According to the net ionic equation, one Cl^- ion is required for each Ag^+ ion. Thus 78.1 mol of NaCl are needed to precipitate the silver. The corresponding mass of NaCl is

$$\text{mass NaCl} = 78.1 \text{ mol NaCl} (58.44 \text{ g NaCl/mol NaCl}) = 4560 \text{ g NaCl} = 4.56 \text{ kg NaCl}$$

Note that 78.1 mol of AgCl correspond to 8.43 kg of metallic silver, which is worth about \$7983 at 2011 prices (\$32.84 per troy ounce). Silver recovery may be economically attractive as well as ecologically sound, although the procedure outlined is becoming nearly obsolete for all but artistic purposes with the growth of digital photography.

Exercise

Because of its toxicity, arsenic is the active ingredient in many pesticides. The arsenic content of a pesticide can be measured by oxidizing arsenic compounds to the arsenate ion (AsO_4^{3-}), which forms an insoluble silver salt (Ag_3AsO_4). Suppose you are asked to assess the purity of technical grade sodium

arsenite (NaAsO_2), the active ingredient in a pesticide used against termites. You dissolve a 10.00 g sample in water, oxidize it to arsenate, and dilute it with water to a final volume of 500 mL. You then add excess AgNO_3 solution to a 50.0 mL sample of the arsenate solution. The resulting precipitate of Ag_3AsO_4 has a mass of 3.24 g after drying. What is the percentage by mass of NaAsO_2 in the original sample?

Answer: 91.0%

Summary

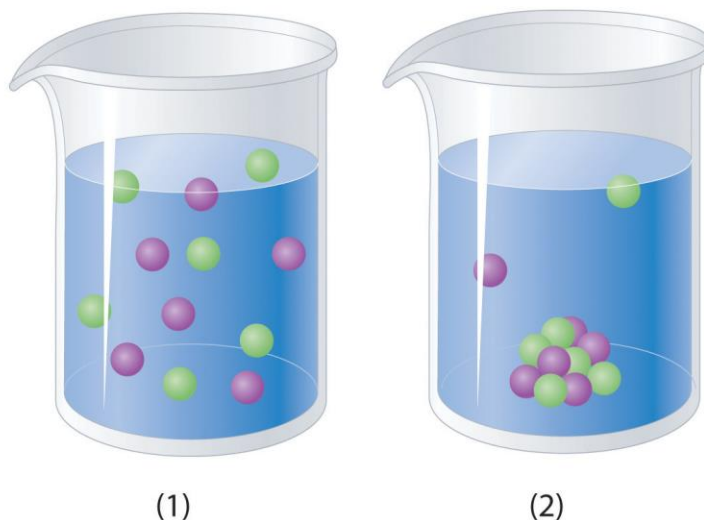
In a **precipitation reaction**, a subclass of exchange reactions, an insoluble material (a **precipitate**) forms when solutions of two substances are mixed. To predict the product of a precipitation reaction, all species initially present in the solutions are identified, as are any combinations likely to produce an insoluble salt.

KEY TAKEAWAY

- Predicting the solubility of ionic compounds in water can give insight into whether or not a reaction will occur.

CONCEPTUAL PROBLEMS

- Predict whether mixing each pair of solutions will result in the formation of a precipitate. If so, identify the precipitate.
 - $\text{FeCl}_2(\text{aq}) + \text{Na}_2\text{S}(\text{aq})$
 - $\text{NaOH}(\text{aq}) + \text{H}_3\text{PO}_4(\text{aq})$
 - $\text{ZnCl}_2(\text{aq}) + (\text{NH}_4)_2\text{S}(\text{aq})$
- Predict whether mixing each pair of solutions will result in the formation of a precipitate. If so, identify the precipitate.
 - $\text{KOH}(\text{aq}) + \text{H}_3\text{PO}_4(\text{aq})$
 - $\text{K}_2\text{CO}_3(\text{aq}) + \text{BaCl}_2(\text{aq})$
 - $\text{Ba}(\text{NO}_3)_2(\text{aq}) + \text{Na}_2\text{SO}_4(\text{aq})$
- Which representation best corresponds to an aqueous solution originally containing each of the following?
 - 1 M NH_4Cl
 - 1 M NaO_2CCH_3
 - 1 M NaOH + 1 M HCl
 - 1 M $\text{Ba}(\text{OH})_2$ + 1 M H_2SO_4



4. Which representation in Problem 3 best corresponds to an aqueous solution originally containing each of the following?

- 1 M $\text{CH}_3\text{CO}_2\text{H}$ + 1 M NaOH
- 1 M NH_3 + 1 M HCl
- 1 M Na_2CO_3 + 1 M H_2SO_4
- 1 M CaCl_2 + 1 M H_3PO_4

ANSWER

3.

- 1
- 1
- 1
- 2

NUMERICAL PROBLEMS

- What mass of precipitate would you expect to obtain by mixing 250 mL of a solution containing 4.88 g of Na_2CrO_4 with 200 mL of a solution containing 3.84 g of AgNO_3 ? What is the final nitrate ion concentration?
- Adding 10.0 mL of a dilute solution of zinc nitrate to 246 mL of 2.00 M sodium sulfide produced 0.279 g of a precipitate. How many grams of zinc(II) nitrate and sodium sulfide were consumed to produce this quantity of product? What was the concentration of each ion in the original solutions? What is the concentration of the sulfide ion in solution after the precipitation reaction, assuming no further reaction?

ANSWER

1. 3.75 g Ag_2CrO_4 ; 5.02×10^{-2} M nitrate

4.6 Acid–Base Reactions

LEARNING OBJECTIVE

1. To know the characteristic properties of acids and bases.

Acid–base reactions are essential in both biochemistry and industrial chemistry. Moreover, many of the substances we encounter in our homes, the supermarket, and the pharmacy are acids or bases. For example, aspirin is an acid (acetylsalicylic acid), and antacids are bases. In fact, every amateur chef who has prepared mayonnaise or squeezed a wedge of lemon to marinate a piece of fish has carried out an acid–base reaction. Before we discuss the characteristics of such reactions, let's first describe some of the properties of acids and bases.

Definitions of Acids and Bases

In Chapter 2 "Molecules, Ions, and Chemical Formulas", we defined **acids** as substances that dissolve in water to produce H^+ ions, whereas **bases** were defined as substances that dissolve in water to produce OH^- ions. In fact, this is only one possible set of definitions. Although the general properties of acids and bases have been known for more than a thousand years, the definitions of *acid* and *base* have changed dramatically as scientists have learned more about them. In ancient times, an acid was any substance that had a sour taste (e.g., vinegar or lemon juice), caused consistent color changes in dyes derived from plants (e.g., turning blue litmus paper red), reacted with certain metals to produce hydrogen gas and a solution of a salt containing a metal cation, and dissolved carbonate salts such as limestone (CaCO_3) with the evolution of carbon dioxide. In contrast, a base was any substance that had a bitter taste, felt slippery to the touch, and caused color changes in plant dyes that differed diametrically from the changes caused by acids (e.g., turning red litmus paper blue). Although these definitions were useful, they were entirely descriptive.

Acid

Sour taste

Turns blue litmus red

reacts with some metals to produce H_2

Dissolves carbonate salts, releasing CO_2



Base

Bitter taste

Turns red litmus blue

Slippery to the touch



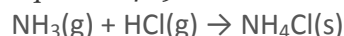
The Arrhenius Definition of Acids and Bases

The first person to define acids and bases in detail was the Swedish chemist Svante Arrhenius (1859–1927; Nobel Prize in Chemistry, 1903). According to the *Arrhenius definition*, an acid is a substance like hydrochloric acid that dissolves in water to produce H^+ ions (protons, and a base is a substance like sodium hydroxide that dissolves in water to produce hydroxide (OH^-) ions:

According to Arrhenius, the characteristic properties of acids and bases are due exclusively to the presence of H^+ and OH^- ions, respectively, in solution.

Although Arrhenius's ideas were widely accepted, his definition of acids and bases had two major limitations. First, because acids and bases were defined in terms of ions obtained from water, the Arrhenius concept applied only to substances in aqueous solution. Second, and more important, the Arrhenius definition predicted that *only* substances that dissolve in water to produce H^+ and OH^- ions should exhibit the properties of acids and bases, respectively. For example, according to the Arrhenius definition, the reaction of ammonia (a base) with gaseous HCl (an acid) to give ammonium chloride (Equation 4.19) is not an acid–base reaction because it does not involve H^+ and OH^- :

Equation 4.19



The Brønsted–Lowry Definition of Acids and Bases

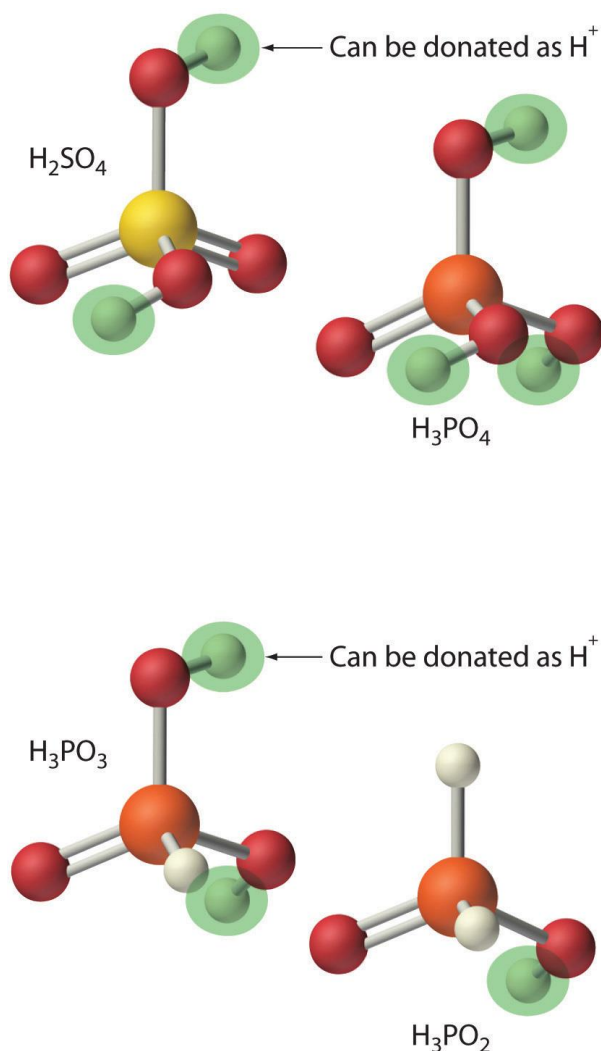
Because of the limitations of the Arrhenius definition, a more general definition of acids and bases was needed. One was proposed independently in 1923 by the Danish chemist J. N. Brønsted (1879–1947) and the British chemist T. M. Lowry (1874–1936), who defined acid–base reactions in terms of the transfer of a proton (H^+ ion) from one substance to another.

According to Brønsted and Lowry, an acid is any substance that can donate a proton, and a base is any substance that can accept a proton. The Brønsted–Lowry definition of an acid is essentially the same as the Arrhenius definition, except that it is not restricted to aqueous solutions. The Brønsted–Lowry definition of a base, however, is far more general because the hydroxide ion is just one of many substances that can accept a proton. Ammonia, for example, reacts with a proton to form NH_4^+ , so in Equation 4.19, NH_3 is a Brønsted–Lowry base and HCl is a Brønsted–Lowry acid. Because of its more general nature, the Brønsted–Lowry definition is used throughout this text unless otherwise specified. We will present a third definition—Lewis acids and bases—in Chapter 8 "Ionic versus Covalent Bonding" when we discuss molecular structure.

Polyprotic Acids

Acids differ in the number of protons they can donate. For example, monoprotic acids are compounds that are capable of donating a single proton per molecule. Monoprotic acids include HF , HCl , HBr , HI , HNO_3 , and HNO_2 . All carboxylic acids that contain a single $-\text{CO}_2\text{H}$ group, such as acetic acid ($\text{CH}_3\text{CO}_2\text{H}$), are monoprotic acids, dissociating to form RCO_2^- and H^+ (Section 4.1 "Aqueous Solutions"). Polyprotic acids can donate more than one proton per molecule. For example, H_2SO_4 can donate two H^+ ions in separate steps, so it is a diprotic acid, and H_3PO_4 , which is capable of donating three protons in successive steps, is a triprotic acid:

Equation 4.20



In chemical equations such as these, a double arrow is used to indicate that both the forward and reverse reactions occur simultaneously, so the forward reaction does not go to completion. Instead, the solution contains significant amounts of both reactants and products. Over time, the reaction reaches a state in which the concentration of each species in solution remains constant. The reaction is then said to be in equilibrium. We will return to the concept of equilibrium in more detail in Chapter 15 "Chemical Equilibrium".

Strengths of Acids and Bases

We will not discuss the strengths of acids and bases quantitatively until Chapter 16 "Aqueous Acid–Base Equilibria". Qualitatively, however, we can state that strong acids react essentially completely with water to give H^+ and the corresponding anion. Similarly, strong bases dissociate essentially completely in water to give OH^- and the corresponding cation. Strong acids and strong bases are both strong electrolytes.

In contrast, only a fraction of the molecules of weak acids and weak bases react with water to produce ions, so weak acids and weak bases are also weak electrolytes. Typically less than 5% of a weak electrolyte dissociates into ions in solution, whereas more than 95% is present in undissociated form.

In practice, only a few strong acids are commonly encountered: HCl, HBr, HI, HNO₃, HClO₄, and H₂SO₄ (H₃PO₄ is only moderately strong). The most common strong bases are ionic compounds that contain the hydroxide ion as the anion; three examples are NaOH, KOH, and Ca(OH)₂. Common weak acids include HCN, H₂S, HF, oxoacids such as HNO₂ and HClO, and carboxylic acids such as acetic acid. Most of the ammonia (>99%) is present in the form of NH₃(g). Amines, which are organic analogues of ammonia, are also weak bases, as are ionic compounds that contain anions derived from weak acids (such as S²⁻).

Table 4.3 "Common Strong Acids and Bases" lists some common strong acids and bases. Acids other than the six common strong acids are almost invariably weak acids. The only common strong bases are the hydroxides of the alkali metals and the heavier alkaline earths (Ca, Sr, and Ba); any other bases you encounter are most likely weak. Remember that *there is no correlation between solubility and whether a substance is a strong or a weak electrolyte!* Many weak acids and bases are extremely soluble in water.

Note the Pattern

There is *no* correlation between the solubility of a substance and whether it is a strong electrolyte, a weak electrolyte, or a nonelectrolyte.

Table 4.3 Common Strong Acids and Bases

Strong Acids		Strong Bases	
Hydrogen Halides	Oxoacids	Group 1 Hydroxides	Hydroxides of the Heavier Group 2 Elements
HCl	HNO ₃	LiOH	Ca(OH) ₂
HBr	H ₂ SO ₄	NaOH	Sr(OH) ₂
HI	HClO ₄	KOH	Ba(OH) ₂
		RbOH	
		CsOH	

EXAMPLE 13

Classify each compound as a strong acid, a weak acid, a strong base, a weak base, or none of these.

- CH₃CH₂CO₂H
- CH₃OH

- c. $\text{Sr}(\text{OH})_2$
- d. $\text{CH}_3\text{CH}_2\text{NH}_2$
- e. HBrO_4

Given: compound

Asked for: acid or base strength

Strategy:

A Determine whether the compound is organic or inorganic.

B If inorganic, determine whether the compound is acidic or basic by the presence of dissociable H^+ or OH^- ions, respectively. If organic, identify the compound as a weak base or a weak acid by the presence of an amine or a carboxylic acid group, respectively. Recall that all polyprotic acids except H_2SO_4 are weak acids.

Solution:

- a. **A** This compound is propionic acid, which is organic. **B** It contains a carboxylic acid group analogous to that in acetic acid, so it must be a weak acid.
- b. **A** CH_3OH is methanol, an organic compound that contains the $-\text{OH}$ group. **B** As a covalent compound, it does not dissociate to form the OH^- ion. Because it does not contain a carboxylic acid ($-\text{CO}_2\text{H}$) group, methanol also cannot dissociate to form $\text{H}^+(\text{aq})$ ions. Thus we predict that in aqueous solution methanol is neither an acid nor a base.
- c. **A** $\text{Sr}(\text{OH})_2$ is an inorganic compound that contains one Sr^{2+} and two OH^- ions per formula unit. **B** We therefore expect it to be a strong base, similar to $\text{Ca}(\text{OH})_2$.
- d. **A** $\text{CH}_3\text{CH}_2\text{NH}_2$ is an amine (ethylamine), an organic compound in which one hydrogen of ammonia has been replaced by an R group. **B** Consequently, we expect it to behave similarly to ammonia (Equation 4.23), reacting with water to produce small amounts of the OH^- ion. Ethylamine is therefore a weak base.
- e. **A** HBrO_4 is perbromic acid, an inorganic compound. **B** It is not listed in Table 4.3 "Common Strong Acids and Bases" as one of the common strong acids, but that does not necessarily mean that it is a weak acid. If you examine the periodic table, you can see that Br lies directly below Cl in group 17. We might therefore expect that HBrO_4 is chemically similar to HClO_4 , a strong acid—and, in fact, it is.

Exercise

Classify each compound as a strong acid, a weak acid, a strong base, a weak base, or none of these.

- a. $\text{Ba}(\text{OH})_2$
- b. HIO_4
- c. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$
- d. $(\text{CH}_3)_2\text{NH}$
- e. CH_2O

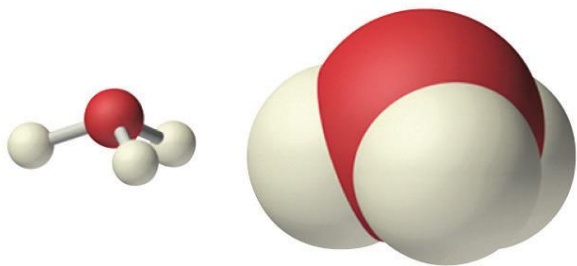
Answer:

- a. strong base
- b. strong acid
- c. weak acid
- d. weak base
- e. none of these; formaldehyde is a neutral molecule

The Hydronium Ion

Because isolated protons are *very* unstable and hence very reactive, an acid never simply “loses” an H^+ ion. Instead, the proton is always transferred to another substance, which acts as a base in the Brønsted–Lowry definition. Thus in every acid–base reaction, one species acts as an acid and one species acts as a base. Occasionally, the same substance performs both roles, as you will see later. When a strong acid dissolves in water, the proton that is released is transferred to a water molecule that acts as a proton acceptor or base, as shown for the dissociation of sulfuric acid.

Technically, therefore, it is imprecise to describe the dissociation of a strong acid as producing $\text{H}^+(\text{aq})$ ions, as we have been doing. The resulting H_3O^+ ion, called the hydronium ion, is a more accurate representation of $\text{H}^+(\text{aq})$. For the sake of brevity, however, in discussing acid dissociation reactions, we will often show the product as $\text{H}^+(\text{aq})$ with the understanding that the product is actually the $\text{H}_3\text{O}^+(\text{aq})$ ion.



Hydronium ion,
 H_3O^+

Conversely, bases that do not contain the hydroxide ion accept a proton from water, so small amounts of OH^- are produced.

Again, the double arrow indicates that the reaction does not go to completion but rather reaches a state of equilibrium. In this reaction, water acts as an acid by donating a proton to ammonia, and ammonia acts as a base by accepting a proton from water. Thus water can act as either an acid or a base by donating a proton to a base or by accepting a proton from an acid. Substances that can behave as both an acid and a base are said to be amphoteric.

The products of an acid–base reaction are also an acid and a base. In Equation 4.27, for example, the products of the reaction are the hydronium ion, here an acid, and the hydrogen sulfate ion, here a weak base. In Equation 4.28, the products are NH_4^+ , an acid, and OH^- , a base. The product NH_4^+ is called the conjugate acid of the base NH_3 , and the product OH^- is called the conjugate base of the acid H_2O . Thus all acid–base reactions actually involve two conjugate acid–base pairs; in Equation 4.28, they are $\text{NH}_4^+/\text{NH}_3$ and $\text{H}_2\text{O}/\text{OH}^-$. We will describe the relationship between conjugate acid–base pairs in more detail in Chapter 16 "Aqueous Acid–Base Equilibria".

Neutralization Reactions

A neutralization reaction is one in which an acid and a base react in stoichiometric amounts to produce water and a salt, the general term for any ionic substance that does not have OH^- as the anion or H^+ as the cation. If the base is a metal hydroxide, then the general formula for the reaction of an acid with a base is described as follows: *Acid plus base yields water plus salt*. For example, the reaction of equimolar amounts of HBr and NaOH to give water and a salt (NaBr) is a neutralization reaction.

Note the Pattern

Acid plus base yields water plus salt.

The strengths of the acid and the base generally determine whether the reaction goes to completion. The reaction of *any* strong acid with *any* strong base goes essentially to completion, as does the reaction of a strong acid with a weak base, and a weak acid with a strong base.

Sodium acetate is written with the organic component first followed by the cation, as is usual for organic salts. Most reactions of a weak acid with a weak base also go essentially to completion.

An example of an acid–base reaction that does not go to completion is the reaction of a weak acid or a weak base with water, which is both an extremely weak acid and an extremely weak base. We will discuss these reactions in more detail in Chapter 16 "Aqueous Acid–Base Equilibria".

Note the Pattern

Except for the reaction of a weak acid or a weak base with water, acid–base reactions essentially go to completion.

In some cases, the reaction of an acid with an anion derived from a weak acid (such as HS^-) produces a gas (in this case, H_2S). Because the gaseous product escapes from solution in the form of bubbles, the reverse reaction cannot occur. Therefore, these reactions tend to be forced, or driven, to completion. Examples include reactions in which an acid is added to ionic compounds that contain the HCO_3^- , CN^- , or S^{2-} anions, all of which are driven to completion (Figure 4.14 "The Reaction of Dilute Aqueous HNO_3 ").

EXAMPLE 14

Calcium propionate is used to inhibit the growth of molds in foods, tobacco, and some medicines. Write a balanced chemical equation for the reaction of aqueous propionic acid ($\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$) with aqueous calcium hydroxide [$\text{Ca}(\text{OH})_2$] to give calcium propionate. Do you expect this reaction to go to completion, making it a feasible method for the preparation of calcium propionate?

Given: reactants and product

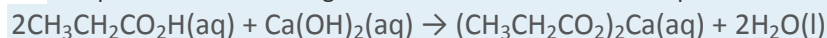
Asked for: balanced chemical equation and whether the reaction will go to completion

Strategy:

Write the balanced chemical equation for the reaction of propionic acid with calcium hydroxide. Based on their acid and base strengths, predict whether the reaction will go to completion.

Solution:

Propionic acid is an organic compound that is a weak acid, and calcium hydroxide is an inorganic compound that is a strong base. The balanced chemical equation is as follows:



The reaction of a weak acid and a strong base will go to completion, so it is reasonable to prepare calcium propionate by mixing solutions of propionic acid and calcium hydroxide in a 2:1 mole ratio.

Exercise

Write a balanced chemical equation for the reaction of solid sodium acetate with dilute sulfuric acid to give sodium sulfate.

Answer: $2\text{CH}_3\text{CO}_2\text{Na(s)} + \text{H}_2\text{SO}_4\text{(aq)} \rightarrow \text{Na}_2\text{SO}_4\text{(aq)} + 2\text{CH}_3\text{CO}_2\text{H(aq)}$

One of the most familiar and most heavily advertised applications of acid–base chemistry is *antacids*, which are bases that neutralize stomach acid. The human stomach contains an approximately 0.1 M solution of hydrochloric acid that helps digest foods. If the protective lining of the stomach breaks down, this acid can attack the stomach tissue, resulting in the formation of an *ulcer*. Because one factor that is believed to contribute to the formation of stomach ulcers is the production of excess acid in the stomach, many individuals routinely consume large quantities of antacids. The active ingredients in antacids include sodium bicarbonate and potassium bicarbonate (NaHCO_3 and KHCO_3 ; Alka-Seltzer); a mixture of magnesium hydroxide and aluminum hydroxide [Mg(OH)_2 and Al(OH)_3 ; Maalox, Mylanta]; calcium carbonate (CaCO_3 ; Tums); and a complex salt, dihydroxyaluminum sodium carbonate [$\text{NaAl(OH)}_2\text{CO}_3$; original Rolaids]. Each has certain advantages and disadvantages. For example, Mg(OH)_2 is a powerful laxative (it is the active ingredient in milk of magnesia), whereas Al(OH)_3 causes constipation. When mixed, each tends to counteract the unwanted effects of the other. Although all antacids contain both an anionic base (OH^- , CO_3^{2-} , or HCO_3^-) and an appropriate cation, they differ substantially in the amount of active ingredient in a given mass of product.

EXAMPLE 15

Assume that the stomach of someone suffering from acid indigestion contains 75 mL of 0.20 M HCl. How many Tums tablets are required to neutralize 90% of the stomach acid, if each tablet contains 500 mg of CaCO_3 ? (Neutralizing all of the stomach acid is not desirable because that would completely shut down digestion.)

Given: volume and molarity of acid and mass of base in an antacid tablet

Asked for: number of tablets required for 90% neutralization

Strategy:

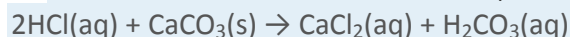
A Write the balanced chemical equation for the reaction and then decide whether the reaction will go to completion.

B Calculate the number of moles of acid present. Multiply the number of moles by the percentage to obtain the quantity of acid that must be neutralized. Using mole ratios, calculate the number of moles of base required to neutralize the acid.

C Calculate the number of moles of base contained in one tablet by dividing the mass of base by the corresponding molar mass. Calculate the number of tablets required by dividing the moles of base by the moles contained in one tablet.

Solution:

A We first write the balanced chemical equation for the reaction:



Each carbonate ion can react with 2 mol of H^+ to produce H_2CO_3 , which rapidly decomposes to H_2O and CO_2 . Because HCl is a strong acid and CO_3^{2-} is a weak base, the reaction will go to completion.

B Next we need to determine the number of moles of HCl present:

Because we want to neutralize only 90% of the acid present, we multiply the number of moles of HCl by 0.90:

$$(0.015 \text{ mol HCl})(0.90) = 0.014 \text{ mol HCl}$$

Exercise

Assume that as a result of overeating, a person's stomach contains 300 mL of 0.25 M HCl. How many Rolaids tablets must be consumed to neutralize 95% of the acid, if each tablet contains 400 mg of

$\text{NaAl}(\text{OH})_2\text{CO}_3$? The neutralization reaction can be written as follows:

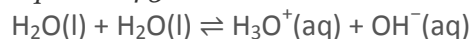


Answer: 6.4 tablets

The pH Scale

One of the key factors affecting reactions that occur in dilute solutions of acids and bases is the concentration of H^+ and OH^- ions. The pH scale provides a convenient way of expressing the hydrogen ion (H^+) concentration of a solution and enables us to describe acidity or basicity in quantitative terms. Pure liquid water contains extremely low but measurable concentrations of $\text{H}_3\text{O}^+(\text{aq})$ and $\text{OH}^-(\text{aq})$ ions produced via an *autoionization reaction*, in which water acts simultaneously as an acid and as a base:

Equation 4.38



The concentration of hydrogen ions in pure water is only $1.0 \times 10^{-7} \text{ M}$ at 25°C . Because the autoionization reaction produces both a proton and a hydroxide ion, the OH^- concentration in pure water is also $1.0 \times 10^{-7} \text{ M}$. Pure water is a neutral solution, in which $[\text{H}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$.

The pH scale describes the hydrogen ion concentration of a solution in a way that avoids the use of exponential notation; pH is defined as the negative base-10 logarithm of the hydrogen ion concentration:^[1]

Equation 4.39

$$\text{pH} = -\log[\text{H}^+]$$

Conversely,

Equation 4.40

$$[\text{H}^+] = 10^{-\text{pH}}$$

(If you are not familiar with logarithms or using a calculator to obtain logarithms and antilogarithms, consult Essential Skills 3 in Section 4.1 "Aqueous Solutions".)

Because the hydrogen ion concentration is $1.0 \times 10^{-7} \text{ M}$ in pure water at 25°C , the pH of pure liquid water (and, by extension, of any neutral solution) is

Equation 4.41

$$\text{pH} = -\log[1.0 \times 10^{-7}] = 7.00$$

Adding an acid to pure water increases the hydrogen ion concentration and decreases the hydroxide ion concentration because a neutralization reaction occurs, such as that shown in Equation 4.31. Because the negative exponent of $[\text{H}^+]$ becomes smaller as $[\text{H}^+]$ increases, the pH *decreases* with increasing $[\text{H}^+]$. For example, a 1.0 M solution of a strong monoprotic acid such as HCl or HNO_3 has a pH of 0.00:

Equation 4.42

$$\text{pH} = -\log[1.0] = 0.00$$

Note the Pattern

pH decreases with increasing $[\text{H}^+]$.

Conversely, adding a base to pure water increases the hydroxide ion concentration and decreases the hydrogen ion concentration. Because the autoionization reaction of water does not go to completion, neither does the neutralization reaction. Even a strongly basic solution contains a detectable amount of

H⁺ ions. For example, a 1.0 M OH⁻ solution has [H⁺] = 1.0 × 10⁻¹⁴ M. The pH of a 1.0 M NaOH solution is therefore

Equation 4.43

$$\text{pH} = -\log[1.0 \times 10^{-14}] = 14.00$$

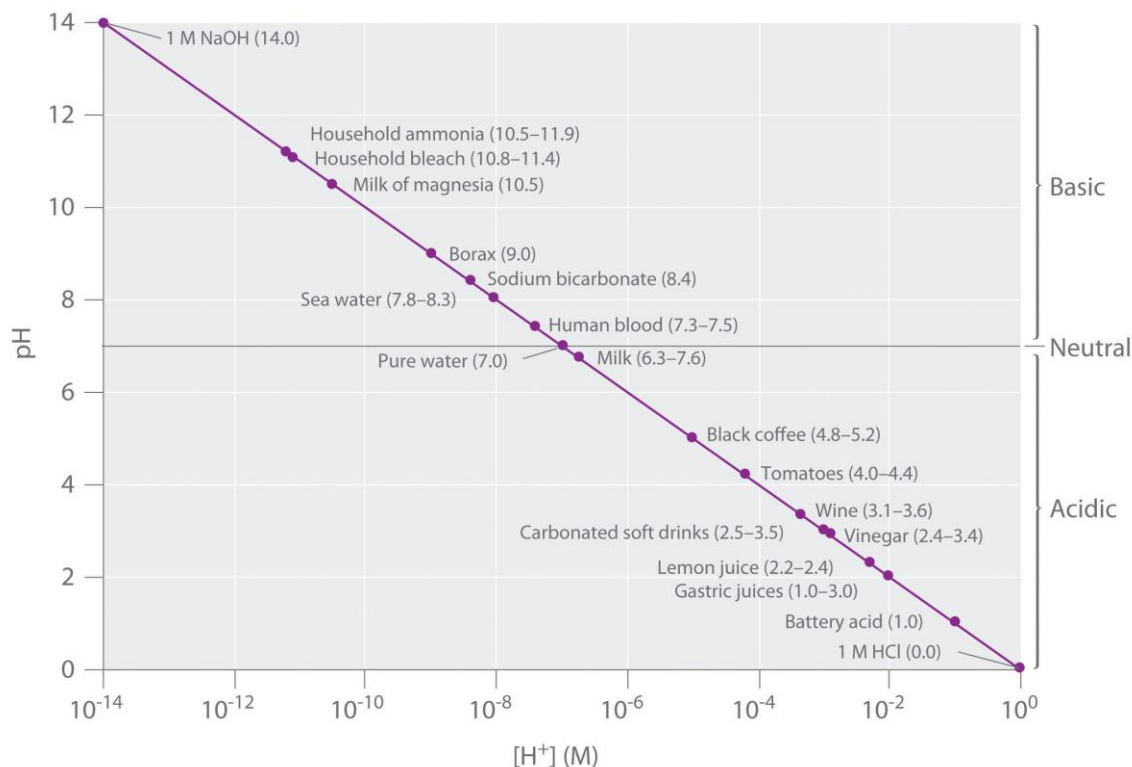
For practical purposes, the pH scale runs from pH = 0 (corresponding to 1 M H⁺) to pH 14 (corresponding to 1 M OH⁻), although pH values less than 0 or greater than 14 are possible.

We can summarize the relationships between acidity, basicity, and pH as follows:

- If pH = 7.0, the solution is neutral.
- If pH < 7.0, the solution is acidic.
- If pH > 7.0, the solution is basic.

Keep in mind that the pH scale is logarithmic, so a change of 1.0 in the pH of a solution corresponds to a *tenfold* change in the hydrogen ion concentration. The foods and consumer products we encounter daily represent a wide range of pH values, as shown in Figure 4.15 "A Plot of pH versus [H⁺]."

Figure 4.15 A Plot of pH versus [H⁺] for Some Common Aqueous Solutions



Although many substances exist in a range of pH values (indicated in parentheses), they are plotted using typical values.

EXAMPLE 16

- a. What is the pH of a 2.1×10^{-2} M aqueous solution of HClO_4 ?
- b. The pH of a vinegar sample is 3.80. What is its hydrogen ion concentration?

Given: molarity of acid or pH

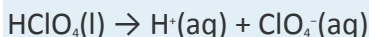
Asked for: pH or $[\text{H}^+]$

Strategy:

Using the balanced chemical equation for the acid dissociation reaction and Equation 4.41 or 4.40, determine $[\text{H}^+]$ and convert it to pH or vice versa.

Solution:

- a. HClO_4 (perchloric acid) is a strong acid, so it dissociates completely into H^+ ions and ClO_4^- ions:



The H^+ ion concentration is therefore the same as the perchloric acid concentration. The pH of the perchloric acid solution is thus

$$\text{pH} = -\log[\text{H}^+] = -\log(2.1 \times 10^{-2}) = 1.68$$

The result makes sense: the H^+ ion concentration is between 10^{-1} M and 10^{-2} M, so the pH must be between 1 and 2.

Note: The assumption that $[\text{H}^+]$ is the same as the concentration of the acid is valid for *only* strong acids. Because weak acids do *not* dissociate completely in aqueous solution, a more complex procedure is needed to calculate the pH of their solutions, which we will describe in Chapter 16 "Aqueous Acid–Base Equilibria".

- b. We are given the pH and asked to calculate the hydrogen ion concentration. From Equation 4.40,

$$10^{-\text{pH}} = [\text{H}^+]$$

$$\text{Thus } [\text{H}^+] = 10^{-3.80} = 1.6 \times 10^{-4} \text{ M.}$$

Exercise

- a. What is the pH of a 3.0×10^{-5} M aqueous solution of HNO_3 ?
- b. What is the hydrogen ion concentration of turnip juice, which has a pH of 5.41?

Answer:

- a. $\text{pH} = 4.52$
- b. $[\text{H}^+] = 3.9 \times 10^{-6} \text{ M}$

Tools have been developed that make the measurement of pH simple and convenient (Figure 4.16 "Two Ways of Measuring the pH of a Solution: pH Paper and a pH Meter"). For example, pH paper consists of strips of paper impregnated with one or more acid–base indicators, which are intensely colored organic molecules whose colors change dramatically depending on the pH of the solution. Placing a drop of a solution on a strip of pH paper and comparing its color with standards give the solution's approximate pH. A more accurate tool, the pH meter, uses a glass electrode, a device whose voltage depends on the H^+ ion concentration.

KEY EQUATIONS

definition of pH

Equation 4.39: $pH = -\log[H^+]$

Equation 4.40: $[H^+] = 10^{-pH}$

Summary

Acid–base reactions require both an acid and a base. In Brønsted–Lowry terms, an **acid** is a substance that can donate a proton (H^+), and a **base** is a substance that can accept a proton. All acid–base reactions contain two acid–base pairs: the reactants and the products. Acids can donate one proton (**monoprotic acids**), two protons (**diprotic acids**), or three protons (**triprotic acids**). Compounds that are capable of donating more than one proton are generally called **polyprotic acids**. Acids also differ in their tendency to donate a proton, a measure of their acid strength. **Strong acids** react completely with water to produce $H_3O^+(aq)$ (the **hydronium ion**), whereas **weak acids** dissociate only partially in water. Conversely, **strong bases** react completely with water to produce the hydroxide ion, whereas **weak bases** react only partially with water to form hydroxide ions. The reaction of a strong acid with a strong base is a **neutralization reaction**, which produces water plus a **salt**.

The acidity or basicity of an aqueous solution is described quantitatively using the **pH scale**. The **pH** of a solution is the negative logarithm of the H^+ ion concentration and typically ranges from 0 for strongly acidic solutions to 14 for strongly basic ones. Because of the *autoionization reaction* of water, which produces small amounts of hydronium ions and hydroxide ions, a **neutral solution** of water contains $1 \times 10^{-7} M$ H^+ ions and has a pH of 7.0. An **indicator** is an intensely colored organic substance whose color is pH dependent; it is used to determine the pH of a solution.

KEY TAKEAWAY

- An acidic solution and a basic solution react together in a neutralization reaction that also forms a salt.

CONCEPTUAL PROBLEMS

1. Why was it necessary to expand on the Arrhenius definition of an acid and a base? What specific point does the Brønsted–Lowry definition address?
2. State whether each compound is an acid, a base, or a salt.
 - a. CaCO_3
 - b. NaHCO_3
 - c. H_2SO_4
 - d. CaCl_2
 - e. $\text{Ba}(\text{OH})_2$
3. State whether each compound is an acid, a base, or a salt.
 - a. NH_3
 - b. NH_4Cl
 - c. H_2CO_3
 - d. CH_3COOH
 - e. NaOH
4. Classify each compound as a strong acid, a weak acid, a strong base, or a weak base in aqueous solution.
 - a. sodium hydroxide
 - b. acetic acid
 - c. magnesium hydroxide
 - d. tartaric acid
 - e. sulfuric acid
 - f. ammonia
 - g. hydroxylamine (NH_2OH)
 - h. hydrocyanic acid
5. Decide whether each compound forms an aqueous solution that is strongly acidic, weakly acidic, strongly basic, or weakly basic.
 - a. propanoic acid

- b. hydrobromic acid
 - c. methylamine
 - d. lithium hydroxide
 - e. citric acid
 - f. sodium acetate
 - g. ammonium chloride
 - h. barium hydroxide
6. What is the relationship between the strength of an acid and the strength of the conjugate base derived from that acid? Would you expect the CH_3CO_2^- ion to be a strong base or a weak base? Why? Is the hydronium ion a strong acid or a weak acid? Explain your answer.
 7. What are the products of an acid–base reaction? Under what circumstances is one of the products a gas?
 8. Explain how an aqueous solution that is strongly basic can have a pH, which is a measure of the *acidity* of a solution.

ANSWER

5.
 - a. weakly acidic
 - b. strongly acidic
 - c. weakly basic
 - d. strongly basic
 - e. weakly acidic
 - f. weakly basic
 - g. weakly acidic
 - h. strongly basic

NUMERICAL PROBLEMS

Please be sure you are familiar with the topics discussed in Essential Skills 3 (Section 4.1 "Aqueous Solutions") before proceeding to the Numerical Problems.

1. Derive an equation to relate the hydrogen ion concentration to the molarity of a solution of a strong monoprotic acid.

2. Derive an equation to relate the hydroxide ion concentration to the molarity of a solution of
 - a. a group I hydroxide.
 - b. a group II hydroxide.
3. Given the following salts, identify the acid and the base in the neutralization reactions and then write the complete ionic equation:
 - a. barium sulfate
 - b. lithium nitrate
 - c. sodium bromide
 - d. calcium perchlorate
4. What is the pH of each solution?
 - a. 5.8×10^{-3} mol of HNO_3 in 257 mL of water
 - b. 0.0079 mol of HI in 750 mL of water
 - c. 0.011 mol of HClO_4 in 500 mL of water
 - d. 0.257 mol of HBr in 5.00 L of water
5. What is the hydrogen ion concentration of each substance in the indicated pH range?
 - a. black coffee (pH 5.10)
 - b. milk (pH 6.30–7.60)
 - c. tomatoes (pH 4.00–4.40)
6. What is the hydrogen ion concentration of each substance in the indicated pH range?
 - a. orange juice (pH 3–4)
 - b. fresh egg white (pH 7.60–7.80)
 - c. lemon juice (pH 2.20–2.40)
7. What is the pH of a solution prepared by diluting 25.00 mL of 0.879 M HCl to a volume of 555 mL?
8. Vinegar is primarily an aqueous solution of acetic acid. Commercial vinegar typically contains 5.0 g of acetic acid in 95.0 g of water. What is the concentration of commercial vinegar? If only 3.1% of the acetic acid dissociates to CH_3CO_2^- and H^+ , what is the pH of the solution? (Assume the density of the solution is 1.00 g/mL.)
9. If a typical household cleanser is 0.50 M in strong base, what volume of 0.998 M strong monoprotic acid is needed to neutralize 50.0 mL of the cleanser?

10. A 25.00 mL sample of a 0.9005 M solution of HCl is diluted to 500.0 mL. What is the molarity of the final solution? How many milliliters of 0.223 M NaOH are needed to neutralize 25.00 mL of this final solution?
11. If 20.0 mL of 0.10 M NaOH are needed to neutralize 15.0 mL of gastric fluid, what is the molarity of HCl in the fluid? (Assume all the acidity is due to the presence of HCl.) What other base might be used instead of NaOH?
12. Malonic acid ($\text{C}_3\text{H}_4\text{O}_4$) is a diprotic acid used in the manufacture of barbiturates. How many grams of malonic acid are in a 25.00 mL sample that requires 32.68 mL of 1.124 M KOH for complete neutralization to occur? Malonic acid is a dicarboxylic acid; propose a structure for malonic acid.
13. Describe how you would prepare 500 mL of a 1.00 M stock solution of HCl from an HCl solution that is 12.11 M. Using your stock solution, how would you prepare 500 mL of a solution that is 0.012 M in HCl?
14. Given a stock solution that is 8.52 M in HBr, describe how you would prepare a 500 mL solution with each concentration.
- 2.50 M
 - 4.00×10^{-3} M
 - 0.989 M
15. How many moles of solute are contained in each?
- 25.00 mL of 1.86 M NaOH
 - 50.00 mL of 0.0898 M HCl
 - 13.89 mL of 0.102 M HBr
16. A chemist needed a solution that was approximately 0.5 M in HCl but could measure only 10.00 mL samples into a 50.00 mL volumetric flask. Propose a method for preparing the solution. (Assume that concentrated HCl is 12.0 M.)
17. Write the balanced chemical equation for each reaction.
- perchloric acid with potassium hydroxide
 - nitric acid with calcium hydroxide
18. Write the balanced chemical equation for each reaction.
- solid strontium hydroxide with hydrobromic acid
 - aqueous sulfuric acid with solid sodium hydroxide

19. A neutralization reaction gives calcium nitrate as one of the two products. Identify the acid and the base in this reaction. What is the second product? If the product had been cesium iodide, what would have been the acid and the base? What is the complete ionic equation for each reaction?

ANSWERS

1. $[\text{H}_3\text{O}^+] = [\text{HA}] \text{ M}$
- 2.
3.
 - a. H_2SO_4 and $\text{Ba}(\text{OH})_2$; $2\text{H}^+ + \text{SO}_4^{2-} + \text{Ba}^{2+} + 2\text{OH}^- \rightarrow 2\text{H}_2\text{O} + \text{Ba}^{2+} + \text{SO}_4^{2-}$
 - b. HNO_3 and LiOH ; $\text{H}^+ + \text{NO}_3^- + \text{Li}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{Li}^+ + \text{NO}_3^-$
 - c. HBr and NaOH ; $\text{H}^+ + \text{Br}^- + \text{Na}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{Na}^+ + \text{Br}^-$
 - d. HClO_4 and $\text{Ca}(\text{OH})_2$; $2\text{H}^+ + 2\text{ClO}_4^- + \text{Ca}^{2+} + 2\text{OH}^- \rightarrow 2\text{H}_2\text{O} + \text{Ca}^{2+} + 2\text{ClO}_4^-$
- 4.
5.
 - a. $7.9 \times 10^{-6} \text{ M H}^+$
 - b. 5.0×10^{-7} to $2.5 \times 10^{-8} \text{ M H}^+$
 - c. 1.0×10^{-4} to $4.0 \times 10^{-5} \text{ M H}^+$
- 6.
7. $\text{pH} = 1.402$
- 8.
9. 25 mL
- 10.
11. 0.13 M HCl; magnesium carbonate, MgCO_3 , or aluminum hydroxide, $\text{Al}(\text{OH})_3$
- 12.
13. 1.00 M solution: dilute 41.20 mL of the concentrated solution to a final volume of 500 mL. 0.012 M solution: dilute 12.0 mL of the 1.00 M stock solution to a final volume of 500 mL.
- 14.
15.
 - a. $4.65 \times 10^{-2} \text{ mol NaOH}$
 - b. $4.49 \times 10^{-3} \text{ mol HCl}$

c. 1.42×10^{-3} mol HBr

16.

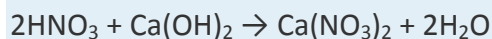
17.

a. $\text{HClO}_4 + \text{KOH} \rightarrow \text{KClO}_4 + \text{H}_2\text{O}$

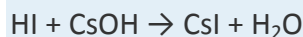
b. $2\text{HNO}_3 + \text{Ca}(\text{OH})_2 \rightarrow \text{Ca}(\text{NO}_3)_2 + 2\text{H}_2\text{O}$

18.

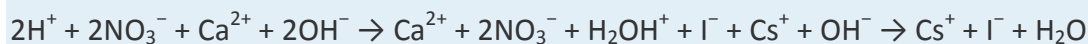
19. The acid is nitric acid, and the base is calcium hydroxide. The other product is water.



The acid is hydroiodic acid, and the base is cesium hydroxide. The other product is water.



The complete ionic equations are



[1] pH is actually defined as the negative base-10 logarithm of hydrogen ion *activity*. As you will learn in a more advanced course, the activity of a substance in solution is related to its concentration. For dilute solutions such as those we are discussing, the activity and the concentration are approximately the same.

4.7 The Chemistry of Acid Rain

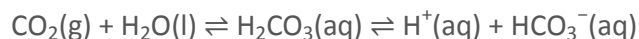
LEARNING OBJECTIVE

1. To understand the chemistry of acid rain.

Acid–base reactions can have a strong environmental impact. For example, a dramatic increase in the acidity of rain and snow over the past 150 years is dissolving marble and limestone surfaces, accelerating the corrosion of metal objects, and decreasing the pH of natural waters. This environmental problem is called acid rain and has significant consequences for all living organisms. To understand acid rain requires an understanding of acid–base reactions in aqueous solution.

The term *acid rain* is actually somewhat misleading because even pure rainwater collected in areas remote from civilization is slightly acidic ($\text{pH} \approx 5.6$) due to dissolved carbon dioxide, which reacts with water to give carbonic acid, a weak acid:

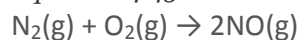
Equation 4.44



The English chemist Robert Angus Smith is generally credited with coining the phrase *acid rain* in 1872 to describe the increased acidity of the rain in British industrial centers (such as Manchester), which was apparently caused by the unbridled excesses of the early Industrial Revolution, although the connection was not yet understood. At that time, there was no good way to measure hydrogen ion concentrations, so it is difficult to know the actual pH of the rain observed by Smith. Typical pH values for rain in the continental United States now range from 4 to 4.5, with values as low as 2.0 reported for areas such as Los Angeles. Recall from Figure 4.15 "A Plot of pH versus [H]" that rain with a pH of 2 is comparable in acidity to lemon juice, and even "normal" rain is now as acidic as tomato juice or black coffee.

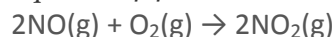
What is the source of the increased acidity in rain and snow? Chemical analysis shows the presence of large quantities of sulfate (SO_4^{2-}) and nitrate (NO_3^-) ions, and a wide variety of evidence indicates that a significant fraction of these species come from nitrogen and sulfur oxides produced during the combustion of fossil fuels. At the high temperatures found in both internal combustion engines and lightning discharges, molecular nitrogen and molecular oxygen react to give nitric oxide:

Equation 4.45



Nitric oxide then reacts rapidly with excess oxygen to give nitrogen dioxide, the compound responsible for the brown color of smog:

Equation 4.46



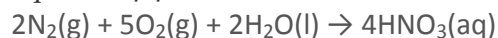
When nitrogen dioxide dissolves in water, it forms a 1:1 mixture of nitrous acid and nitric acid:

Equation 4.47



Because molecular oxygen eventually oxidizes nitrous acid to nitric acid, the overall reaction is

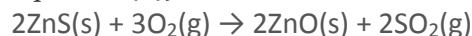
Equation 4.48



Large amounts of sulfur dioxide have always been released into the atmosphere by natural sources, such as volcanoes, forest fires, and the microbial decay of organic materials, but for most of Earth's recorded history the natural cycling of sulfur from the atmosphere into oceans and rocks kept the acidity of rain and snow in check. Unfortunately, the burning of fossil fuels seems to have tipped the balance. Many coals contain as much as 5%–6% pyrite (FeS_2) by mass, and fuel oils typically contain at least 0.5% sulfur by mass. Since the mid-19th century, these fuels have been burned

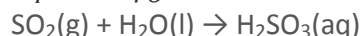
on a huge scale to supply the energy needs of our modern industrial society, releasing tens of millions of tons of additional SO_2 into the atmosphere annually. In addition, roasting sulfide ores to obtain metals such as zinc and copper produces large amounts of SO_2 via reactions such as

Equation 4.49

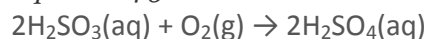


Regardless of the source, the SO_2 dissolves in rainwater to give sulfurous acid (Equation 4.50), which is eventually oxidized by oxygen to sulfuric acid (Equation 4.51):

Equation 4.50

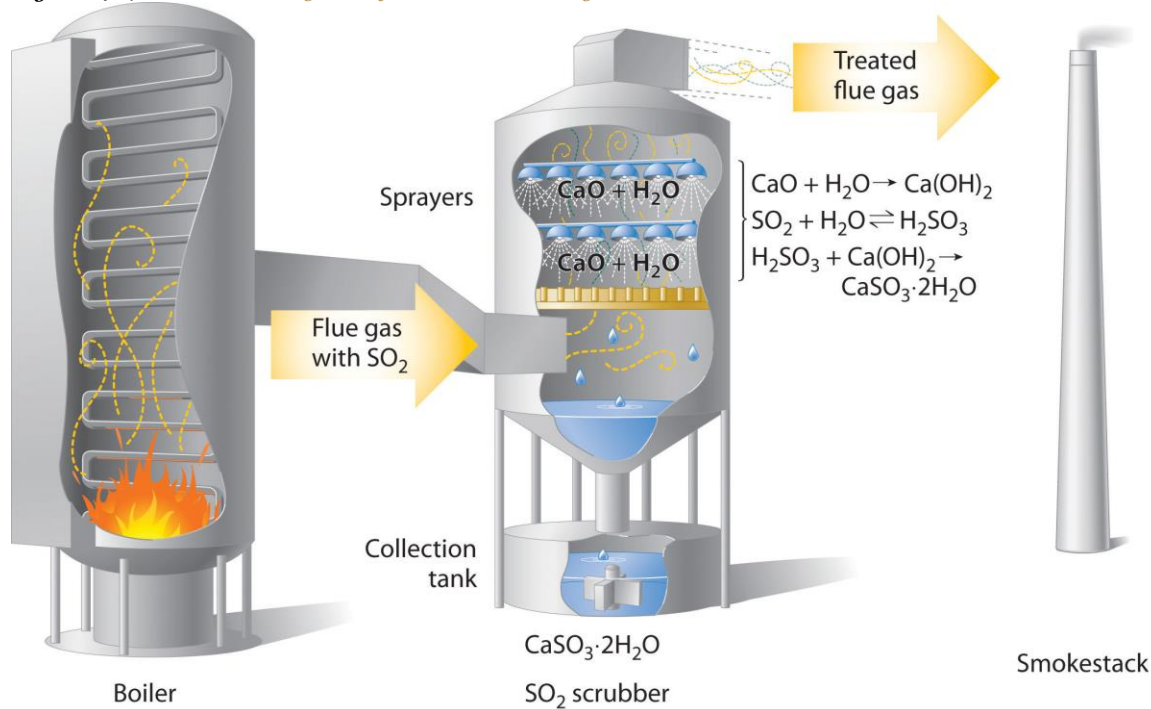


Equation 4.51



Concerns about the harmful effects of acid rain have led to strong pressure on industry to minimize the release of SO_2 and NO . For example, coal-burning power plants now use SO_2 “scrubbers,” which trap SO_2 by its reaction with lime (CaO) to produce calcium sulfite dihydrate ($\text{CaSO}_3 \cdot 2\text{H}_2\text{O}$; Figure 4.17 "Schematic Diagram of a Wet Scrubber System").

Figure 4.17 Schematic Diagram of a Wet Scrubber System



In coal-burning power plants, SO_2 can be removed (“scrubbed”) from exhaust gases by its reaction with a lime (CaO) and water spray to produce calcium sulfite dihydrate ($\text{CaSO}_3 \cdot 2\text{H}_2\text{O}$). Removing SO_2 from the gases prevents

its conversion to SO₃ and subsequent reaction with rainwater (acid rain). Scrubbing systems are now commonly used to minimize the environmental effects of large-scale fossil fuel combustion.

The damage that acid rain does to limestone and marble buildings and sculptures is due to a classic acid–base reaction. Marble and limestone both consist of calcium carbonate (CaCO₃), a salt derived from the weak acid H₂CO₃. As we saw in Section 4.6 "Acid–Base Reactions", the reaction of a strong acid with a salt of a weak acid goes to completion. Thus we can write the reaction of limestone or marble with dilute sulfuric acid as follows:

Equation 4.52

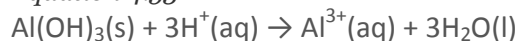


Because CaSO₄ is sparingly soluble in water, the net result of this reaction is to dissolve the marble or limestone. The Lincoln Memorial in Washington, DC, which was built in 1922, already shows significant damage from acid rain, and many older objects are exhibiting even greater damage (Figure 4.18 "Acid Rain Damage to a Statue of George Washington"). Metal objects can also suffer damage from acid rain through oxidation–reduction reactions, which are discussed in Section 4.8 "Oxidation–Reduction Reactions in Solution".

The biological effects of acid rain are more complex. As indicated in Figure 4.15 "A Plot of pH versus [H]", biological fluids, such as blood, have a pH of 7–8. Organisms such as fish can maintain their internal pH in water that has a pH in the range of 6.5–8.5. If the external pH is too low, however, many aquatic organisms can no longer maintain their internal pH, so they die. A pH of 4 or lower is fatal for virtually all fish, most invertebrate animals, and many microorganisms. As a result of acid rain, the pH of some lakes in Europe and the United States has dropped below 4. Recent surveys suggest that up to 6% of the lakes in the Adirondack Mountains of upstate New York and 4% of the lakes in Sweden and Norway are essentially dead and contain no fish. Neither location contains large concentrations of industry, but New York lies downwind of the industrial Midwest, and Scandinavia is downwind of the most industrialized regions of western Europe. Both regions appear to have borne the brunt of the pollution produced by their upwind neighbors. One possible way to counter the effects of acid rain in isolated lakes is by adding large quantities of finely ground limestone, which neutralizes the acid via the reaction shown in Equation 4.52 (see Section 4.1 "Aqueous Solutions"1, Problem 15).

A second major way in which acid rain can cause biological damage is less direct. Trees and many other plants are sensitive to the presence of aluminum and other metals in groundwater. Under normal circumstances, aluminum hydroxide [Al(OH)₃], which is present in some soils, is insoluble. At lower pH values, however, Al(OH)₃ dissolves via the following reaction:

Equation 4.53



The result is increased levels of Al^{3+} ions in groundwater. Because the Al^{3+} ion is toxic to plants, high concentrations can affect plant growth. Acid rain can also weaken the leaves and roots of plants so much that the plants are unable to withstand other stresses. The combination of the two effects can cause significant damage to established forests, such as the Black Forest in Germany and the forests of the northeastern United States and Canada and other countries (Figure 4.19 "Acid Rain Damage to a Forest in the Czech Republic").

Summary

Acid rain is rainfall whose pH is less than 5.6, the value typically observed, due to the presence of dissolved carbon dioxide. Acid rain is caused by nitrogen oxides and sulfur dioxide produced by both natural processes and the combustion of fossil fuels. Eventually, these oxides react with oxygen and water to give nitric acid and sulfuric acid.

KEY TAKEAWAY

- The damaging effects of acid rain have led to strong pressure on industry to minimize the release of harmful reactants.

CONCEPTUAL PROBLEMS

1. Why is it recommended that marble countertops not be used in kitchens? Marble is composed mostly of CaCO_3 .
2. Explain why desulfurization of fossil fuels is an area of intense research.
3. What is the role of NO_x in the formation of acid rain?

4.8 Oxidation–Reduction Reactions in Solution

LEARNING OBJECTIVE

1. To identify oxidation–reduction reactions in solution.

We described the defining characteristics of oxidation–reduction, or redox, reactions in Chapter 3 "Chemical Reactions". Most of the reactions we considered there were relatively simple, and balancing them was straightforward. When oxidation–reduction reactions occur in aqueous solution, however, the equations are more complex and can be more difficult to balance by inspection. Because a balanced chemical equation is the most

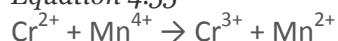
important prerequisite for solving any stoichiometry problem, we need a method for balancing oxidation–reduction reactions in aqueous solution that is generally applicable. One such method uses *oxidation states*, and a second is referred to as the *half-reaction* method. We show you how to balance redox equations using oxidation states in this section; the half-reaction method is described in Chapter 19 "Electrochemistry".

Balancing Redox Equations Using Oxidation States

To balance a redox equation using the oxidation state method, we conceptually separate the overall reaction into two parts: an oxidation—in which the atoms of one element lose electrons—and a reduction—in which the atoms of one element gain electrons. Consider, for example, the reaction of $\text{Cr}^{2+}(\text{aq})$ with manganese dioxide (MnO_2) in the presence of dilute acid. Equation 4.54 is the net ionic equation for this reaction before balancing; the oxidation state of each element in each species has been assigned using the procedure described in Section 3.5 "Classifying Chemical Reactions":

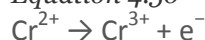
Notice that chromium is oxidized from the +2 to the +3 oxidation state, while manganese is reduced from the +4 to the +2 oxidation state. We can write an equation for this reaction that shows only the atoms that are oxidized and reduced:

Equation 4.55



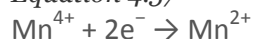
The oxidation can be written as

Equation 4.56



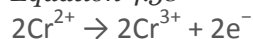
and the reduction as

Equation 4.57



For the overall chemical equation to be balanced, the number of electrons lost by the reductant must equal the number gained by the oxidant. We must therefore multiply the oxidation and the reduction equations by appropriate coefficients to give us the same number of electrons in both. In this example, we must multiply the oxidation equation by 2 to give

Equation 4.58

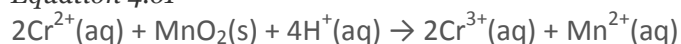


Note the Pattern

In a balanced redox reaction, the number of electrons lost by the reductant equals the number of electrons gained by the oxidant.

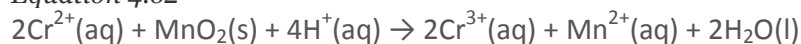
The number of electrons lost in the oxidation now equals the number of electrons gained in the reduction. Although the electrons cancel and the metal atoms are balanced, the total charge on the left side of the equation (+4) does not equal the charge on the right side (+8). Because the reaction is carried out in the presence of aqueous acid, we can add H^+ as necessary to either side of the equation to balance the charge. By the same token, if the reaction were carried out in the presence of aqueous base, we could balance the charge by adding OH^- as necessary to either side of the equation to balance the charges. In this case, adding four H^+ ions to the left side of the equation gives:

Equation 4.61



Although the charges are now balanced, we have two oxygen atoms on the left side of the equation and none on the right. We can balance the oxygen atoms without affecting the overall charge balance by adding H_2O as necessary to either side of the equation. Here, we need to add two H_2O molecules to the right side:

Equation 4.62



Although we did not explicitly balance the hydrogen atoms, we can see by inspection that the overall chemical equation is now balanced. All that remains is to check to make sure that we have not made a mistake. This procedure for balancing reactions is summarized in Table 4.4 "Procedure for Balancing Oxidation–Reduction Reactions by the Oxidation State Method" and illustrated in Example 17.

Table 4.4 Procedure for Balancing Oxidation–Reduction Reactions by the Oxidation State Method

Write the unbalanced chemical equation for the reaction, showing the reactants and the products.

Assign oxidation states to all atoms in the reactants and the products (see Section 3.5 "Classifying Chemical Reactions") and determine which atoms change oxidation state.

Write separate equations for oxidation and reduction, showing (a) the atom(s) that is (are) oxidized and reduced and (b) the number of electrons accepted or donated by each.

Multiply the oxidation and reduction equations by appropriate coefficients so that both contain the same number of electrons.

Write the oxidation and reduction equations showing the actual chemical forms of the reactants and the products, adjusting the coefficients as necessary to give the numbers of atoms in step 4.

Add the two equations and cancel the electrons.

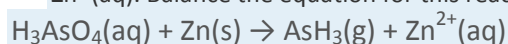
Balance the charge by adding H^+ or OH^- ions as necessary for reactions in acidic or basic solution, respectively.

Balance the oxygen atoms by adding H_2O molecules to one side of the equation.

Check to make sure that the equation is balanced in both atoms and total charges.

EXAMPLE 17

Arsenic acid (H_3AsO_4) is a highly poisonous substance that was once used as a pesticide. The reaction of elemental zinc with arsenic acid in acidic solution yields arsine (AsH_3 , a highly toxic and unstable gas) and $\text{Zn}^{2+}(\text{aq})$. Balance the equation for this reaction using oxidation states:



Given: reactants and products in acidic solution

Asked for: balanced chemical equation using oxidation states

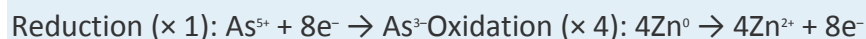
Strategy:

Follow the procedure given in Table 4.4 "Procedure for Balancing Oxidation–Reduction Reactions by the Oxidation State Method" for balancing a redox equation using oxidation states. When you are done, be certain to check that the equation is balanced.

Solution:

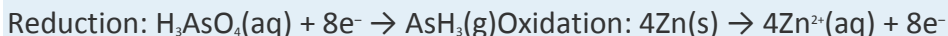
1. **Write a chemical equation showing the reactants and the products.** Because we are given this information, we can skip this step.
2. **Assign oxidation states using the procedure described in Section 3.5 "Classifying Chemical Reactions" and determine which atoms change oxidation state.** The oxidation state of arsenic in arsenic acid is +6, and the oxidation state of arsenic in arsine is –3. Conversely, the oxidation state of zinc in elemental zinc is 0, and the oxidation state of zinc in $\text{Zn}^{2+}(\text{aq})$ is +2.
3. **Write separate equations for oxidation and reduction.** The arsenic atom in H_3AsO_4 is reduced from the +6 to the –3 oxidation state, which requires the addition of eight electrons.
4. Each zinc atom in elemental zinc is oxidized from 0 to +2, which requires the loss of two electrons per zinc atom.

Multiply the oxidation and reduction equations by appropriate coefficients so that both contain the same number of electrons. The reduction equation has eight electrons, and the oxidation equation has two electrons, so we need to multiply the oxidation equation by 4 to obtain



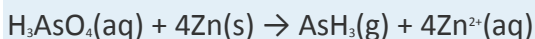
5. **Write the oxidation and reduction equations showing the actual chemical forms of the reactants and the products, adjusting coefficients as necessary to give the numbers of atoms shown in**

step 4. Inserting the actual chemical forms of arsenic and zinc and adjusting the coefficients gives

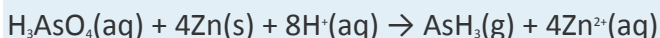


6. *Add the two equations and cancel the electrons.* The sum of the two equations in step 5 is

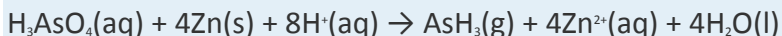
which then yields



7. *Balance the charge by adding H⁺ or OH⁻ ions as necessary for reactions in acidic or basic solution, respectively.* Because the reaction is carried out in acidic solution, we can add H⁺ ions to whichever side of the equation requires them to balance the charge. The overall charge on the left side is zero, and the total charge on the right side is $4 \times (+2) = +8$. Adding eight H⁺ ions to the left side gives a charge of +8 on both sides of the equation:



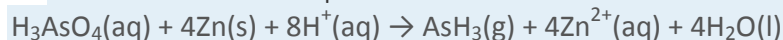
8. *Balance the oxygen atoms by adding H₂O molecules to one side of the equation.* There are 4 O atoms on the left side of the equation. Adding 4 H₂O molecules to the right side balances the O atoms:



Although we have not explicitly balanced H atoms, each side of the equation has 11 H atoms.

9. *Check to make sure that the equation is balanced in both atoms and total charges.* To guard against careless errors, it is important to check that both the total number of atoms of each element and the total charges are the same on both sides of the equation:
Atoms: $1\text{As} + 4\text{Zn} + 4\text{O} + 11\text{H} = 1\text{As} + 4\text{Zn} + 4\text{O} + 11\text{H}$ Total charge: $8(+1) = 4(+2) = +8$

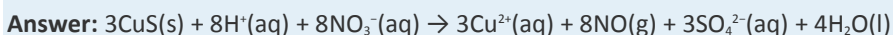
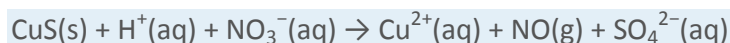
The balanced chemical equation for the reaction is therefore:



Exercise

Copper commonly occurs as the sulfide mineral CuS. The first step in extracting copper from CuS is to dissolve the mineral in nitric acid, which oxidizes the sulfide to sulfate and reduces nitric acid to NO.

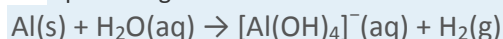
Balance the equation for this reaction using oxidation states:



Reactions in basic solutions are balanced in exactly the same manner. To make sure you understand the procedure, consider Example 18.

EXAMPLE 18

The commercial solid drain cleaner, Drano, contains a mixture of sodium hydroxide and powdered aluminum. The sodium hydroxide dissolves in standing water to form a strongly basic solution, capable of slowly dissolving organic substances, such as hair, that may be clogging the drain. The aluminum dissolves in the strongly basic solution to produce bubbles of hydrogen gas that agitate the solution to help break up the clogs. The reaction is as follows:



Balance this equation using oxidation states.

Given: reactants and products in a basic solution

Asked for: balanced chemical equation

Strategy:

Follow the procedure given in Table 4.4 "Procedure for Balancing Oxidation–Reduction Reactions by the Oxidation State Method" for balancing a redox reaction using oxidation states. When you are done, be certain to check that the equation is balanced.

Solution:

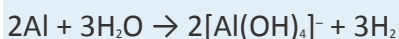
We will apply the same procedure used in Example 17 but in a more abbreviated form.

1. The equation for the reaction is given, so we can skip this step.
2. The oxidation state of aluminum changes from 0 in metallic Al to +3 in $[\text{Al(OH)}_4]^-$. The oxidation state of hydrogen changes from +1 in H_2O to 0 in H_2 . Aluminum is oxidized, while hydrogen is reduced.
3. Multiply the reduction equation by 3 to obtain an equation with the same number of electrons as the oxidation equation:
Reduction: $3\text{H}^+ + 3\text{e}^- \rightarrow 3\text{H}^0$ (in H_2) Oxidation: $\text{Al}^0 \rightarrow \text{Al}^{3+} + 3\text{e}^-$
4. Insert the actual chemical forms of the reactants and products, adjusting the coefficients as necessary to obtain the correct numbers of atoms as in step 4. Because a molecule of H_2O

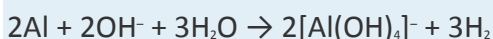
contains two protons, in this case, 3H^+ corresponds to $3/2\text{H}_2\text{O}$. Similarly, each molecule of hydrogen gas contains two H atoms, so 3H corresponds to $3/2\text{H}_2$.

5. Adding the equations and canceling the electrons gives

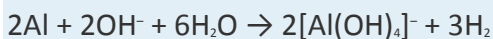
To remove the fractional coefficients, multiply both sides of the equation by 2:



6. The right side of the equation has a total charge of -2 , whereas the left side has a total charge of 0. Because the reaction is carried out in basic solution, we can balance the charge by adding two OH^- ions to the left side:



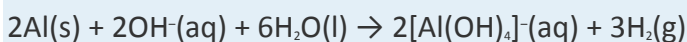
7. The left side of the equation contains five O atoms, and the right side contains eight O atoms. We can balance the O atoms by adding three H_2O molecules to the left side:



8. Be sure the equation is balanced:

Atoms: $2\text{Al} + 8\text{O} + 14\text{H} = 2\text{Al} + 8\text{O} + 14\text{H}$
Total charge: $(2)(0) + (2)(-1) + (6)(0) = (2)(-1) + (3)(0) - 2 = -2$

The balanced chemical equation is therefore



Thus 3 mol of H_2 gas are produced for every 2 mol of Al.

Exercise

The permanganate ion reacts with nitrite ion in basic solution to produce manganese(IV) oxide and nitrate ion. Write a balanced chemical equation for the reaction.

Answer: $2\text{MnO}_4^-(\text{aq}) + 3\text{NO}_2^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2\text{MnO}_2(\text{s}) + 3\text{NO}_3^-(\text{aq}) + 2\text{OH}^-(\text{aq})$

As suggested in Example 17 and Example 18, a wide variety of redox reactions are possible in aqueous solutions. The identity of the products obtained from a given set of reactants often depends on both the ratio of oxidant to reductant and whether the reaction is carried out in acidic or basic solution, which is one reason it can be difficult to predict the outcome of a reaction. Because oxidation–reduction reactions

in solution are so common and so important, however, chemists have developed two general guidelines for predicting whether a redox reaction will occur and the identity of the products:

1. Compounds of elements in high oxidation states (such as ClO_4^- , NO_3^- , MnO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, and UF_6) tend to act as *oxidants* and *become reduced* in chemical reactions.
2. Compounds of elements in low oxidation states (such as CH_4 , NH_3 , H_2S , and HI) tend to act as *reductants* and *become oxidized* in chemical reactions.

Note the Pattern

Species in high oxidation states act as oxidants, whereas species in low oxidation states act as reductants.

When an aqueous solution of a compound that contains an element in a high oxidation state is mixed with an aqueous solution of a compound that contains an element in a low oxidation state, an oxidation–reduction reaction is likely to occur.

Redox Reactions of Solid Metals in Aqueous Solution

A widely encountered class of oxidation–reduction reactions is the reaction of aqueous solutions of acids or metal salts with solid metals. An example is the corrosion of metal objects, such as the rusting of an automobile (Figure 4.20 "Rust Formation"). Rust is formed from a complex oxidation–reduction reaction involving dilute acid solutions that contain Cl^- ions (effectively, dilute HCl), iron metal, and oxygen. When an object rusts, iron metal reacts with $\text{HCl}(\text{aq})$ to produce iron(II) chloride and hydrogen gas:

Equation 4.63



In subsequent steps, FeCl_2 undergoes oxidation to form a reddish-brown precipitate of $\text{Fe}(\text{OH})_3$.

Many metals dissolve through reactions of this type, which have the general form

Equation 4.64



Some of these reactions have important consequences. For example, it has been proposed that one factor that contributed to the fall of the Roman Empire was the widespread use of lead in cooking utensils and pipes that carried water. Rainwater, as we have seen, is slightly acidic, and foods such as fruits, wine, and vinegar contain organic acids.

In the presence of these acids, lead dissolves:

Equation 4.65

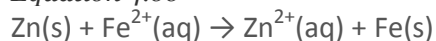


Consequently, it has been speculated that both the water and the food consumed by Romans contained toxic levels of lead, which resulted in widespread lead poisoning and eventual madness. Perhaps this explains why the Roman Emperor Caligula appointed his favorite horse as consul!

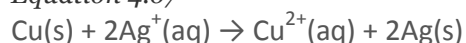
Single-Displacement Reactions

Certain metals are oxidized by aqueous acid, whereas others are oxidized by aqueous solutions of various metal salts. Both types of reactions are called single-displacement reactions, in which the ion in solution is displaced through oxidation of the metal. Two examples of single-displacement reactions are the reduction of iron salts by zinc (Equation 4.66) and the reduction of silver salts by copper (Equation 4.67 and Figure 4.21 "The Single-Displacement Reaction of Metallic Copper with a Solution of Silver Nitrate"):

Equation 4.66

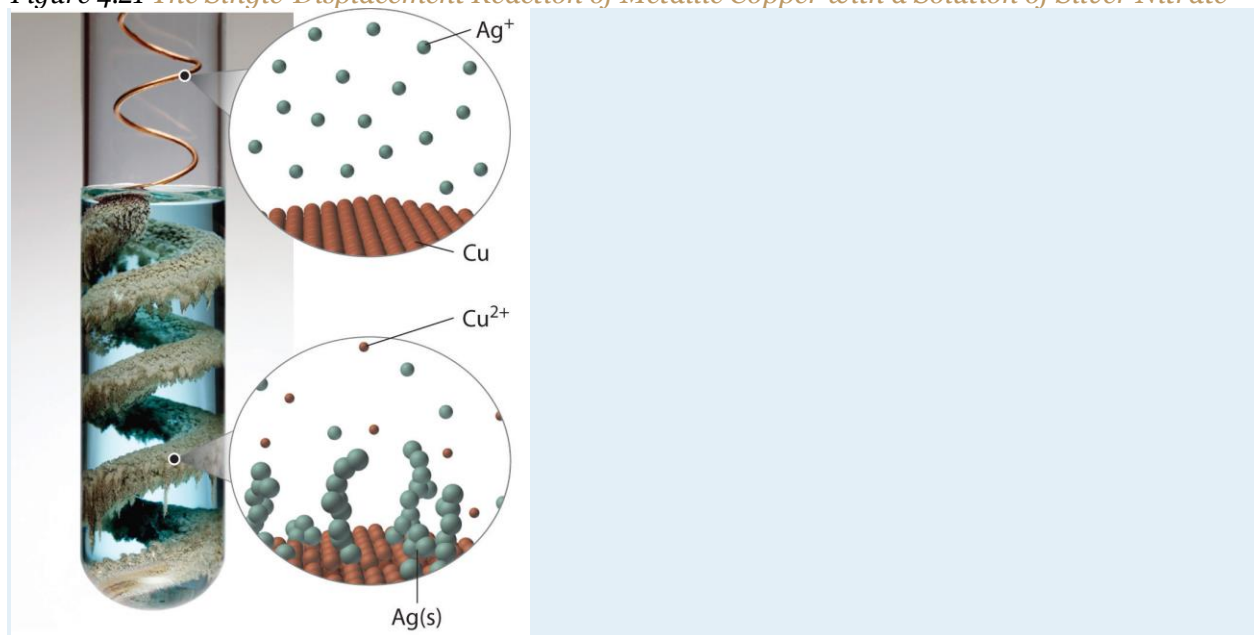


Equation 4.67



The reaction in Equation 4.66 is widely used to prevent (or at least postpone) the corrosion of iron or steel objects, such as nails and sheet metal. The process of “galvanizing” consists of applying a thin coating of zinc to the iron or steel, thus protecting it from oxidation as long as zinc remains on the object.

Figure 4.21 *The Single-Displacement Reaction of Metallic Copper with a Solution of Silver Nitrate*

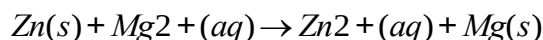


When a copper coil is placed in a solution of silver nitrate, silver ions are reduced to metallic silver on the copper surface, and some of the copper metal dissolves. Note the formation of a metallic silver precipitate on the copper coil and a blue color in the surrounding solution due to the presence of aqueous Cu^{2+} ions. (Water molecules and nitrate ions have been omitted from molecular views of the solution for clarity.)

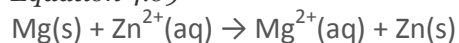
The Activity Series

By observing what happens when samples of various metals are placed in contact with solutions of other metals, chemists have arranged the metals according to the relative ease or difficulty with which they can be oxidized in a single-displacement reaction. For example, we saw in Equation 4.66 and Equation 4.67 that metallic zinc reacts with iron salts, and metallic copper reacts with silver salts. Experimentally, it is found that zinc reacts with both copper salts and silver salts, producing Zn^{2+} . Zinc therefore has a greater tendency to be oxidized than does iron, copper, or silver. Although zinc will not react with magnesium salts to give magnesium metal, magnesium metal will react with zinc salts to give zinc metal:

Equation 4.68



Equation 4.69



Magnesium has a greater tendency to be oxidized than zinc does.

Pairwise reactions of this sort are the basis of the activity series (Figure 4.22 "The Activity Series"), which lists metals and hydrogen in order of their relative tendency to be oxidized. The metals at the top of the series, which have the greatest tendency to lose electrons, are the alkali metals (group 1), the alkaline earth metals (group 2), and Al (group 13). In contrast, the metals at the bottom of the series, which have the lowest tendency to be oxidized, are the precious metals or coinage metals—platinum, gold, silver, and copper, and mercury, which are located in the lower right portion of the metals in the periodic table. You should be generally familiar with which kinds of metals are active metals (located at the top of the series) and which are inert metals (at the bottom of the series).

Figure 4.22 The Activity Series

	Element	Oxidation Reaction	
React vigorously with cold H₂O to form H₂ React with steam to form H₂ React with simple acids to form H₂ Will not dissolve in simple acids	Lithium	$\text{Li} \rightarrow \text{Li}^+ + \text{e}^-$	Increasing ease of oxidation
	Potassium	$\text{K} \rightarrow \text{K}^+ + \text{e}^-$	
	Barium	$\text{Ba} \rightarrow \text{Ba}^{2+} + 2\text{e}^-$	
	Calcium	$\text{Ca} \rightarrow \text{Ca}^{2+} + 2\text{e}^-$	
	Sodium	$\text{Na} \rightarrow \text{Na}^+ + \text{e}^-$	
	Magnesium	$\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^-$	
	Aluminum	$\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^-$	
	Manganese	$\text{Mn} \rightarrow \text{Mn}^{2+} + 2\text{e}^-$	
	Zinc	$\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$	
	Chromium	$\text{Cr} \rightarrow \text{Cr}^{3+} + 3\text{e}^-$	
	Iron	$\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$	
	Cadmium	$\text{Cd} \rightarrow \text{Cd}^{2+} + 2\text{e}^-$	
	Cobalt	$\text{Co} \rightarrow \text{Co}^{2+} + 2\text{e}^-$	
	Nickel	$\text{Ni} \rightarrow \text{Ni}^{2+} + 2\text{e}^-$	
	Tin	$\text{Sn} \rightarrow \text{Sn}^{2+} + 2\text{e}^-$	
	Lead	$\text{Pb} \rightarrow \text{Pb}^{2+} + 2\text{e}^-$	
	Hydrogen	$\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$	
	Copper	$\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$	
	Silver	$\text{Ag} \rightarrow \text{Ag}^+ + \text{e}^-$	
	Mercury	$\text{Hg} \rightarrow \text{Hg}^{2+} + 2\text{e}^-$	
	Platinum	$\text{Pt} \rightarrow \text{Pt}^{2+} + 2\text{e}^-$	
	Gold	$\text{Au} \rightarrow \text{Au}^+ + \text{e}^-$	

When using the activity series to predict the outcome of a reaction, keep in mind that *any element will reduce compounds of the elements below it in the series*. Because magnesium is above zinc in Figure 4.22 "The Activity Series", magnesium metal will reduce zinc salts but not vice versa. Similarly, the precious metals are at the bottom of the activity series, so virtually any other metal will reduce precious metal salts to the pure precious metals. Hydrogen is included in the series, and the tendency of a metal to react with an acid is indicated by its position relative to hydrogen in the activity series. *Only those metals that lie above hydrogen in the activity series dissolve in acids to produce H₂*. Because the precious metals lie below hydrogen, they do not dissolve in dilute acid and therefore do not corrode readily. Example 19 demonstrates how a familiarity with the activity series allows you to predict the products of many single-displacement reactions. We will return to the activity series when we discuss oxidation–reduction reactions in more detail in Chapter 19 "Electrochemistry".

EXAMPLE 19

Using the activity series, predict what happens in each situation. If a reaction occurs, write the net ionic equation.

- A strip of aluminum foil is placed in an aqueous solution of silver nitrate.
- A few drops of liquid mercury are added to an aqueous solution of lead(II) acetate.
- Some sulfuric acid from a car battery is accidentally spilled on the lead cable terminals.

Given: reactants

Asked for: overall reaction and net ionic equation

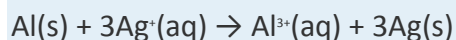
Strategy:

A Locate the reactants in the activity series in Figure 4.22 "The Activity Series" and from their relative positions, predict whether a reaction will occur. If a reaction does occur, identify which metal is oxidized and which is reduced.

B Write the net ionic equation for the redox reaction.

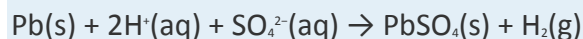
Solution:

- A** Aluminum is an active metal that lies above silver in the activity series, so we expect a reaction to occur. According to their relative positions, aluminum will be oxidized and dissolve, and silver ions will be reduced to silver metal. **B** The net ionic equation is as follows:



Recall from our discussion of solubilities that most nitrate salts are soluble. In this case, the nitrate ions are spectator ions and are not involved in the reaction.

- A** Mercury lies below lead in the activity series, so no reaction will occur.
- A** Lead is above hydrogen in the activity series, so the lead terminals will be oxidized, and the acid will be reduced to form H_2 . **B** From our discussion of solubilities, recall that Pb^{2+} and SO_4^{2-} form insoluble lead(II) sulfate. In this case, the sulfate ions are *not* spectator ions, and the reaction is as follows:



Lead(II) sulfate is the white solid that forms on corroded battery terminals.

Exercise

Using the activity series, predict what happens in each situation. If a reaction occurs, write the net ionic equation.

- A strip of chromium metal is placed in an aqueous solution of aluminum chloride.

- b. A strip of zinc is placed in an aqueous solution of chromium(III) nitrate.
- c. A piece of aluminum foil is dropped into a glass that contains vinegar (the active ingredient is acetic acid).

Answer:

- a. no reaction
- b. $3\text{Zn(s)} + 2\text{Cr}^{3+}(\text{aq}) \rightarrow 3\text{Zn}^{2+}(\text{aq}) + 2\text{Cr(s)}$
- c. $2\text{Al(s)} + 6\text{CH}_3\text{CO}_2\text{H(aq)} \rightarrow 2\text{Al}^{3+}(\text{aq}) + 6\text{CH}_3\text{CO}_2^{-}(\text{aq}) + 3\text{H}_2(\text{g})$

Summary

In oxidation–reduction reactions, electrons are transferred from one substance or atom to another. We can balance oxidation–reduction reactions in solution using the **oxidation state method** (Table 4.4 "Procedure for Balancing Oxidation–Reduction Reactions by the Oxidation State Method"), in which the overall reaction is separated into an oxidation equation and a reduction equation. **Single-displacement reactions** are reactions of metals with either acids or another metal salt that result in dissolution of the first metal and precipitation of a second (or evolution of hydrogen gas). The outcome of these reactions can be predicted using the **activity series** (Figure 4.22 "The Activity Series"), which arranges metals and H_2 in decreasing order of their tendency to be oxidized. Any metal will reduce metal ions below it in the activity series. **Active metals** lie at the top of the activity series, whereas **inert metals** are at the bottom of the activity series.

KEY TAKEAWAY

- Oxidation–reduction reactions are balanced by separating the overall chemical equation into an oxidation equation and a reduction equation.

CONCEPTUAL PROBLEMS

1. Which elements in the periodic table tend to be good oxidants? Which tend to be good reductants?
2. If two compounds are mixed, one containing an element that is a poor oxidant and one with an element that is a poor reductant, do you expect a redox reaction to occur? Explain your answer. What do you predict if one is a strong oxidant and the other is a weak reductant? Why?
3. In each redox reaction, determine which species is oxidized and which is reduced:
 - a. $\text{Zn(s)} + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{ZnSO}_4(\text{aq}) + \text{H}_2(\text{g})$
 - b. $\text{Cu(s)} + 4\text{HNO}_3(\text{aq}) \rightarrow \text{Cu}(\text{NO}_3)_2(\text{aq}) + 2\text{NO}_2(\text{g}) + 2\text{H}_2\text{O(l)}$

- c. $\text{BrO}_3^-(\text{aq}) + 2\text{MnO}_2(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Br}^-(\text{aq}) + 2\text{MnO}_4^-(\text{aq}) + 2\text{H}^+(\text{aq})$
4. Single-displacement reactions are a subset of redox reactions. In this subset, what is oxidized and what is reduced? Give an example of a redox reaction that is *not* a single-displacement reaction.
5. Of the following elements, which would you expect to have the greatest tendency to be oxidized: Zn, Li, or S? Explain your reasoning.
6. Of these elements, which would you expect to be easiest to reduce: Se, Sr, or Ni? Explain your reasoning.
7. Which of these metals produces H_2 in acidic solution?
- Ag
 - Cd
 - Ca
 - Cu
8. Using the activity series, predict what happens in each situation. If a reaction occurs, write the net ionic equation.
- $\text{Mg}(\text{s}) + \text{Cu}^{2+}(\text{aq}) \rightarrow$
 - $\text{Au}(\text{s}) + \text{Ag}^+(\text{aq}) \rightarrow$
 - $\text{Cr}(\text{s}) + \text{Pb}^{2+}(\text{aq}) \rightarrow$
 - $\text{K}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow$
 - $\text{Hg}(\text{l}) + \text{Pb}^{2+}(\text{aq}) \rightarrow$

NUMERICAL PROBLEMS

- Balance each redox reaction under the conditions indicated.
 - $\text{CuS}(\text{s}) + \text{NO}_3^-(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) + \text{NO}(\text{g})$; acidic solution
 - $\text{Ag}(\text{s}) + \text{HS}^-(\text{aq}) + \text{CrO}_4^{2-}(\text{aq}) \rightarrow \text{Ag}_2\text{S}(\text{s}) + \text{Cr}(\text{OH})_3(\text{s})$; basic solution
 - $\text{Zn}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{H}_2(\text{g})$; acidic solution
 - $\text{O}_2(\text{g}) + \text{Sb}(\text{s}) \rightarrow \text{H}_2\text{O}_2(\text{aq}) + \text{SbO}_2^-(\text{aq})$; basic solution
 - $\text{UO}_2^{2+}(\text{aq}) + \text{Te}(\text{s}) \rightarrow \text{U}^{4+}(\text{aq}) + \text{TeO}_4^{2-}(\text{aq})$; acidic solution
- Balance each redox reaction under the conditions indicated.
 - $\text{MnO}_4^-(\text{aq}) + \text{S}_2\text{O}_3^{2-}(\text{aq}) \rightarrow \text{Mn}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$; acidic solution
 - $\text{Fe}^{2+}(\text{aq}) + \text{Cr}_2\text{O}_7^{2-}(\text{aq}) \rightarrow \text{Fe}^{3+}(\text{aq}) + \text{Cr}^{3+}(\text{aq})$; acidic solution
 - $\text{Fe}(\text{s}) + \text{CrO}_4^{2-}(\text{aq}) \rightarrow \text{Fe}_2\text{O}_3(\text{s}) + \text{Cr}_2\text{O}_3(\text{s})$; basic solution

- d. $\text{Cl}_2(\text{aq}) \rightarrow \text{ClO}_3^-(\text{aq}) + \text{Cl}^-(\text{aq})$; acidic solution
 - e. $\text{CO}_3^{2-}(\text{aq}) + \text{N}_2\text{H}_4(\text{aq}) \rightarrow \text{CO}(\text{g}) + \text{N}_2(\text{g})$; basic solution
3. Using the activity series, predict what happens in each situation. If a reaction occurs, write the net ionic equation; then write the complete ionic equation for the reaction.
 - a. Platinum wire is dipped in hydrochloric acid.
 - b. Manganese metal is added to a solution of iron(II) chloride.
 - c. Tin is heated with steam.
 - d. Hydrogen gas is bubbled through a solution of lead(II) nitrate.
 4. Using the activity series, predict what happens in each situation. If a reaction occurs, write the net ionic equation; then write the complete ionic equation for the reaction.
 - a. A few drops of NiBr_2 are dropped onto a piece of iron.
 - b. A strip of zinc is placed into a solution of HCl .
 - c. Copper is dipped into a solution of ZnCl_2 .
 - d. A solution of silver nitrate is dropped onto an aluminum plate.
 5. Dentists occasionally use metallic mixtures called *amalgams* for fillings. If an amalgam contains zinc, however, water can contaminate the amalgam as it is being manipulated, producing hydrogen gas under basic conditions. As the filling hardens, the gas can be released, causing pain and cracking the tooth. Write a balanced chemical equation for this reaction.
 6. Copper metal readily dissolves in dilute aqueous nitric acid to form blue $\text{Cu}^{2+}(\text{aq})$ and nitric oxide gas.
 - a. What has been oxidized? What has been reduced?
 - b. Balance the chemical equation.
 7. Classify each reaction as an acid–base reaction, a precipitation reaction, or a redox reaction, or state if there is no reaction; then complete and balance the chemical equation:
 - a. $\text{Pt}^{2+}(\text{aq}) + \text{Ag}(\text{s}) \rightarrow$
 - b. $\text{HCN}(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow$
 - c. $\text{Fe}(\text{NO}_3)_3(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow$
 - d. $\text{CH}_4(\text{g}) + \text{O}_2(\text{g}) \rightarrow$
 8. Classify each reaction as an acid–base reaction, a precipitation reaction, or a redox reaction, or state if there is no reaction; then complete and balance the chemical equation:

- a. $\text{Zn(s)} + \text{HCl(aq)} \rightarrow$
- b. $\text{HNO}_3\text{(aq)} + \text{AlCl}_3\text{(aq)} \rightarrow$
- c. $\text{K}_2\text{CrO}_4\text{(aq)} + \text{Ba(NO}_3)_2\text{(aq)} \rightarrow$
- d. $\text{Zn(s)} + \text{Ni}^{2+}\text{(aq)} \rightarrow \text{Zn}^{2+}\text{(aq)} + \text{Ni(s)}$

4.9 Quantitative Analysis Using Titrations

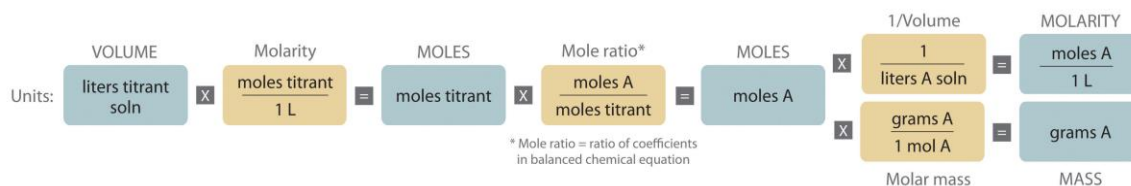
LEARNING OBJECTIVE

1. To use titration methods to analyze solutions quantitatively.

To determine the amounts or concentrations of substances present in a sample, chemists use a combination of chemical reactions and stoichiometric calculations in a methodology called quantitative analysis. Suppose, for example, we know the identity of a certain compound in a solution but not its concentration. If the compound reacts rapidly and completely with another reactant, we may be able to use the reaction to determine the concentration of the compound of interest. In a titration, a carefully measured volume of a solution of known concentration, called the titrant, is added to a measured volume of a solution containing a compound whose concentration is to be determined (the *unknown*). The reaction used in a titration can be an acid–base reaction, a precipitation reaction, or an oxidation–reduction reaction. In all cases, the reaction chosen for the analysis must be fast, complete, and *specific*; that is, *only* the compound of interest should react with the titrant. The equivalence point is reached when a stoichiometric amount of the titrant has been added—the amount required to react completely with the unknown.

Determining the Concentration of an Unknown Solution Using a Titration

The chemical nature of the species present in the unknown dictates which type of reaction is most appropriate and also how to determine the equivalence point. The volume of titrant added, its concentration, and the coefficients from the balanced chemical equation for the reaction allow us to calculate the total number of moles of the unknown in the original solution. Because we have measured the volume of the solution that contains the unknown, we can calculate the molarity of the unknown substance. This procedure is summarized graphically here:



EXAMPLE 20

The calcium salt of oxalic acid [$\text{Ca}(\text{O}_2\text{CCO}_2)$] is found in the sap and leaves of some vegetables, including spinach and rhubarb, and in many ornamental plants. Because oxalic acid and its salts are toxic, when a food such as rhubarb is processed commercially, the leaves must be removed, and the oxalate content carefully monitored.

The reaction of MnO_4^- with oxalic acid ($\text{HO}_2\text{CCO}_2\text{H}$) in acidic aqueous solution produces Mn^{2+} and CO_2

Because this reaction is rapid and goes to completion, potassium permanganate (KMnO_4) is widely used as a reactant for determining the concentration of oxalic acid.

Suppose you stirred a 10.0 g sample of canned rhubarb with enough dilute $\text{H}_2\text{SO}_4(\text{aq})$ to obtain 127 mL of colorless solution. Because the added permanganate is rapidly consumed, adding small volumes of a 0.0247 M KMnO_4 solution, which has a deep purple color, to the rhubarb extract does not initially change the color of the extract. When 15.4 mL of the permanganate solution have been added, however, the solution becomes a faint purple due to the presence of a slight excess of permanganate (Figure 4.23 "The Titration of Oxalic Acid with Permanganate"). If we assume that oxalic acid is the only species in solution that reacts with permanganate, what percentage of the mass of the original sample was calcium oxalate?

Given: equation, mass of sample, volume of solution, and molarity and volume of titrant

Asked for: mass percentage of unknown in sample

Strategy:

A Balance the chemical equation for the reaction using oxidation states.

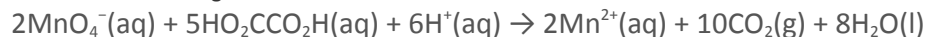
B Calculate the number of moles of permanganate consumed by multiplying the volume of the titrant by its molarity.

Then calculate the number of moles of oxalate in the solution by multiplying by the ratio of the coefficients in the balanced chemical equation. Because calcium oxalate contains a 1:1 ratio of $\text{Ca}^{2+}:\text{O}_2\text{CCO}_2^-$, the number of moles of oxalate in the solution is the same as the number of moles of calcium oxalate in the original sample.

C Find the mass of calcium oxalate by multiplying the number of moles of calcium oxalate in the sample by its molar mass. Divide the mass of calcium oxalate by the mass of the sample and convert to a percentage to calculate the percentage by mass of calcium oxalate in the original sample.

Solution:

A As in all other problems of this type, the first requirement is a balanced chemical equation for the reaction. Using oxidation states gives



Thus each mole of MnO_4^- added consumes 2.5 mol of oxalic acid.

B Because we know the concentration of permanganate (0.0247 M) and the volume of permanganate solution that was needed to consume all the oxalic acid (15.4 mL), we can calculate the number of moles of MnO_4^- consumed. The number of moles of oxalic acid, and thus oxalate, present can be calculated from the mole ratio of the reactants in the balanced chemical equation.

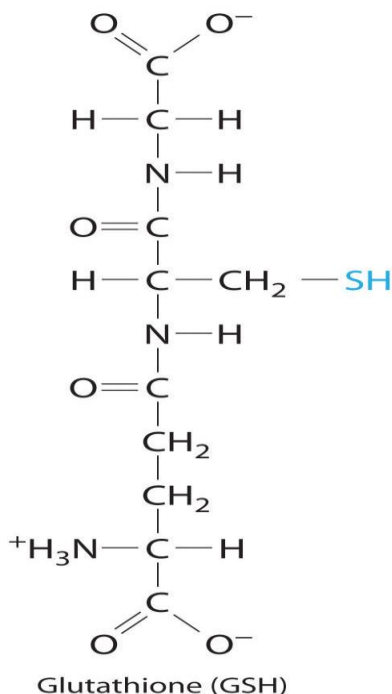
C The problem asks for the *percentage* of calcium oxalate by mass in the original 10.0 g sample of rhubarb, so we need to know the mass of calcium oxalate that produced 9.50×10^{-4} mol of oxalic acid. Because calcium oxalate is $\text{Ca}(\text{O}_2\text{CCO}_2)$, 1 mol of calcium oxalate gave 1 mol of oxalic acid in the initial acid extraction:



Because the problem asked for the percentage by mass of calcium oxalate in the original sample rather than for the *concentration* of oxalic acid in the extract, we do not need to know the volume of the oxalic acid solution for this calculation.

Exercise

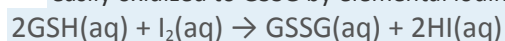
Glutathione is a low-molecular-weight compound found in living cells that is produced naturally by the liver. Health-care providers give it to patients to counter the side effects of chemotherapy and to prevent kidney problems.



after heart bypass

s surgery. Its structure is as follows:

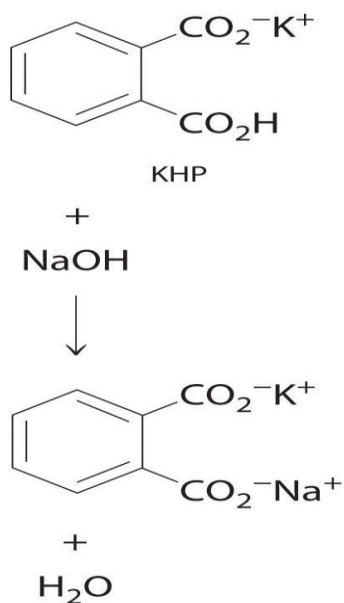
Glutathione is found in two forms: one abbreviated as GSH (indicating the presence of an -SH group) and the other as GSSG (the *disulfide* form, in which an S-S bond links two glutathione units). The GSH form is easily oxidized to GSSG by elemental iodine:



A small amount of soluble starch is added as an indicator. Because starch reacts with excess I_2 to give an intense blue color, the appearance of a blue color indicates that the equivalence point of the reaction has been reached.

Adding small volumes of a 0.0031 M aqueous solution of I_2 to 194 mL of a solution that contains glutathione and a trace of soluble starch initially causes no change. After 16.3 mL of iodine solution have been added, however, a permanent pale blue color appears because of the formation of the starch-iodine complex. What is the concentration of glutathione in the original solution?

Answer: $5.2 \times 10^{-4} \text{ M}$



Standard Solutions

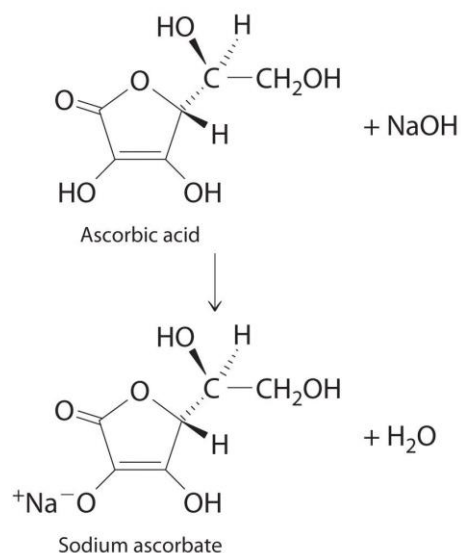
In Example 20, the concentration of the titrant (I_2) was accurately known. The accuracy of any titration analysis depends on an accurate knowledge of the concentration of the titrant. Most titrants are first *standardized*; that is, their concentration is measured by titration with a standard solution, which is a solution whose concentration is known precisely. Only pure crystalline compounds that do not react with water or carbon dioxide are suitable for use in preparing a standard solution. One such compound is potassium hydrogen phthalate (KHP), a weak monoprotic acid suitable for standardizing solutions of bases such as sodium hydroxide. The reaction of KHP with NaOH is a simple acid–base reaction. If the concentration of the KHP solution is known accurately and the titration of a NaOH solution with the KHP solution is carried out carefully, then the concentration of the NaOH solution can be calculated precisely. The standardized NaOH solution can then be used to titrate a solution of an acid whose concentration is unknown.

Acid–Base Titrations

Because most common acids and bases are not intensely colored, a small amount of an acid–base **indicator** is usually added to detect the equivalence point in an acid–base titration. The point in the titration at which an indicator changes color is called the endpoint. The procedure is illustrated in Example 21.

EXAMPLE 21

The structure of vitamin C (ascorbic acid, a monoprotic acid) is as follows:



Ascorbic acid. The upper figure shows the three-dimensional representation of ascorbic acid. Hatched lines indicate bonds that are behind the plane of the paper, and wedged lines indicate bonds that are out of the plane of the paper.

An absence of vitamin C in the diet leads to the disease known as scurvy, a breakdown of connective tissue throughout the body and of dentin in the teeth. Because fresh fruits and vegetables rich in vitamin C are readily available in developed countries today, scurvy is not a major problem. In the days of slow voyages in wooden ships, however, scurvy was common. Ferdinand Magellan, the first person to sail around the world, lost more than 90% of his crew, many to scurvy. Although a diet rich in fruits and vegetables contains more than enough vitamin C to prevent scurvy, many people take supplemental doses of vitamin C, hoping that the extra amounts will help prevent colds and other illness.

Suppose a tablet advertised as containing 500 mg of vitamin C is dissolved in 100.0 mL of distilled water that contains a small amount of the acid–base indicator bromothymol blue, an indicator that is yellow in acid solution and blue in basic solution, to give a yellow solution. The addition of 53.5 mL of a 0.0520 M solution of NaOH results in a change to green at the endpoint, due to a mixture of the blue and yellow forms of the indicator (Figure 4.24 "The Titration of Ascorbic Acid with a Solution of NaOH"). What is the actual mass of vitamin C in the tablet? (The molar mass of ascorbic acid is 176.13 g/mol.)

Given: reactant, volume of sample solution, and volume and molarity of titrant

Asked for: mass of unknown

Strategy:

A Write the balanced chemical equation for the reaction and calculate the number of moles of base needed to neutralize the ascorbic acid.

B Using mole ratios, determine the amount of ascorbic acid consumed. Calculate the mass of vitamin C by multiplying the number of moles of ascorbic acid by its molar mass.

Solution:

A Because ascorbic acid acts as a monoprotic acid, we can write the balanced chemical equation for the reaction as $\text{HAsc(aq)} + \text{OH}^-(\text{aq}) \rightarrow \text{Asc}^-(\text{aq}) + \text{H}_2\text{O(l)}$

Because 0.490 g equals 490 mg, the tablet contains about 2% less vitamin C than advertised.

Exercise

Vinegar is essentially a dilute solution of acetic acid in water. Vinegar is usually produced in a concentrated form and then diluted with water to give a final concentration of 4%–7% acetic acid; that is, a 4% m/v solution contains 4.00 g of acetic acid per 100 mL of solution. If a drop of bromothymol blue indicator is added to 50.0 mL of concentrated vinegar stock and 31.0 mL of 2.51 M NaOH are needed to turn the solution from yellow to green, what is the percentage of acetic acid in the vinegar stock? (Assume that the density of the vinegar solution is 1.00 g/mL.)

Answer: 9.35%

Summary

The concentration of a species in solution can be determined by **quantitative analysis**. One such method is a **titration**, in which a measured volume of a solution of one substance, the **titrant**, is added to a solution of another substance to determine its concentration. The **equivalence point** in a titration is the point at which exactly enough reactant has been added for the reaction to go to completion.

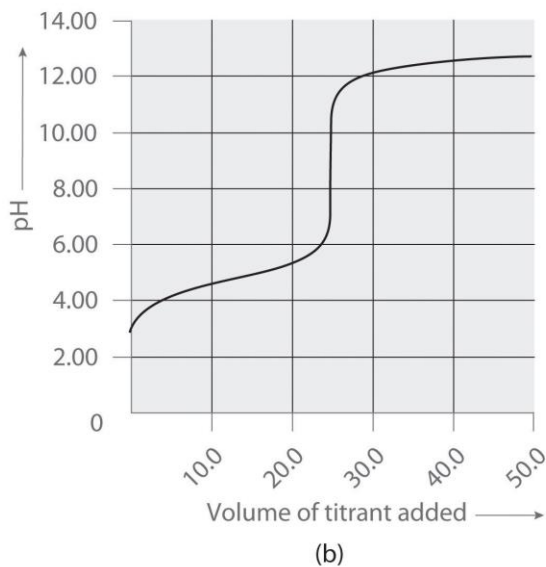
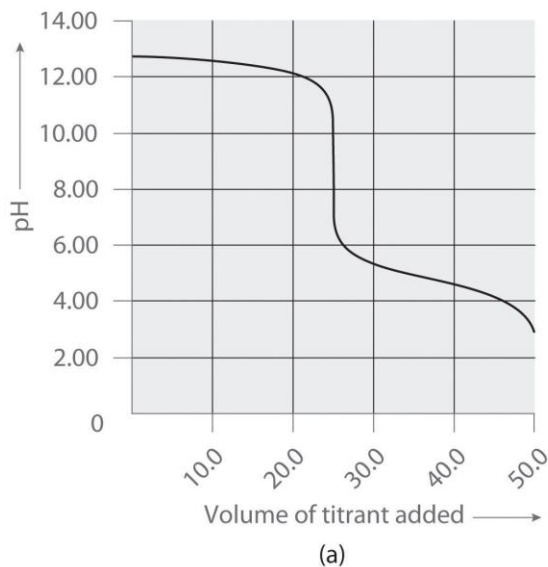
A **standard solution**, a solution whose concentration is known precisely, is used to determine the concentration of the titrant. Many titrations, especially those that involve acid–base reactions, rely on an indicator. The point at which a color change is observed is the **endpoint**, which is close to the equivalence point if the indicator is chosen properly.

KEY TAKEAWAY

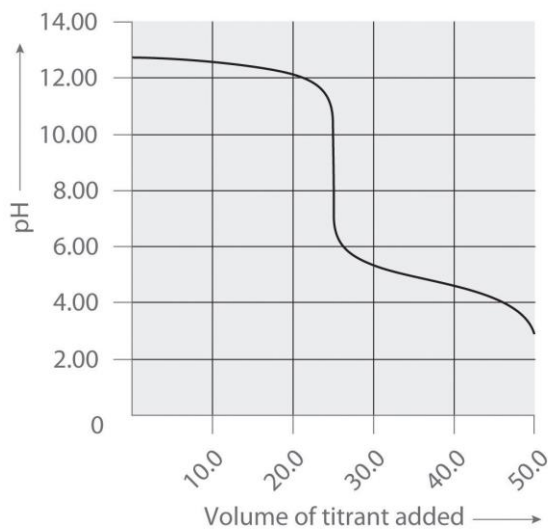
- Quantitative analysis of an unknown solution can be achieved using titration methods.

CONCEPTUAL PROBLEMS

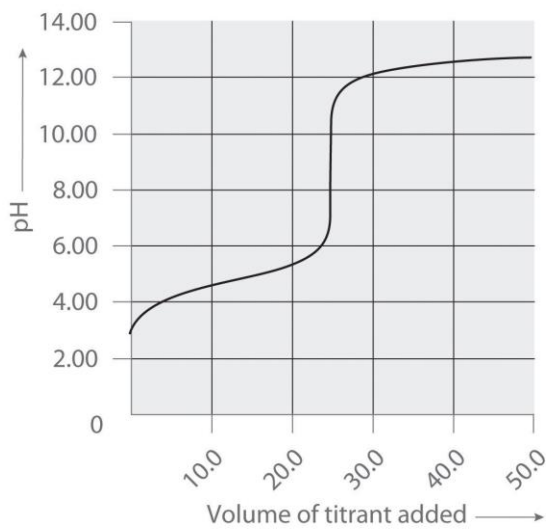
1. The titration procedure is an application of the use of limiting reactants. Explain why this is so.
2. Explain how to determine the concentration of a substance using a titration.
3. Following are two graphs that illustrate how the pH of a solution varies during a titration. One graph corresponds to the titration of 100 mL 0.10 M acetic acid with 0.10 M NaOH, and the other corresponds to the titration of 100 mL 0.10 M NaOH with 0.10 M acetic acid. Which graph corresponds to which titration? Justify your answer.



4. Following are two graphs that illustrate how the pH of a solution varies during a titration. One graph corresponds to the titration of 100 mL 0.10 M ammonia with 0.10 M HCl, and the other corresponds to the titration of 100 mL 0.10 M NH_4Cl with 0.10 M NaOH. Which graph corresponds to which titration? Justify your answer.

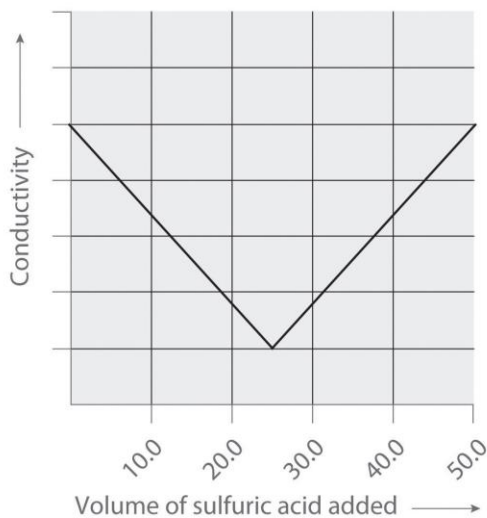


(a)

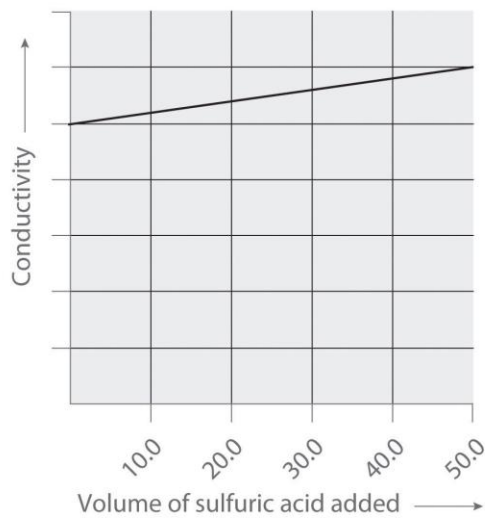


(b)

5. Following are two graphs that illustrate how the electrical conductivity of a solution varies during a titration. One graph corresponds to the titration of 100 mL 0.10 M $\text{Ba}(\text{OH})_2$ with 0.10 M H_2SO_4 , and the other corresponds to the titration of 100 mL of 0.10 M NaOH with 0.10 M H_2SO_4 . Which graph corresponds to which titration? Justify your answer.



(a)



(b)

ANSWERS

1.

2.

3.

a. titration of NaOH with acetic acid

b. titration of acetic acid with NaOH

- 4.
- 5.
- a. titration of $\text{Ba}(\text{OH})_2$ with sulfuric acid
- b. titration of NaOH with sulfuric acid

NUMERICAL PROBLEMS

1. A 10.00 mL sample of a 1.07 M solution of potassium hydrogen phthalate (KHP, formula mass = 204.22 g/mol) is diluted to 250.0 mL. What is the molarity of the final solution? How many grams of KHP are in the 10.00 mL sample?
2. What volume of a 0.978 M solution of NaOH must be added to 25.0 mL of 0.583 M HCl to completely neutralize the acid? How many moles of NaOH are needed for the neutralization?
3. A student was titrating 25.00 mL of a basic solution with an HCl solution that was 0.281 M. The student ran out of the HCl solution after having added 32.46 mL, so she borrowed an HCl solution that was labeled as 0.317 M. An additional 11.5 mL of the second solution was needed to complete the titration. What was the concentration of the basic solution?

4.10 Essential Skills 3

TOPICS

- Base-10 Logarithms
- Calculations Using Common Logarithms

Essential Skills 1 in Chapter 1 "Introduction to Chemistry", Section 1.9 "Essential Skills 1" and Essential Skills 2 in Chapter 3 "Chemical Reactions", Section 3.7 "Essential Skills 2" described some fundamental mathematical operations used for solving problems in chemistry. This section introduces you to base-10 logarithms, a topic with which you must be familiar to do the Questions and Problems at the end of Chapter 4 "Reactions in Aqueous Solution". We will return to the subject of logarithms in Essential Skills 6 in Chapter 11 "Liquids", Section 11.9 "Essential Skills 6".

Base-10 (Common) Logarithms

Essential Skills 1 introduced exponential notation, in which a base number is multiplied by itself the number of times indicated in the exponent. The number 10^3 , for example, is the base 10 multiplied by

itself three times ($10 \times 10 \times 10 = 1000$). Now suppose that we do not know what the exponent is—that we are given only a base of 10 and the final number. If our answer is 1000, the problem can be expressed as $10^a = 1000$

We can determine the value of a by using an operation called the *base-10 logarithm*, or *common logarithm*, abbreviated as *log*, that represents the power to which 10 is raised to give the number to the right of the equals sign. This relationship is stated as $\log 10^a = a$. In this case, the logarithm is 3 because

$$10^3 = 1000:$$

$$\log 10^3 = 3 \log 1000 = 3$$

Now suppose you are asked to find a when the final number is 659. The problem can be solved as follows (remember that any operation applied to one side of an equality must also be applied to the other side):

$$10^a = 659 \log 10^a = \log 659 a = \log 659$$

If you enter 659 into your calculator and press the “log” key, you get 2.819, which means that $a = 2.819$ and $10^{2.819} = 659$. Conversely, if you enter the value 2.819 into your calculator and press the “10x” key, you get 659.

You can decide whether your answer is reasonable by comparing it with the results you get when $a = 2$ and $a = 3$:

$$a = 2: 10^2 = 100 a = 2.819: 10^{2.819} = 659 a = 3: 10^3 = 1000$$

Because the number 659 is between 100 and 1000, a must be between 2 and 3, which is indeed the case.

Table 4.5 "Relationships in Base-10 Logarithms" lists some base-10 logarithms, their numerical values, and their exponential forms.

Table 4.5 Relationships in Base-10 Logarithms

Numerical Value	Exponential Form	Logarithm (a)
1000	10^3	3
100	10^2	2
10	10^1	1
1	10^0	0
0.1	10^{-1}	-1
0.01	10^{-2}	-2
0.001	10^{-3}	-3

Base-10 logarithms may also be expressed as $\log_{10}$, in which the base is indicated as a subscript. We can write $\log 10^a = a$ in either of two ways:

$$\log 10a = a \log_{10} = (10a) = a$$

The second equation explicitly indicates that we are solving for the base-10 logarithm of $10a$.

The number of significant figures in a logarithmic value is the same as the number of digits *after* the decimal point in its logarithm, so $\log 62.2$, a number with three significant figures, is 1.794, with three significant figures after the decimal point; that is, $10^{1.794} = 62.2$, *not* 62.23. Skill Builder ES1 provides practice converting a value to its exponential form and then calculating its logarithm.

SKILL BUILDER ES1

Express each number as a power of 10 and then find the common logarithm.

- 10,000
- 0.00001
- 10.01
- 2.87
- 0.134

Solution

- $10,000 = 1 \times 10^4$; $\log 1 \times 10^4 = 4.0$
- $0.00001 = 1 \times 10^{-5}$; $\log 1 \times 10^{-5} = -5.0$
- $10.01 = 1.001 \times 10$; $\log 10.01 = 1.0004$ (enter 10.01 into your calculator and press the “log” key); $10^{1.0004} = 10.01$
- $2.87 = 2.87 \times 10^0$; $\log 2.87 = 0.458$ (enter 2.87 into your calculator and press the “log” key); $10^{0.458} = 2.87$
- $0.134 = 1.34 \times 10^{-1}$; $\log 0.134 = -0.873$ (enter 0.134 into your calculator and press the “log” key); $10^{-0.873} = 0.134$

SKILL BUILDER ES2

Convert each base-10 logarithm to its numerical value.

- 3
- 2.0
- 1.62
- 0.23
- 4.872

Solution

- a. 10^3
- b. 10^{-2}
- c. $10^{1.62} = 42$
- d. $10^{-0.23} = 0.59$
- e. $10^{-4.872} = 1.34 \times 10^{-5}$

Calculations Using Common Logarithms

Because logarithms are exponents, the properties of exponents that you learned in Essential Skills 1 apply to logarithms as well, which are summarized in Table 4.6 "Properties of Logarithms". The logarithm of

(4.08×20.67), for example, can be computed as follows:

$$\log(4.08 \times 20.67) = \log 4.08 + \log 20.67 = 0.611 + 1.3153 = 1.926$$

We can be sure that this answer is correct by checking that $10^{1.926}$ is equal to 4.08×20.67 , and it is.

In an alternative approach, we multiply the two values before computing the logarithm:

$$4.08 \times 20.67 = 84.3 \log 84.3 = 1.926$$

We could also have expressed 84.3 as a power of 10 and then calculated the logarithm:

$$\log 84.3 = \log(8.43 \times 10) = \log 8.43 + \log 10 = 0.926 + 1 = 1.926$$

As you can see, *there may be more than one way to correctly solve a problem.*

We can use the properties of exponentials and logarithms to show that the logarithm of the inverse of a number ($1/B$) is the negative logarithm of that number ($-\log B$):

$$\log(1/B) = -\log B$$

If we use the formula for division given Table 4.6 "Properties of Logarithms" and recognize that $\log 1 = 0$, then the logarithm is:

Table 4.6 Properties of Logarithms

Operation	Exponential Form	Logarithm
multiplication	$(10^a)(10^b) = 10^{a+b}$	$\log(ab) = \log a + \log b$

SKILL BUILDER ES3

Convert each number to exponential form and then calculate the logarithm (assume all trailing zeros on whole numbers are not significant).

- a. 100×1000
- b. $0.100 \div 100$

c. 1000×0.010

d. 200×3000

e. $20.5 \div 0.026$

Solution

a. $100 \times 1000 = (1 \times 10^2)(1 \times 10^3)$

$$\log[(1 \times 10^2)(1 \times 10^3)] = 2.0 + 3.0 = 5.0$$

Alternatively, $(1 \times 10^2)(1 \times 10^3) = 1 \times 10^{2+3} = 1 \times 10^5$

$$\log(1 \times 10^5) = 5.0$$

b. $0.100 \div 100 = (1.00 \times 10^{-1}) \div (1 \times 10^2)$

$$\log[(1.00 \times 10^{-1}) \div (1 \times 10^2)] = 1 \times 10^{-1-2} = 1 \times 10^{-3}$$

Alternatively, $(1.00 \times 10^{-1}) \div (1 \times 10^2) = 1 \times 10^{[-1] - [2]} = 1 \times 10^{-3}$

$$\log(1 \times 10^{-3}) = -3.0$$

c. $1000 \times 0.010 = (1 \times 10^3)(1.0 \times 10^{-2})$

$$\log[(1 \times 10^3)(1 \times 10^{-2})] = 3.0 + (-2.0) = 1.0$$

Alternatively, $(1 \times 10^3)(1.0 \times 10^{-2}) = 1 \times 10^{[3] + [-2]} = 1 \times 10^1$

$$\log(1 \times 10^1) = 1.0$$

d. $200 \times 3000 = (2 \times 10^2)(3 \times 10^3)$

$$\log[(2 \times 10^2)(3 \times 10^3)] = \log(2 \times 10^2) + \log(3 \times 10^3)$$

$$= (\log 2 + \log 10^2) + (\log 3 + \log 10^3)$$

$$= 0.30 + 2 + 0.48 + 3 = 5.8$$

Alternatively, $(2 \times 10^2)(3 \times 10^3) = 6 \times 10^{2+3} = 6 \times 10^5$

$$\log(6 \times 10^5) = \log 6 + \log 10^5 = 0.78 + 5 = 5.8$$

e. $20.5 \div 0.026 = (2.05 \times 10) \div (2.6 \times 10^{-2})$

$$\log[(2.05 \times 10) \div (2.6 \times 10^{-2})] = (\log 2.05 + \log 10) - (\log 2.6 + \log 10^{-2})$$

$$= (0.3118 + 1) - [0.415 + (-2)]$$

$$= 1.3118 + 1.585 = 2.90$$

Alternatively, $(2.05 \times 10) \div (2.6 \times 10^{-2}) = 0.788 \times 10^{[1] - [-2]} = 0.788 \times 10^3$

$$\log(0.79 \times 10^3) = \log 0.79 + \log 10^3 = -0.102 + 3 = 2.90$$

SKILL BUILDER ES4

Convert each number to exponential form and then calculate its logarithm (assume all trailing zeros on whole numbers are not significant).

- a. $10 \times 100,000$
- b. $1000 \div 0.10$
- c. $25,000 \times 150$
- d. $658 \div 17$

Solution

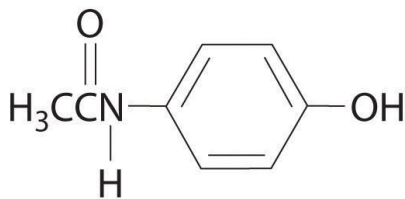
- a. $(1 \times 10)(1 \times 10^5)$; logarithm = 6.0
- b. $(1 \times 10^3) \div (1.0 \times 10^{-1})$; logarithm = 4.00
- c. $(2.5 \times 10^4)(1.50 \times 10^2)$; logarithm = 6.57
- d. $(6.58 \times 10^2) \div (1.7 \times 10)$; logarithm = 1.59

4.11 End-of-Chapter Material

APPLICATION PROBLEMS

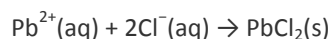
Please be sure you are familiar with the topics discussed in Essential Skills 3 (Section 4.1 "Aqueous Solutions") before proceeding to the Application Problems. Problems marked with a ♦ involve multiple concepts.

1. ♦ Acetaminophen (molar mass = 151 g/mol) is an analgesic used as a substitute for aspirin. If a child's dose contains 80.0 mg of acetaminophen/5.00 mL of an ethanol-water solution, what is the molar concentration? Acetaminophen is frequently packaged as an ethanol-water solution rather than as an aqueous one. Why?

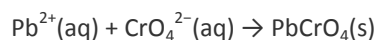


Acetaminophen

2. ♦ Lead may have been the first metal ever recovered from its ore by humans. Its cation (Pb^{2+}) forms a precipitate with Cl^- according to the following equation:



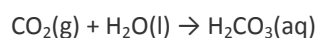
When PbCl_2 is dissolved in hot water, its presence can be confirmed by its reaction with CrO_4^{2-} , with which it forms a yellow precipitate:



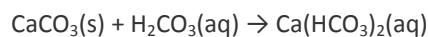
The precipitate is used as a rust inhibitor and in pigments.

- What type of reaction does each equation represent?
- If 100 mL of a Pb^{2+} solution produce 1.65 g of lead chromate, what was the concentration of the lead solution?
- What volume of a potassium chromate solution containing 0.503 g of solute per 250.0 mL is needed for this reaction?
- If all the PbCrO_4 originated from PbCl_2 , what volume of a 1.463 M NaCl solution was needed for the initial reaction?
- Why is there environmental concern over the use of PbCrO_4 ?

3. ♦ Reactions that affect buried marble artifacts present a problem for archaeological chemists. Groundwater dissolves atmospheric carbon dioxide to produce an aqueous solution of carbonic acid:



This weakly acidic carbonic acid solution dissolves marble, converting it to soluble calcium bicarbonate:



Evaporation of water causes carbon dioxide to be driven off, resulting in the precipitation of calcium carbonate:



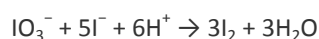
The reprecipitated calcium carbonate forms a hard scale, or incrustation, on the surface of the object.

- If 8.5 g of calcium carbonate were obtained by evaporating 250 mL of a solution of calcium bicarbonate followed by drying, what was the molarity of the initial calcium bicarbonate solution, assuming complete reaction?
 - If the overall reaction sequence was 75% efficient, how many grams of carbonic acid were initially dissolved in the 250 mL to produce the calcium bicarbonate?
4. How many Maalox tablets are needed to neutralize 5.00 mL of 0.100 M HCl stomach acid if each tablet contains 200 mg $\text{Mg}(\text{OH})_2$ + 200 mg $\text{Al}(\text{OH})_3$? Each Rolaids tablet contains 412 mg CaCO_3 + 80.0 mg $\text{Mg}(\text{OH})_2$.

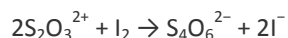
How many Roloids tablets are needed? Suggest another formula (and approximate composition) for an effective antacid tablet.

5. Citric acid ($\text{C}_6\text{H}_8\text{O}_7$, molar mass = 192.12 g/mol) is a triprotic acid extracted from citrus fruits and pineapple waste that provides tartness in beverages and jellies. How many grams of citric acid are contained in a 25.00 mL sample that requires 38.43 mL of 1.075 M NaOH for neutralization to occur? What is the formula of the calcium salt of this compound?

6. ♦ A method for determining the molarity of a strongly acidic solution has been developed based on the fact that a standard solution of potassium iodide and potassium iodate yields iodine when treated with acid:



Starch is used as the indicator in this titration because starch reacts with iodine in the presence of iodide to form an intense blue complex. The amount of iodine produced from this reaction can be determined by subsequent titration with thiosulfate:



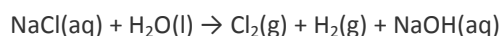
The endpoint is reached when the solution becomes colorless.

- h. The thiosulfate solution was determined to be 1.023 M. If 37.63 mL of thiosulfate solution were needed to titrate a 25.00 mL sample of an acid, what was the H^+ ion concentration of the acid?
 - i. If the 25.00 mL sample that was titrated had been produced by dilution of a 10.00 mL sample of acid, what was the molarity of the acid in the original solution?
 - j. Why might this be an effective method for determining the molarity of a strong acid, such as H_2SO_4 ?
7. ♦ Sewage processing occurs in three stages. Primary treatment removes suspended solids, secondary treatment involves biological processes that decompose organic matter, and tertiary treatment removes specific pollutants that arise from secondary treatment (generally phosphates). Phosphate can be removed by treating the HPO_4^{2-} solution produced in the second stage with lime (CaO) to precipitate hydroxyapatite $[\text{Ca}_5(\text{PO}_4)_3\text{OH}]$.
- k. Write a balanced chemical equation for the reaction that occurs in the tertiary treatment process.
 - l. What has been neutralized in this process?
 - m. Four pounds of hydroxyapatite precipitated from the water. What mass of lime was used in the reaction?
 - n. Assuming a volume of water of 30 m^3 , what was the hydrogen phosphate anion concentration in the water?

8. Calcium hydroxide and calcium carbonate are effective in neutralizing the effects of acid rain on lakes.

Suggest other compounds that might be effective in treating lakes. Give a plausible reason to explain why Ca(OH)_2 and CaCO_3 are used.

9. ♦ Approximately 95% of the chlorine produced industrially comes from the electrolysis of sodium chloride solutions (brine):



Chlorine is a respiratory irritant whose presence is easily detected by its penetrating odor and greenish-yellow color. One use for the chlorine produced is in the manufacture of hydrochloric acid.

- o. In the chemical equation shown, what has been oxidized and what has been reduced?
- p. Write the oxidation and reduction equations for this reaction.
- q. Balance the net ionic equation.
- r. Name another salt that might produce chlorine by electrolysis and give the expected products. Identify those products as gases, liquids, or solids.

10. ♦ The lead/acid battery used in automobiles consists of six cells that produce a 12 V electrical system.

During discharge, lead(IV) oxide, lead, and aqueous sulfuric acid react to form lead(II) sulfate and water.

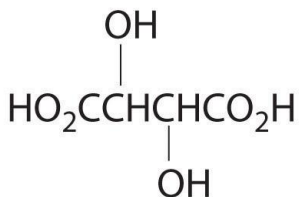
- s. What has been oxidized and what has been reduced?
- t. Write and balance the equation for the reaction.
- u. What is the net ionic equation?
- v. What is the complete ionic equation?
- w. What hazard is associated with handling automobile batteries?

11. ♦ The use of iron, which is abundant in Earth's crust, goes back to prehistoric times. In fact, it is believed that the Egyptians used iron implements approximately 5000 years ago. One method for quantifying the iron concentration in a sample involves three steps. The first step is to dissolve a portion of the sample in concentrated hydrochloric acid to produce ferric chloride; the second is to reduce Fe^{3+} to Fe^{2+} using zinc metal; and the third is to titrate Fe^{2+} with permanganate, producing $\text{Mn}^{2+}(\text{aq})$ and ferric iron in the form of Fe_2O_3 .

- x. Write chemical equations for all three steps.
- y. Write the net ionic equations for these three reactions.
- z. If 27.64 mL of a 1.032 M solution of permanganate are required to titrate 25.00 mL of Fe^{2+} in the third step, how many grams of Fe were in the original sample?

aa. Based on your answer to part c, if the original sample weighed 50.32 g, what was the percentage of iron?

12. Baking powder, which is a mixture of tartaric acid and sodium bicarbonate, is used in baking cakes and bread. Why does bread rise when you use baking powder? What type of reaction is involved?



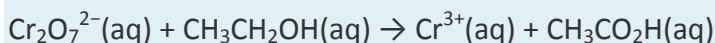
Tartaric acid

1. An activity series exists for the halogens, which is based on the ease of *reducing* the diatomic halogen molecule (X_2) to X^- . Experimentally, it is found that fluorine is the easiest halogen to reduce (i.e., F_2 is the best oxidant), and iodine is the hardest halogen to reduce (i.e., I_2 is the worst oxidant). Consequently, the addition of any diatomic halogen, Y_2 , to solutions containing a halide ion (X^-) that lies below Y in the periodic table will result in the reduction of Y_2 to Y^- and the oxidation of X^- . Describe what you would expect to occur when

- chlorine is added to an aqueous solution of bromide.
- iodine crystals are added to a solution of potassium bromide.

Bromide is present in naturally occurring salt solutions called *brines*. Based on your answers, propose an effective method to remove bromide from brine.

- ♦ Marble is composed of mostly calcium carbonate. Assuming that acid rain contains $4.0 \times 10^{-5} \text{ M H}_2\text{SO}_4$, approximately what volume of rain is necessary to dissolve a 250 lb marble statue?
- ♦ One of the “first-aid” measures used to neutralize lakes whose pH has dropped to critical levels is to spray them with slaked lime ($\text{Ca}(\text{OH})_2$) or limestone (CaCO_3). (A slower but effective alternative is to add limestone boulders.) How much slaked lime would be needed to neutralize the acid in a lake that contains $4.0 \times 10^{-5} \text{ M H}_2\text{SO}_4$ and has a volume of 1.2 cubic miles ($5.0 \times 10^{12} \text{ L}$)?
- Recall from Section 4.3 “Stoichiometry of Reactions in Solution” that the reaction of ethanol with dichromate ion in acidic solution yields acetic acid and $\text{Cr}^{3+}(\text{aq})$:



Balance the equation for this reaction using oxidation states. (*Hint*: the oxidation state of carbon in the CH_3 group remains unchanged, as do the oxidation states of hydrogen and oxygen.)

ANSWERS

1. 0.106 M acetaminophen; acetaminophen is an organic compound that is much more soluble in ethanol than water, so using an ethanol/water mixture as the solvent allows a higher concentration of the drug to be used.
 - 2.
 - 3.
 - a. 0.34 M $\text{Ca}(\text{HCO}_3)_2$
 - b. 7.0 g H_2CO_3
 - 4.
 5. 2.646 g citric acid, $\text{Ca}_3(\text{C}_6\text{H}_5\text{O}_7)_2$
 - 6.
 - 7.
 - a. $5\text{CaO} + 3\text{HPO}_4^{2-} + 2\text{H}_2\text{O} \rightarrow \text{Ca}_5(\text{PO}_4)_3\text{OH} + 6\text{OH}^-$
 - b. This is an acid–base reaction, in which the acid is the HPO_4^{2-} ion and the base is CaO. Transferring a proton from the acid to the base produces the PO_4^{3-} ion and the hydroxide ion.
 - c. 2.2 lbs (1 kg) of lime
 - d. 3.6×10^{-4} M HPO_4^{2-}
 - 8.
 - 9.
 - a. Chloride is oxidized, and protons are reduced.
 - b.
- Oxidation: $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$ –Reduction: $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$
- c.
- $2\text{Cl}^- + 2\text{H}_2\text{O} \rightarrow \text{Cl}_2 + \text{H}_2 + 2\text{OH}^-$

Chapter 5

Energy Changes in Chemical Reactions

In Chapter 3 "Chemical Reactions", Section 3.3 "Chemical Equations", you learned that applying a small amount of heat to solid ammonium dichromate initiates a vigorous reaction that produces chromium(III) oxide, nitrogen gas, and water vapor. These are not the only products of this reaction that interest chemists, however; the reaction also releases energy in the form of heat and light. So our description of this reaction was incomplete. A complete description of a chemical reaction includes not only the identity, amount, and chemical form of the reactants and products but also the quantity of energy produced or consumed. In combustion reactions, heat is always a product; in other reactions, heat may be produced or consumed.

This chapter introduces you to thermochemistry, a branch of chemistry that describes the energy changes that occur during chemical reactions. In some situations, the energy produced by chemical reactions is actually of greater interest to chemists than the material products of the reaction. For example, the controlled combustion of organic molecules, primarily sugars and fats, within our cells provides the energy for physical activity, thought, and other complex chemical transformations that occur in our bodies. Similarly, our energy-intensive society extracts energy from the combustion of fossil fuels, such as coal, petroleum, and natural gas, to manufacture clothing and furniture, heat your home in winter and cool it in summer, and power the car or bus that gets you to class and to the movies. By the end of this chapter, you will know enough about thermochemistry to explain why ice cubes cool a glass of soda, how instant cold packs and hot packs work, and why swimming pools and waterbeds are heated. You will also understand what factors determine the caloric content of your diet and why even "nonpolluting" uses of fossil fuels may be affecting the environment.

Thermodynamic spontaneity. *The highly exothermic and dramatic thermite reaction is thermodynamically spontaneous. Reactants of aluminum and a metal oxide, usually iron, which are stable at room temperature, are ignited either in the presence of heat or by the reaction of potassium permanganate and glycerin. The resulting products are aluminum oxide, free and molten elemental metal, and a great deal of heat, which makes this an excellent method for on-site welding. Because this reaction has its own oxygen supply, it can be used for underwater welding as well.*

5.1 Energy and Work

LEARNING OBJECTIVES

1. To understand the concept of energy and its various forms.
2. To know the relationship between energy, work, and heat.

Because energy takes many forms, only some of which can be seen or felt, it is defined by its effect on matter. For example, microwave ovens produce energy to cook food, but we cannot see that energy. In contrast, we can see the energy produced by a light bulb when we switch on a lamp. In this section, we describe the forms of energy and discuss the relationship between energy, heat, and work.

Forms of Energy

The forms of energy include thermal energy, radiant energy, electrical energy, nuclear energy, and chemical energy (Figure 5.1 "Forms of Energy"). Thermal energy results from atomic and molecular motion; the faster the motion, the greater the thermal energy. The temperature of an object is a measure of its thermal energy content. Radiant energy is the energy carried by light, microwaves, and radio waves. Objects left in bright sunshine or exposed to microwaves become warm because much of the radiant energy they absorb is converted to thermal energy. Electrical energy results from the flow of electrically charged particles. When the ground and a cloud develop a separation of charge, for example, the resulting flow of electrons from one to the other produces lightning, a natural form of electrical energy. Nuclear energy is stored in the nucleus of an atom, and chemical energy is stored within a chemical compound because of a particular arrangement of atoms.

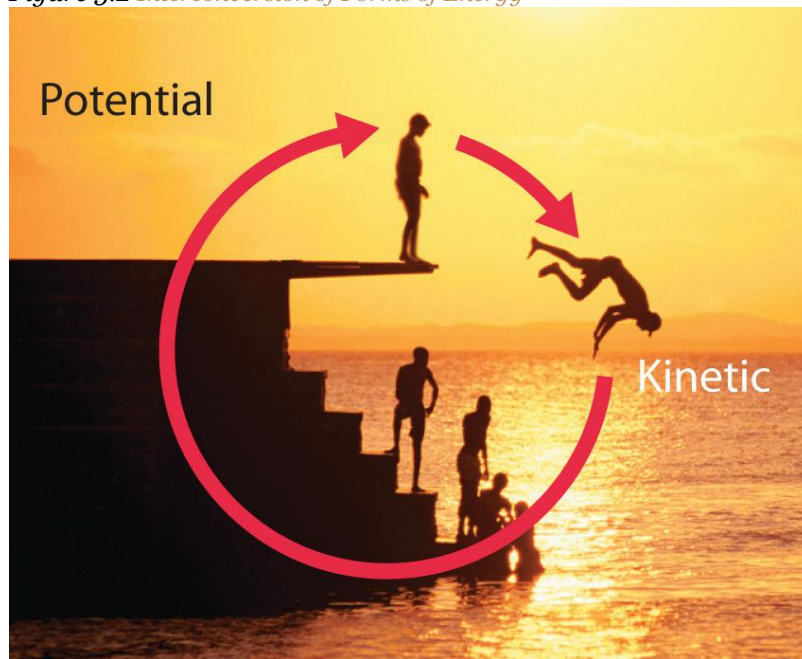
(a) Thermal energy results from atomic and molecular motion; molten steel at 2000°C has a very high thermal energy content. (b) Radiant energy (e.g., from the sun) is the energy in light, microwaves, and radio waves. (c) Lightning is an example of electrical energy, which is due to the flow of electrically charged particles. (d) Nuclear energy is released when particles in the nucleus of the atom are rearranged. (e) Chemical energy results from the particular arrangement of atoms in a chemical compound; the heat and light produced in this reaction are due to energy released during the breaking and reforming of chemical bonds.

Electrical energy, nuclear energy, and chemical energy are different forms of potential energy (**PE**), which is energy stored in an object because of the relative positions or orientations of its components. A brick lying on the windowsill of a 10th-floor office has a great deal of potential energy, but until its position changes by falling, the energy is contained. In contrast, kinetic energy (**KE**) is energy due to the *motion* of an object. When the brick falls, its potential energy is transformed to kinetic energy, which is then transferred to the object on the ground that it strikes.

The electrostatic attraction between oppositely charged particles is a form of potential energy, which is converted to kinetic energy when the charged particles move toward each other.

Energy can be converted from one form to another (Figure 5.2 "Interconversion of Forms of Energy") or, as we saw with the brick, transferred from one object to another. For example, when you climb a ladder to a high diving board, your body uses chemical energy produced by the combustion of organic molecules. As you climb, the chemical energy is converted to *mechanical work* to overcome the force of gravity. When you stand on the end of the diving board, your potential energy is greater than it was before you climbed the ladder: the greater the distance from the water, the greater the potential energy. When you then dive into the water, your potential energy is converted to kinetic energy as you fall, and when you hit the surface, some of that energy is transferred to the water, causing it to splash into the air. Chemical energy can also be converted to radiant energy; one common example is the light emitted by fireflies, which is produced from a chemical reaction.

Figure 5.2 *Interconversion of Forms of Energy*



When a swimmer steps off the platform to dive into the water, potential energy is converted to kinetic energy. As the swimmer climbs back up to the top of the diving platform, chemical energy is converted to mechanical work.

Although energy can be converted from one form to another, *the total amount of energy in the universe remains constant*. This is known as the law of conservation of energy.^[1] *Energy cannot be created or destroyed.*

Energy, Heat, and Work

One definition of energy is the capacity to do work. The easiest form of work to visualize is mechanical work (Figure 5.3 "An Example of Mechanical Work"), which is the energy required to move an object a distance d when opposed by a force F , such as gravity:

Equation 5.1: work = force x distance

Because the force (F) that opposes the action is equal to the mass (m) of the object times its acceleration (a), we can also write Equation 5.1 as follows:^[2]

$$\text{Work} = \text{mass} \times \text{acceleration} \times \text{distance}$$

Consider the mechanical work required for you to travel from the first floor of a building to the second. Whether you take an elevator or an escalator, trudge upstairs, or leap up the stairs two at a time, energy is expended to overcome the force of gravity. The amount of work done (w) and thus the energy required depends on three things: (1) the height of the second floor (the distance d); (2) your mass, which must be raised that distance against the downward acceleration due to gravity; and (3) your path, as you will learn in Section 5.2 "Enthalpy".

In contrast, heat (q) is thermal energy that can be transferred from an object at one temperature to an object at another temperature. The net transfer of thermal energy stops when the two objects reach the same temperature. The energy of an object can be changed only by the transfer of energy to or from another object in the form of heat,^[3] work performed on or by the object, or some combination of heat and work. Consider, for example, the energy stored in a fully charged battery. As shown in Figure 5.4 "Energy Transfer", this energy can be used primarily to perform work (e.g., running an electric fan) or to generate light and heat (e.g., illuminating a light bulb). When the battery is fully discharged in either case, the total change in energy is the same, even though the fraction released as work or heat varies greatly. The sum of the heat produced and the work performed equals the change in energy (ΔE):

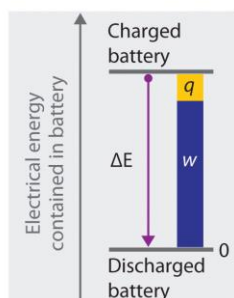
Equation 5.3

Energy change = heat + work

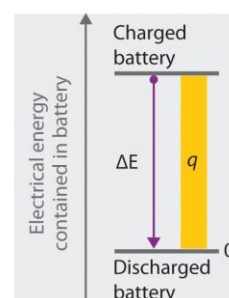
Note the Pattern

Energy can be transferred only in the form of heat, work performed on or by an object, or some combination of heat and work.

Figure 5.4 Energy Transfer



(a) Energy (E) released as work (w) and heat (q)



(b) Energy (E) released as heat (q) and light

Discharging a fully charged battery releases the same amount of energy whether the battery is used to run a fan (a) or illuminate a light bulb (b). In (a), most of the energy is used to perform work, which turns the blades of the fan and thus moves the air; only a small portion of the energy is released as heat by the electric motor. In (b), all the energy is released as heat and light; no work is done.

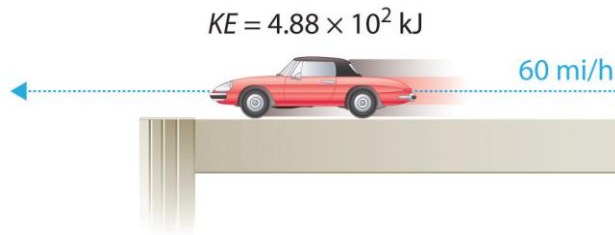
Energy is an extensive property of matter—for example, the amount of **thermal energy** in an object is proportional to both its mass and its temperature. (For more information on the properties of matter, see Chapter 1 "Introduction to Chemistry".) A water heater that holds 150 L of water at 50°C contains much more thermal energy than does a 1 L pan of water at 50°C. Similarly, a bomb contains much more chemical energy than does a firecracker. We now present a more detailed description of kinetic and potential energy.

Kinetic and Potential Energy

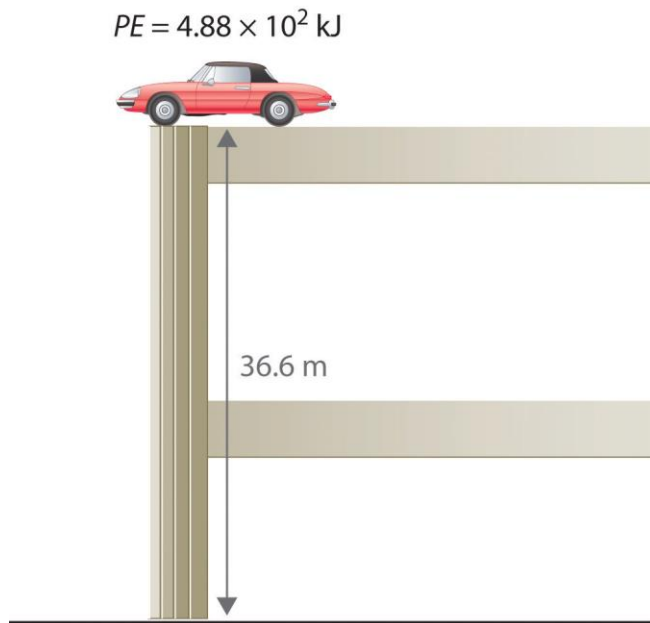
The kinetic energy of an object is related to its mass m and velocity v .

Because all forms of energy can be interconverted, energy in any form can be expressed using the same units as kinetic energy. The SI unit of energy, the joule (J),^[4] is defined as 1

kilogram·meter²/second² (kg·m²/s²). Because a joule is such a small quantity of energy, chemists usually express energy in kilojoules (1 kJ = 10³ J). For example, the kinetic energy of the 1360 kg car traveling at 26.8 m/s is 4.88 × 10⁵ J or 4.88 × 10² kJ. It is important to remember that *the units of energy are the same regardless of the form of energy*, whether thermal, radiant, chemical, or any other form. Because heat and work result in changes in energy, their units must also be the same.



To demonstrate, let's calculate the potential energy of the same 1360 kg automobile if it were parked on the top level of a parking garage 36.6 m (120 ft) high. Its potential energy is equivalent to the amount of work required to raise the vehicle from street level to the top level of the parking garage, which is given by Equation 5.1 ($w = Fd$). According to Equation 5.2, the force (F) exerted by gravity on any object is equal to its mass (m , in this case, 1360 kg) times the acceleration (a) due to gravity (g , 9.81 m/s² at Earth's surface). The distance (d) is the height (h) above street level (in this case, 36.6 m).

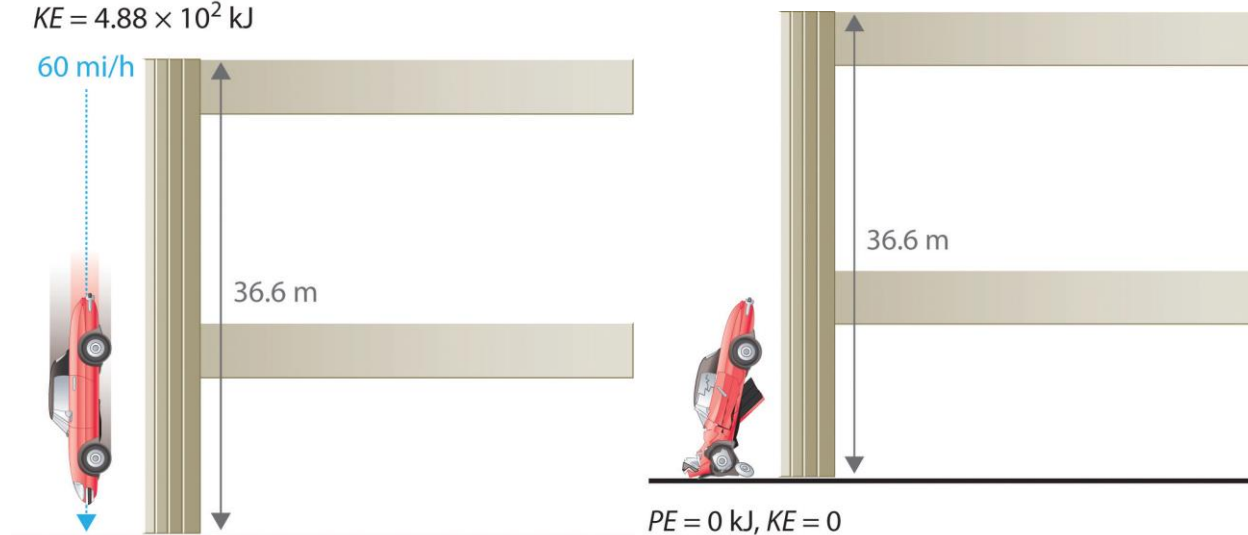


The units of potential energy are the same as the units of kinetic energy. Notice that in this case the potential energy of the stationary automobile at the top of a 36.6 m high parking garage is the same as its kinetic energy at 60 mi/h. If the vehicle fell from the roof of the parking garage, its potential energy would be converted to kinetic energy, and it is reasonable to infer that the vehicle would be traveling at 60 mi/h just before it hit the ground, neglecting air resistance. After the car hit the ground, its potential and kinetic energy would both be zero.

Potential energy is usually defined relative to an arbitrary standard position (in this case, the street was assigned an elevation of zero). As a result, we usually calculate only differences in potential energy: in this case, the difference

between the potential energy of the car on the top level of the parking garage and the potential energy of the same car on the street at the base of the garage.

$$KE = 4.88 \times 10^2 \text{ kJ}$$



A recent and spectacular example of the conversion of potential energy to kinetic energy was seen by the earthquake near the east coast of Honshu, Japan, on March 11, 2011. The magnitude 9.0 earthquake occurred along the Japan Trench subduction zone, the interface boundary between the Pacific and North American geological plates. During its westward movement, the Pacific plate became trapped under the North American plate, and its further movement was prevented. When there was sufficient potential energy to allow the Pacific plate to break free, approximately 7.1×10^{15} kJ of potential energy was released as kinetic energy, the equivalent of 4.75×10^8 tn of TNT (trinitrotoluene) or 25,003 nuclear bombs. The island of Japan experienced the worst devastation in its history from the earthquake, resulting tsunami, and aftershocks. Historical records indicate that an earthquake of such force occurs in some region of the globe approximately every 1000 years. One such earthquake and resulting tsunami is speculated to have caused the destruction of the lost city of Atlantis, referred to by the ancient Greek philosopher Plato.

Note the Pattern

The units of energy are the same for all forms of energy.

Energy can also be expressed in the non-SI units of calories (cal), where 1 cal was originally defined as the amount of energy needed to raise the temperature of exactly 1 g of water from 14.5°C to 15.5°C.^[5] The name is derived from the Latin *calor*, meaning “heat.” Although energy may be expressed as either calories or joules, calories were defined in terms of heat, whereas joules were defined in terms of motion. Because calories and joules are both units of energy, however, the calorie is now defined in terms of the joule

$$1 \text{ cal} = 4.184 \text{ J exactly}$$
$$1 \text{ J} = 0.2390 \text{ cal}$$

In this text, we will use the SI units—joules (J) and kilojoules (kJ)—exclusively, except when we deal with nutritional information, addressed in Section 5.4 "Thermochemistry and Nutrition".

EXAMPLE 1

- If the mass of a baseball is 149 g, what is the kinetic energy of a fastball clocked at 100 mi/h?
- A batter hits a pop fly, and the baseball (with a mass of 149 g) reaches an altitude of 250 ft. If we assume that the ball was 3 ft above home plate when hit by the batter, what is the increase in its potential energy?

Exercise

- In a bowling alley, the distance from the foul line to the head pin is 59 ft, 10 13/16 in. (18.26 m). If a 16 lb (7.3 kg) bowling ball takes 2.0 s to reach the head pin, what is its kinetic energy at impact? (Assume its speed is constant.)
- What is the potential energy of a 16 lb bowling ball held 3.0 ft above your foot?

Answer:

- $3.10 \times 10^2 \text{ J}$
- 65 J

KEY EQUATIONS

general definition of work

Equation 5.1: $w = Fd$

Equation 5.2: $w = mad$

relationship between energy, heat, and work

Equation 5.3: $\Delta E = q + w$

kinetic energy

$KE = \frac{1}{2} mv^2$

potential energy in a gravitational field

Equation 5.6: $PE = mgh$

Summary

Thermochemistry is a branch of chemistry that qualitatively and quantitatively describes the energy changes that occur during chemical reactions. **Energy** is the capacity to do work. **Mechanical work** is the amount of energy required to move an object a given distance when opposed by a force. **Thermal energy** is due to the random motions of atoms, molecules, or ions in a substance. The **temperature** of an object is a measure of the amount of thermal energy it contains. **Heat (q)** is the transfer of thermal energy from a hotter object to a cooler one. Energy can take many forms; most are different varieties of **potential energy (PE)**, energy caused by the relative position or orientation of an object. **Kinetic energy (KE)** is the energy an object possesses due to its motion. Energy can be converted from one form to another, but the **law of conservation of energy** states that energy can be neither created nor destroyed. The most common units of energy are the **joule (J)**, defined as $1 \text{ (kg}\cdot\text{m}^2\text{)/s}^2$, and the **calorie**, defined as the amount of energy needed to raise the temperature of 1 g of water by 1°C ($1 \text{ cal} = 4.184 \text{ J}$).

KEY TAKEAWAY

- All forms of energy can be interconverted. Three things can change the energy of an object: the transfer of heat, work performed on or by an object, or some combination of heat and work.

CONCEPTUAL PROBLEMS

1. What is the relationship between mechanical work and energy?
2. Does a person with a mass of 50 kg climbing a height of 15 m do work? Explain your answer. Does that same person do work while descending a mountain?
3. If a person exerts a force on an immovable object, does that person do work? Explain your answer.
4. Explain the differences between electrical energy, nuclear energy, and chemical energy.
5. The chapter describes thermal energy, radiant energy, electrical energy, nuclear energy, and chemical energy. Which form(s) of energy are represented by each of the following?
 - a. sunlight
 - b. the energy produced by a cathode ray tube, such as that found in a television
 - c. the energy emitted from radioactivity
 - d. the energy emitted from a burning candle
 - e. the energy associated with a steam engine

- f. the energy emitted by a cellular phone
 - g. the energy associated with a stick of dynamite
6. Describe the various forms of energy that are interconverted when a flashlight is switched on.
 7. Describe the forms of energy that are interconverted when the space shuttle lifts off.
 8. Categorize each of the following as representing kinetic energy or potential energy.
 - a. the energy associated with a laptop computer sitting on the edge of a desk
 - b. shoveling snow
 - c. water pouring out of a fire hydrant
 - d. the energy released by an earthquake
 - e. the energy in a volcano about to erupt
 - f. the energy associated with a coiled spring
 9. Are the units for potential energy the same as the units for kinetic energy? Can an absolute value for potential energy be obtained? Explain your answer.
 10. Categorize each of the following as representing kinetic energy or potential energy.
 - a. water cascading over Niagara Falls
 - b. a beaker balanced on the edge of a sink
 - c. the energy released during a mudslide
 - d. rollerblading
 - e. the energy in a block of ice on a rooftop before a thaw
 11. Why does hammering a piece of sheet metal cause the metal to heat up?

ANSWERS

3. Technically, the person is not doing any work, since the object does not move.
12. The kinetic energy of the hammer is transferred to the metal.

NUMERICAL PROBLEMS

Please be sure you are familiar with the topics discussed in Essential Skills 4 (Section 5.6 "Essential Skills 4") before proceeding to the Numerical Problems.

1. Describe the mathematical relationship between (a) the thermal energy stored in an object and that object's mass and (b) the thermal energy stored in an object and that object's temperature.
2. How much energy (in kilojoules) is released or stored when each of the following occurs?

- a. A 230 lb football player is lifted to a height of 4.00 ft.
 - b. An 11.8 lb cat jumps from a height of 6.50 ft.
 - c. A 3.75 lb book falls off of a shelf that is 5.50 ft high.
3. Calculate how much energy (in kilojoules) is released or stored when each of the following occurs:
 - a. A 130 lb ice skater is lifted 7.50 ft off the ice.
 - b. A 48 lb child jumps from a height of 4.0 ft.
 - c. An 18.5 lb light fixture falls from a 10.0 ft ceiling.
 4. A car weighing 1438 kg falls off a bridge that is 211 ft high. Ignoring air resistance, how much energy is released when the car hits the water?
 5. A 1 tn roller coaster filled with passengers reaches a height of 28 m before accelerating downhill. How much energy is released when the roller coaster reaches the bottom of the hill? Assume no energy is lost due to friction.

ANSWERS

1.
 - a. The thermal energy content of an object is directly proportional to its mass.
 - b. The thermal energy content of an object is directly proportional to its temperature.
- 2.
3.
 - a. 1.3 kJ stored
 - b. 0.26 kJ released
 - c. 0.251 kJ released
- 4.
5. 250 kJ released
6. [1] As you will learn in Chapter 18 "Chemical Thermodynamics", the law of conservation of energy is also known as the first law of thermodynamics.
7. [2] Recall from Chapter 1 "Introduction to Chemistry" that weight is a force caused by the gravitational attraction between two masses, such as you and Earth.

8. [3] As you will learn in Chapter 6 "The Structure of Atoms", hot objects can also lose energy as radiant energy, such as heat or light. This energy is converted to heat when it is absorbed by another object. Hence radiant energy is equivalent to heat.
9. [4] The joule is named after the British physicist James Joule (1818–1889), an early worker in the field of energy.
10. [5] We specify the exact temperatures because the amount of energy needed to raise the temperature of 1 g of water 1°C varies slightly with elevation. To three significant figures, however, this amount is 1.00 cal over the temperature range 0°C–100°C.

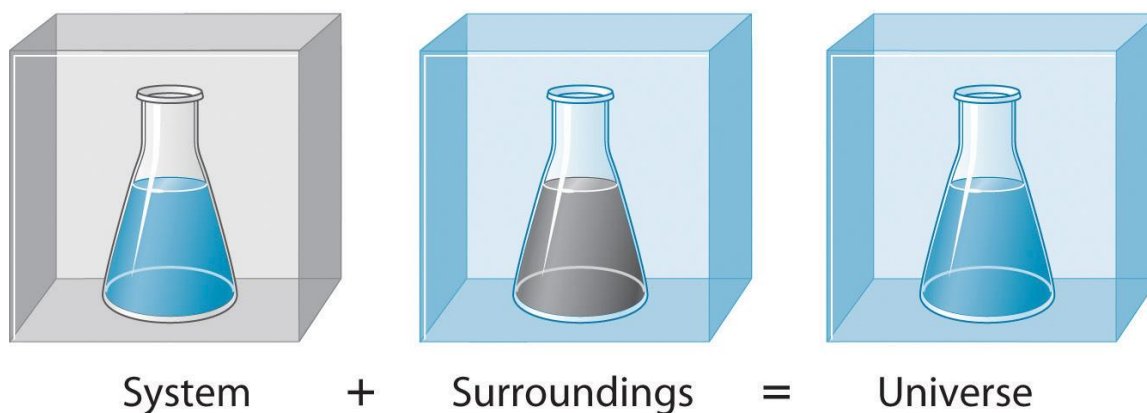
5.2 Enthalpy

LEARNING OBJECTIVES

1. To know the key features of a state function.
2. To use Hess's law and thermochemical cycles to calculate enthalpy changes of chemical reactions.

To study the flow of energy during a chemical reaction, we need to distinguish between a system, the small, well-defined part of the universe in which we are interested (such as a chemical reaction), and its surroundings, the rest of the universe, including the container in which the reaction is carried out (). In the discussion that follows, the mixture of chemical substances that undergoes a reaction is always the system, and the flow of heat can be from the system to the surroundings or vice versa.

Figure 5.5 A System and Its Surroundings



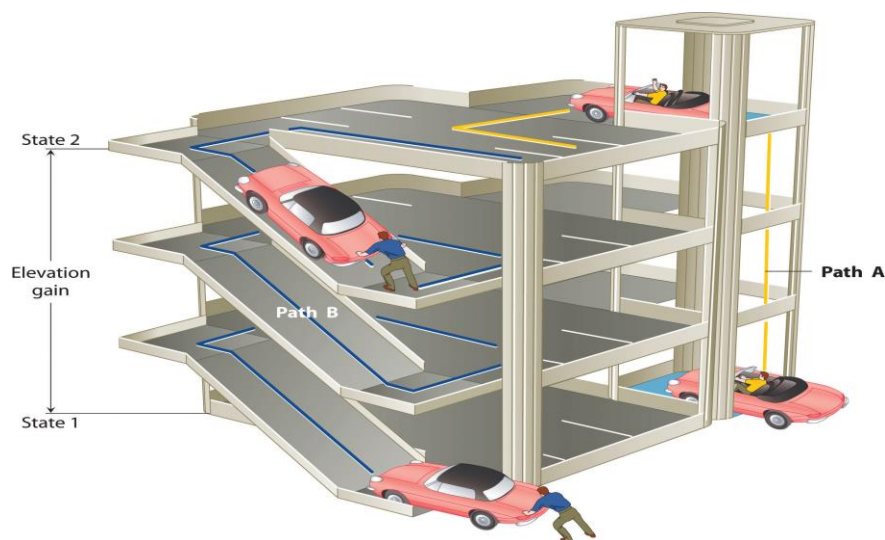
The system is that part of the universe we are interested in studying, such as a chemical reaction inside a flask. The surroundings are the rest of the universe, including the container in which the reaction is carried out.

Three kinds of systems are important in chemistry. An open system can exchange both matter and energy with its surroundings. A pot of boiling water is an open system because a burner supplies energy in the form of heat, and matter in the form of water vapor is lost as the water boils. A closed system can exchange energy but not matter with its surroundings. The sealed pouch of a ready-made dinner that is dropped into a pot of boiling water is a closed system because thermal energy is transferred to the system from the boiling water but no matter is exchanged (unless the pouch leaks, in which case it is no longer a closed system). An isolated system exchanges neither energy nor matter with the surroundings. Energy is always exchanged between a system and its surroundings, although this process may take place very slowly. A truly isolated system does not actually exist. An insulated thermos containing hot coffee approximates an isolated system, but eventually the coffee cools as heat is transferred to the surroundings. In all cases, the amount of heat lost by a system is equal to the amount of heat gained by its surroundings and vice versa. That is, *the total energy of a system plus its surroundings is constant*, which must be true if *energy is conserved*.

The state of a system is a complete description of a system at a given time, including its temperature and pressure, the amount of matter it contains, its chemical composition, and the physical state of the matter. A state function is a property of a system whose magnitude depends on only the present state of the system, not its previous history.

Temperature, pressure, volume, and potential energy are all state functions. The temperature of an oven, for example, is independent of however many steps it may have taken for it to reach that temperature. Similarly, the pressure in a tire is independent of how often air is pumped into the tire for it to reach that pressure, as is the final volume of air in the tire. Heat and work, on the other hand, are not state functions because they are *path dependent*. For example, a car sitting on the top level of a parking garage has the same potential energy whether it was lifted by a crane, set there by a helicopter, driven up, or pushed up by a group of students (). The amount of work expended to get it there, however, can differ greatly depending on the path chosen. If the students decided to carry the car to the top of the ramp, they would perform a great deal more work than if they simply pushed the car up the ramp (unless, of course, they neglected to release the parking brake, in which case the work expended would increase substantially!). The potential energy of the car is the same, however, no matter which path they choose.

Figure 5.6 Elevation as an Example of a State Function

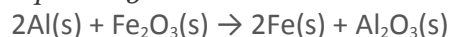


The change in elevation between state 1 (at the bottom of the parking garage) and state 2 (at the top level of the parking garage) is the same for both paths A and B; it does not depend on which path is taken from the bottom to the top. In contrast, the distance traveled and the work needed to reach the top do depend on which path is taken. Elevation is a state function, but distance and work are not state functions.

Direction of Heat Flow

The reaction of powdered aluminum with iron(III) oxide, known as the thermite reaction, generates an enormous amount of heat—enough, in fact, to melt steel (see chapter opening image). The balanced chemical equation for the reaction is as follows:

Equation 5.8



We can also write this chemical equation as

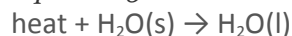
Equation 5.9



to indicate that heat is one of the products. Chemical equations in which heat is shown as either a reactant or a product are called *thermochemical equations*. In this reaction, the system consists of aluminum, iron, and oxygen atoms; everything else, including the container, makes up the surroundings. During the reaction, so much heat is produced that the iron liquefies. Eventually, the system cools; the iron solidifies as heat is transferred to the surroundings. A process in which heat (q) is transferred *from* a system *to* its surroundings is described as exothermic. By convention, $q < 0$ for an exothermic reaction.

When you hold an ice cube in your hand, heat from the surroundings (including your hand) is transferred to the system (the ice), causing the ice to melt and your hand to become cold. We can describe this process by the following thermochemical equation:

Equation 5.10



When heat is transferred *to* a system *from* its surroundings, the process is endothermic. By convention, $q > 0$ for an endothermic reaction.

Enthalpy of Reaction

We have stated that the change in energy (ΔE) is equal to the sum of the heat produced and the work performed (). Work done by an expanding gas is called *pressure-volume work*, also called *PV work*.

Consider, for example, a reaction that produces a gas, such as dissolving a piece of copper in concentrated nitric acid. The chemical equation for this reaction is as follows:

Equation 5.11



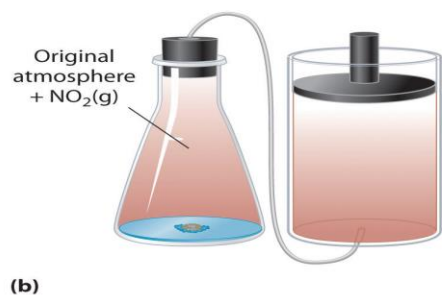
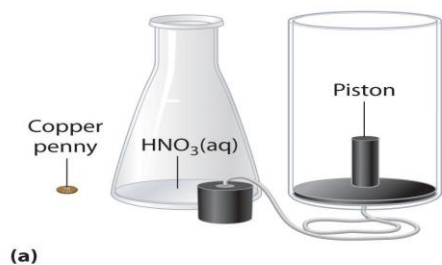
If the reaction is carried out in a closed system that is maintained at constant pressure by a movable piston, the piston will rise as nitrogen dioxide gas is formed (). The system is performing work by lifting the piston against the downward force exerted by the atmosphere (i.e., *atmospheric pressure*). We find the amount of *PV work* done by multiplying the external pressure P by the change in volume caused by movement of the piston (ΔV). At a constant external pressure (here, atmospheric pressure)

Equation 5.12

$$w = -P\Delta V$$

The negative sign associated with *PV work* done indicates that the system loses energy. If the volume increases at constant pressure ($\Delta V > 0$), the work done by the system is negative, indicating that a system has lost energy by performing work on its surroundings. Conversely, if the volume decreases ($\Delta V < 0$), the work done by the system is positive, which means that the surroundings have performed work on the system, thereby increasing its energy.

Figure 5.7 An Example of Work Performed by a Reaction Carried Out at Constant Pressure



(a) Initially, the system (a copper penny and concentrated nitric acid) is at atmospheric pressure. (b) When the penny is added to the nitric acid, the volume of NO_2 gas that is formed causes the piston to move upward to maintain the system at atmospheric pressure. In doing so, the system is performing work on its surroundings.

The symbol E represents the internal energy of a system, which is the sum of the kinetic energy and potential energy of all its components. It is the change in internal energy that produces heat plus work. To measure the energy changes that occur in chemical reactions, chemists usually use a related thermodynamic quantity called enthalpy (H) (from the Greek *enthalpein*, meaning “to warm”). The enthalpy of a system is defined as the sum of its internal energy E plus the product of its pressure P and volume V :

Equation 5.13

$$H = E + PV$$

Because internal energy, pressure, and volume are all state functions, enthalpy is also a state function.

If a chemical change occurs at constant pressure (for a given P , $\Delta P = 0$), the change in enthalpy (ΔH) is

Equation 5.14

$$\Delta H = \Delta(E + PV) = \Delta E + \Delta PV = \Delta E + P\Delta V$$

Substituting $q + w$ for ΔE and $-w$ for $P\Delta V$, we obtain

Equation 5.15

$$\Delta H = \Delta E + P\Delta V = q_p + w - w = q_p$$

The subscript p is used here to emphasize that this equation is true only for a process that occurs at constant pressure.

From we see that at constant pressure the change in enthalpy, ΔH of the system, defined as $H_{\text{final}} - H_{\text{initial}}$, is equal to the heat gained or lost.

Equation 5.16

$$\Delta H = H_{\text{final}} - H_{\text{initial}} = q_p$$

Just as with ΔE , because enthalpy is a state function, the magnitude of ΔH depends on only the initial and final states of the system, not on the path taken. Most important, the enthalpy change is the same even if the process does *not* occur at constant pressure.

Note the Pattern

To find ΔH , measure q_p .

When we study energy changes in chemical reactions, the most important quantity is usually the enthalpy of reaction (ΔH_{rxn}), the change in enthalpy that occurs during a reaction (such as the dissolution of a piece of copper in nitric acid). If heat flows from a system to its surroundings, the enthalpy of the system decreases, so ΔH_{rxn} is negative. Conversely, if heat flows from the surroundings to a system, the enthalpy of the system increases, so ΔH_{rxn} is positive. Thus $\Delta H_{\text{rxn}} < 0$ for an exothermic reaction, and $\Delta H_{\text{rxn}} > 0$ for an endothermic reaction. In chemical reactions, bond breaking requires an input of energy and is therefore an endothermic process, whereas bond making releases energy, which is an exothermic process. The sign conventions for heat flow and enthalpy changes are summarized in the following table:

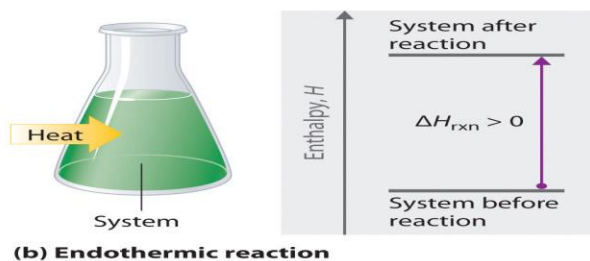
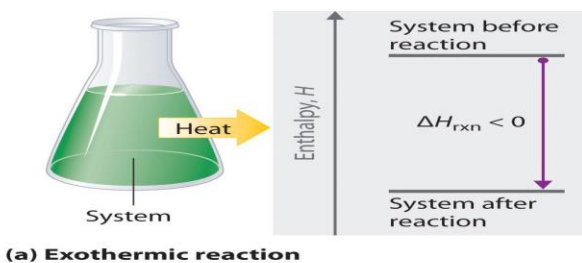
Reaction Type	q	ΔH_{rxn}
exothermic	< 0	< 0 (heat flows from a system to its surroundings)
endothermic	> 0	> 0 (heat flows from the surroundings to a system)

If ΔH_{rxn} is negative, then the enthalpy of the products is less than the enthalpy of the reactants; that is, *an exothermic reaction is energetically downhill* (part (a) in). Conversely, if ΔH_{rxn} is positive, then the enthalpy of the products is greater than the enthalpy of the reactants; thus, *an endothermic reaction is energetically uphill* (part (b) in). Two important characteristics of enthalpy and changes in enthalpy are summarized in the following discussion.

Note the Pattern

Bond breaking requires an input of energy; bond making releases energy.

Figure 5.8 The Enthalpy of Reaction



Reversing a reaction or a process changes the sign of ΔH . Ice *absorbs* heat when it melts (electrostatic interactions are broken), so liquid water must *release* heat when it freezes (electrostatic interactions are formed)

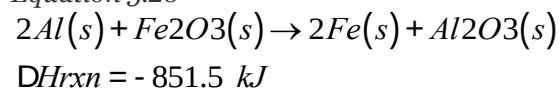
- **Enthalpy is an extensive property (like mass).** The magnitude of ΔH for a reaction is proportional to the amounts of the substances that react. For example, a large fire produces more heat than a single match, even though the chemical reaction—the combustion of wood—is the same in both cases. For this reason, the enthalpy change for a reaction is usually given in kilojoules per mole of a particular reactant or product. Consider , which describes the reaction of aluminum with iron(III) oxide (Fe_2O_3) at constant pressure. According to the reaction stoichiometry, 2 mol of Fe, 1 mol of Al_2O_3 , and 851.5 kJ of heat are produced for every 2 mol of Al and 1 mol of Fe_2O_3 consumed:

Equation 5.19



Thus $\Delta H = -851.5 \text{ kJ/mol}$ of Fe_2O_3 . We can also describe ΔH for the reaction as -425.8 kJ/mol of Al: because 2 mol of Al are consumed in the balanced chemical equation, we divide -851.5 kJ by 2. When a value for ΔH , in kilojoules rather than kilojoules per mole, is written after the reaction, as in , it is the value of ΔH corresponding to the reaction of the molar quantities of reactants as given in the balanced chemical equation:

Equation 5.20



If 4 mol of Al and 2 mol of Fe_2O_3 react, the change in

enthalpy is $2 \times (-851.5 \text{ kJ}) = -1703 \text{ kJ}$.

We can summarize the relationship between the amount of each substance and the enthalpy change for this reaction as follows:

Equation 5.21

$$-851.5 \text{ kJ} / 2 \text{ mol Al} = -425.8 \text{ kJ} / 1 \text{ mol Al} = -1703 \text{ kJ} / 4 \text{ mol Al}$$

The relationship between the magnitude of the enthalpy change and the mass of reactants is illustrated in Example 2.

EXAMPLE 2

Certain parts of the world, such as southern California and Saudi Arabia, are short of freshwater for drinking. One possible solution to the problem is to tow icebergs from Antarctica and then melt them as needed. If ΔH is 6.01 kJ/mol for the reaction $\text{H}_2\text{O(s)} \rightarrow \text{H}_2\text{O(l)}$ at 0°C and constant pressure, how much energy would be required to melt a moderately large iceberg with a mass of 1.00 million metric tons (1.00×10^6 metric tons)? (A metric ton is 1000 kg.)

Given: energy per mole of ice and mass of iceberg

Asked for: energy required to melt iceberg

Strategy:

A Calculate the number of moles of ice contained in 1 million metric tons (1.00×10^6 metric tons) of ice.

B Calculate the energy needed to melt the ice by multiplying the number of moles of ice in the iceberg by the amount of energy required to melt 1 mol of ice.

Solution:

A Because enthalpy is an extensive property, the amount of energy required to melt ice depends on the amount of ice present. We are given ΔH for the process—that is, the amount of energy needed to melt 1 mol (or 18.015 g) of ice—so we need to calculate the number of moles of ice in the iceberg and multiply that number by ΔH (+6.01 kJ/mol).

Because so much energy is needed to melt the iceberg, this plan would require a relatively inexpensive source of energy to be practical. To give you some idea of the scale of such an operation, the amounts of different energy sources equivalent to the amount of energy needed to melt the iceberg are shown in the table below.

Possible sources of the approximately 3.34×10^{11} kJ needed to melt a 1.00×10^6 metric ton iceberg

Combustion of 3.8×10^3 ft³ of natural gas

Combustion of 68,000 barrels of oil

Possible sources of the approximately 3.34×10^{11} kJ needed to melt a 1.00×10^6 metric ton iceberg

Combustion of 15,000 tons of coal

1.1×10^8 kilowatt-hours of electricity

Exercise

If 17.3 g of powdered aluminum are allowed to react with excess Fe_2O_3 , how much heat is produced?

Answer: 273 kJ

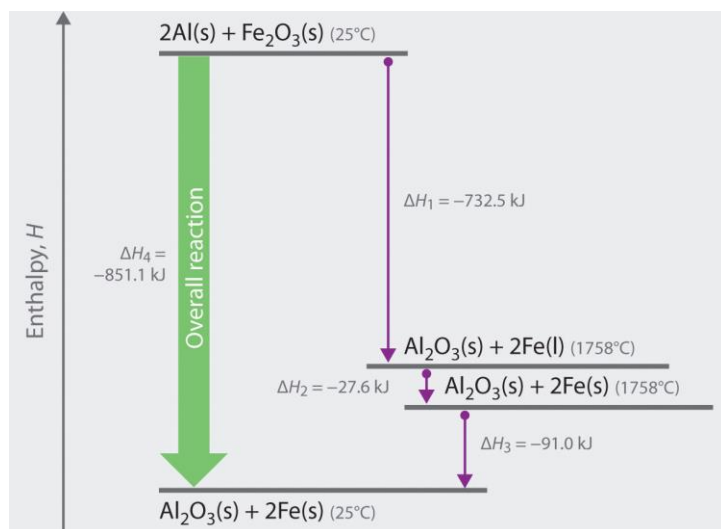
Hess's Law

Because enthalpy is a state function, the enthalpy change for a reaction depends on *only* two things: (1) the masses of the reacting substances and (2) the physical states of the reactants and products. It does *not* depend on the path by which reactants are converted to products. If you climbed a mountain, for example, the altitude change would not depend on whether you climbed the entire way without stopping or you stopped many times to take a break. If you stopped often, the overall change in altitude would be the sum of the changes in altitude for each short stretch climbed. Similarly, when we add two or more balanced chemical equations to obtain a net chemical equation, ΔH for the net reaction is the sum of the ΔH values for the individual reactions. This principle is called Hess's law, after the Swiss-born Russian chemist Germain Hess (1802–1850), a pioneer in the study of thermochemistry. Hess's law allows us to calculate ΔH values for reactions that are difficult to carry out directly by adding together the known ΔH values for individual steps that give the overall reaction, even though the overall reaction may not actually occur via those steps.

We can illustrate Hess's law using the thermite reaction. The overall reaction shown in can be viewed as occurring in three distinct steps with known ΔH values.

The net reaction in part (d) in is identical to . By Hess's law, the enthalpy change for part (d) is the sum of the enthalpy changes for parts (a), (b), and (c). In essence, Hess's law enables us to calculate the enthalpy change for the sum of a series of reactions without having to draw a diagram like that in

Figure 5.9 Energy Changes Accompanying the Thermite Reaction



Because enthalpy is a state function, the overall enthalpy change for the reaction of 2 mol of Al(s) with 1 mol of Fe₂O₃(s) is -851.1 kJ, whether the reaction occurs in a single step (ΔH₄, shown on the left) or in three hypothetical steps (shown on the right) that involve the successive formation of solid Al₂O₃ and liquid iron (ΔH₁), solid iron at 1758°C (ΔH₂), and solid iron at 25°C (ΔH₃). Thus ΔH₄ = ΔH₁ + ΔH₂ + ΔH₃, as stated by Hess's law.

Comparing parts (a) and (d) in also illustrates an important point: *The magnitude of ΔH for a reaction depends on the physical states of the reactants and the products (gas, liquid, solid, or solution).* When the product is liquid iron at its melting point (part (a) in), only 732.5 kJ of heat are released to the surroundings compared with 852 kJ when the product is solid iron at 25°C (part (d) in). The difference, 120 kJ, is the amount of energy that is released when 2 mol of liquid iron solidifies and cools to 25°C. It is important to specify the physical state of all reactants and products when writing a thermochemical equation.

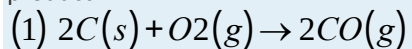
When using Hess's law to calculate the value of ΔH for a reaction, follow this procedure:

1. Identify the equation whose ΔH value is unknown and write individual reactions with known ΔH values that, when added together, will give the desired equation.
2. Arrange the chemical equations so that the reaction of interest is the sum of the individual reactions.
3. If a reaction must be reversed, change the sign of ΔH for that reaction. Additionally, if a reaction must be multiplied by a factor to obtain the correct number of moles of a substance, multiply its ΔH value by that same factor.
4. Add together the individual reactions and their corresponding ΔH values to obtain the reaction of interest and the unknown ΔH.

We illustrate how to use this procedure in Example 3.

EXAMPLE 3

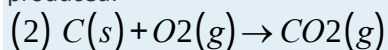
When carbon is burned with limited amounts of oxygen gas (O_2), carbon monoxide (CO) is the main product:



$$\Delta H_1 = -221.0 \text{ kJ}$$

When carbon is burned in excess O_2 , carbon dioxide (CO_2) is

produced:



$$\Delta H_2 = -393.5 \text{ kJ}$$

Use this information to calculate the enthalpy change per mole of CO for the reaction of CO with O_2 to give CO_2 .

Given: two balanced chemical equations and their ΔH values

Asked for: enthalpy change for a third reaction

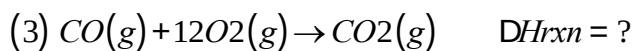
Strategy:

A After balancing the chemical equation for the overall reaction, write two equations whose ΔH values are known and that, when added together, give the equation for the overall reaction. (Reverse the direction of one or more of the equations as necessary, making sure to also reverse the sign of ΔH .)

B Multiply the equations by appropriate factors to ensure that they give the desired overall chemical equation when added together. To obtain the enthalpy change per mole of CO, write the resulting equations as a sum, along with the enthalpy change for each.

Solution:

A We begin by writing the balanced chemical equation for the reaction of interest:



There are at least two ways to solve this problem using Hess's law and the data provided. The simplest is to write two equations that can be added together to give the desired equation and for which the enthalpy changes are known.

Because we have reversed the direction of the reaction, the sign of ΔH is changed.

The sum of reactions A and B is reaction C, which corresponds to the combustion of 2 mol of carbon to give CO_2 . From Hess's law, $\Delta H_A + \Delta H_B = \Delta H_C$, and we are given ΔH for reactions A and C. Substituting the appropriate values gives

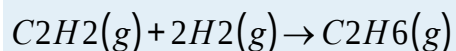
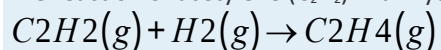
$$-221.0 \text{ kJ} + \Delta H_B = -787.0$$

$$\Delta H_B = -566.0 \text{ kJ}$$

This is again the enthalpy change for the conversion of 2 mol of CO to CO₂. The enthalpy change for the conversion of 1 mol of CO to CO₂ is therefore $-566.0 \div 2 = -283.0$ kJ/mol of CO, which is the same result we obtained earlier. As you can see, *there may be more than one correct way to solve a problem*.

Exercise

The reaction of acetylene (C₂H₂) with hydrogen (H₂) can produce either ethylene (C₂H₄) or ethane (C₂H₆):



What is ΔH for the reaction of C₂H₄ with H₂ to form C₂H₆?

Answer: -136.3 kJ/mol of C₂H₄

Enthalpies of Formation and Reaction

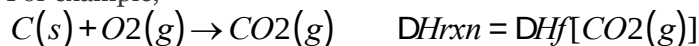
, , and presented a wide variety of chemical reactions, and you learned how to write balanced chemical equations that include all the reactants and the products except heat. One way to report the heat absorbed or released would be to compile a massive set of reference tables that list the enthalpy changes for all possible chemical reactions, which would require an incredible amount of effort. Fortunately, Hess's law allows us to calculate the enthalpy change for virtually any conceivable chemical reaction using a relatively small set of tabulated data, such as the following:

- Enthalpy of combustion (ΔH_{comb}): Enthalpy changes have been measured for the combustion of virtually any substance that will burn in oxygen; these values are usually reported as the enthalpy of combustion per mole of substance.
- Enthalpy of fusion (ΔH_{fus}): The enthalpy change that accompanies the melting, or *fusion*, of 1 mol of a substance; these values have been measured for almost all the elements and for most simple compounds.
- Enthalpy of vaporization (ΔH_{vap}): The enthalpy change that accompanies the vaporization of 1 mol of a substance; these values have also been measured for nearly all the elements and for most volatile compounds.
- Enthalpy of solution (ΔH_{soln}): The enthalpy change when a specified amount of solute dissolves in a given quantity of solvent.
- Enthalpy of formation (ΔH_f): The enthalpy change for the formation of 1 mol of a compound from its component elements, such as the formation of carbon dioxide from carbon and oxygen. The corresponding relationship is

Equation 5.23



For example,



- The sign convention for ΔH_f is the same as for any enthalpy change: $\Delta H_f < 0$ if heat is released when elements combine to form a compound and $\Delta H_f > 0$ if heat is absorbed. The values of ΔH_{vap} and ΔH_{fus} for some common substances are listed in Table 5.1. These values are used in enthalpy calculations when any of the substances undergoes a change of physical state during a reaction.

Table 5.1 Enthalpies of Vaporization and Fusion for Selected Substances at Their Boiling Points and Melting Points

Substance	ΔH_{vap} (kJ/mol)	ΔH_{fus} (kJ/mol)
argon (Ar)	6.3	1.3
methane (CH ₄)	9.2	0.84
ethanol (CH ₃ CH ₂ OH)	39.3	7.6
benzene (C ₆ H ₆)	31.0	10.9
water (H ₂ O)	40.7	6.0
mercury (Hg)	59.0	2.29
iron (Fe)	340	14

Note the Pattern

The sign convention is the same for all enthalpy changes: negative if heat is released by the system and positive if heat is absorbed by the system.

Standard Enthalpies of Formation

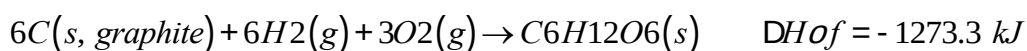
The magnitude of ΔH for a reaction depends on the physical states of the reactants and the products (gas, liquid, solid, or solution), the pressure of any gases present, and the temperature at which the reaction is carried out. To avoid confusion caused by differences in reaction conditions and ensure uniformity of data, the scientific community has selected a specific set of conditions under which enthalpy changes are measured. These standard conditions serve as a reference point for measuring differences in enthalpy, much as sea level is the reference point for measuring the height of a mountain or for reporting the altitude of an airplane.

The standard conditions for which most thermochemical data are tabulated are a pressure of 1 atmosphere (atm) for all gases and a concentration of 1 M for all species in solution (1 mol/L). In addition, each pure

substance must be in its standard state. This is usually its most stable form at a pressure of 1 atm at a specified temperature. We assume a temperature of 25°C (298 K) for all enthalpy changes given in this text, unless otherwise indicated. Enthalpies of formation measured under these conditions are called standard enthalpies of formation. *The standard enthalpy of formation of any element in its standard state is zero by definition.* For example, although oxygen can exist as ozone (O₃), atomic oxygen (O), and molecular oxygen (O₂), O₂ is the most stable form at 1 atm pressure and 25°C. Similarly, hydrogen is H₂(g), not atomic hydrogen (H). Graphite and diamond are both forms of elemental carbon, but because graphite is more stable at 1 atm pressure and 25°C.

The standard enthalpy of formation of glucose from the elements at 25°C is the enthalpy change for the following reaction:

Equation 5.24



It is not possible to measure the value of ΔH_{of} for glucose, -1273.3 kJ/mol, by simply mixing appropriate amounts of graphite, O₂, and H₂ and measuring the heat evolved as glucose is formed; the reaction shown in does not occur at a measurable rate under any known conditions. Glucose is not unique; most compounds cannot be prepared by the chemical equations that define their standard enthalpies of formation. Instead, values of ΔH_{of} are obtained using Hess's law and standard enthalpy changes that have been measured for other reactions, such as combustion reactions. Values of ΔH_{of} for an extensive list of compounds are given in Table 5.2. Note that values are always reported in kilojoules per mole of the substance of interest. Also notice in Table 5.2 that the standard enthalpy of formation of O₂(g) is zero because it is the most stable form of oxygen in its standard state.

EXAMPLE 4

For the formation of each compound, write a balanced chemical equation corresponding to the standard enthalpy of formation of each compound.

- HCl(g)
- MgCO₃(s)
- CH₃(CH₂)₁₄CO₂H(s) (palmitic acid)

Given: compound

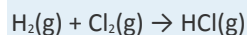
Asked for: balanced chemical equation for its formation from elements in standard states

Strategy:

Use to identify the standard state for each element. Write a chemical equation that describes the formation of the compound from the elements in their standard states and then balance it so that 1 mol of product is made.

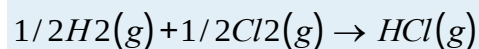
Solution:

a. Hydrogen chloride contains one atom of hydrogen and one atom of chlorine. Because the standard states of elemental hydrogen and elemental chlorine are $H_2(g)$ and $Cl_2(g)$, respectively, the unbalanced chemical equation is

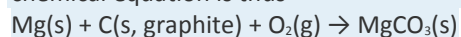


Fractional coefficients are required in this case because values are reported for 1 mol of the product, HCl.

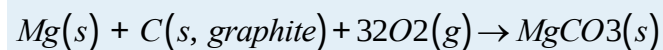
Multiplying both $H_2(g)$ and $Cl_2(g)$ by 1/2 balances the equation:



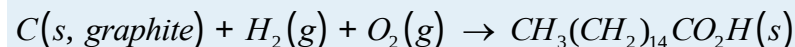
The standard states of the elements in this compound are $Mg(s)$, $C(s, \text{graphite})$, and $O_2(g)$. The unbalanced chemical equation is thus



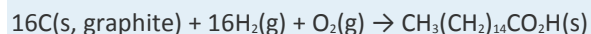
This equation can be balanced by inspection to give



Palmitic acid, the major fat in meat and dairy products, contains hydrogen, carbon, and oxygen, so the unbalanced chemical equation for its formation from the elements in their standard states is as follows:



a. There are 16 carbon atoms and 32 hydrogen atoms in 1 mol of palmitic acid, so the balanced chemical equation is



Exercise

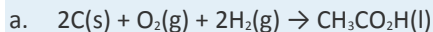
For the formation of each compound, write a balanced chemical equation corresponding to the standard enthalpy of formation of each compound.

a. $NaCl(s)$

b. $H_2SO_4(l)$

c. $CH_3CO_2H(l)$ (acetic acid)

Answer:

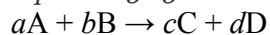


Standard Enthalpies of Reaction

Tabulated values of standard enthalpies of formation can be used to calculate enthalpy changes for *any* reaction involving substances whose values are known.

The standard enthalpy of reaction (ΔH_{rxn}) is the enthalpy change that occurs when a reaction is carried out with all reactants and products in their standard states. Consider the general reaction

Equation 5.25



where A, B, C, and D are chemical substances and *a*, *b*, *c*, and *d* are their stoichiometric coefficients. The magnitude of ΔH_{rxn} is the sum of the standard enthalpies of formation of the products, each multiplied by its appropriate coefficient, minus the sum of the standard enthalpies of formation of the reactants, also multiplied by their coefficients:

Equation 5.26

$$\Delta H_{\text{rxn}} = [c\Delta H_{\text{f}}(\text{C}) + d\Delta H_{\text{f}}(\text{D})]_{\text{products}} - [a\Delta H_{\text{f}}(\text{A}) + b\Delta H_{\text{f}}(\text{B})]_{\text{reactants}}$$

More generally, we can write

Equation 5.27

$$\Delta H_{\text{rxn}} = \Sigma m\Delta H_{\text{f}}(\text{products}) - \Sigma n\Delta H_{\text{f}}(\text{reactants})$$

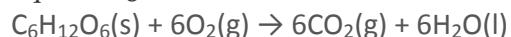
where the symbol Σ means “sum of” and *m* and *n* are the stoichiometric coefficients of each of the products and the reactants, respectively. “Products minus reactants” summations such as arise from the fact that enthalpy is a state function. Because many other thermochemical quantities are also state functions, “products minus reactants” summations are very common in chemistry; we will encounter many others in subsequent chapters.

Note the Pattern

“Products minus reactants” summations are typical of state functions.

To demonstrate the use of tabulated values, we will use them to calculate for the combustion of glucose, the reaction that provides energy for your brain:

Equation 5.28



Using , we write

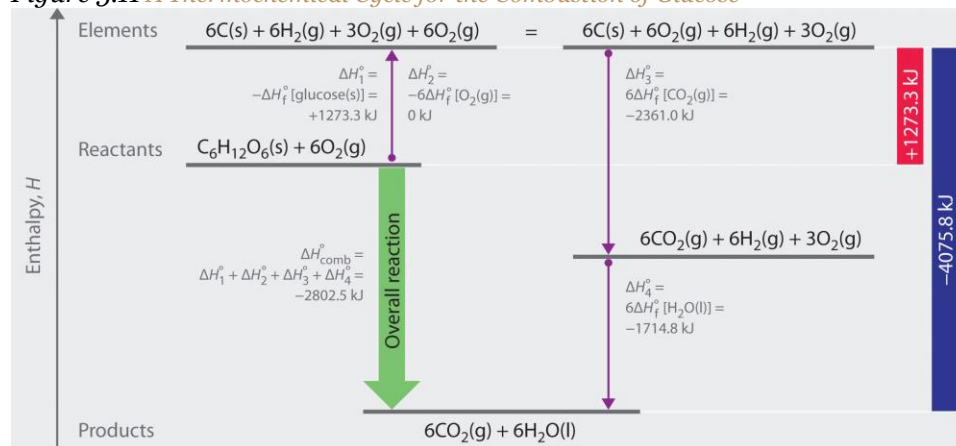
Equation 5.29

$$\Delta H_{\text{rxn}} = \{6\Delta H_f^\circ[\text{CO}_2(\text{g})] + 6\Delta H_f^\circ[\text{H}_2\text{O}(\text{l})]\} - \{\Delta H_f^\circ[\text{C}_6\text{H}_{12}\text{O}_6(\text{s})] + 6\Delta H_f^\circ[\text{O}_2(\text{g})]\}$$

We can use to calculate $\Delta H_{\text{comb}}^\circ$ for glucose because enthalpy is a state function. The figure shows two pathways from reactants (middle left) to products (bottom). The more direct pathway is the downward green arrow labeled Overall reaction. The alternative hypothetical pathway consists of four separate reactions that convert the reactants to the elements in their standard states (upward purple arrow at left) and then convert the elements into the desired products (downward purple arrows at right). The reactions that convert the reactants to the elements are the reverse of the equations that define the values of the reactants.

(Recall that when we reverse a reaction, we must also reverse the sign of the accompanying enthalpy change.) The overall enthalpy change for conversion of the reactants (1 mol of glucose and 6 mol of O_2) to the elements is therefore +1273.3 kJ.

Figure 5.11 A Thermochemical Cycle for the Combustion of Glucose



The reactions that convert the elements to final products (downward purple arrows in) are identical to those used to define the values of the products.

The overall enthalpy change for the conversion of the elements to products (6 mol of carbon dioxide and 6 mol of liquid water) is therefore -4075.8 kJ. Because enthalpy is a state function, the difference in enthalpy between an initial state and a final state can be computed using *any* pathway that connects the two. Thus the enthalpy change for the combustion of glucose to carbon dioxide and water is the sum of the enthalpy changes for the conversion of

glucose and oxygen to the elements (+1273.3 kJ) and for the conversion of the elements to carbon dioxide and water (-4075.8 kJ):

Equation 5.31

$$\Delta H_{\text{comb}} = +1273.3 \text{ kJ} + (-4075.8 \text{ kJ}) = -2802.5 \text{ kJ}$$

This is the same result we obtained using the “products minus reactants” rule () and values. The two results must be the same because is just a more compact way of describing the thermochemical cycle shown in.

EXAMPLE 5

Long-chain fatty acids such as palmitic acid [$\text{CH}_3(\text{CH}_2)_{14}\text{CO}_2\text{H}$] are one of the two major sources of energy in our diet.

Use the data in to calculate for the combustion of palmitic acid. Based on the energy released in combustion *per gram*, which is the better fuel—glucose or palmitic acid?

Given: compound and values ΔH_{of}

Asked for: ΔH_{comb} per mole and per gram

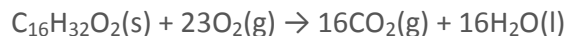
Strategy:

A After writing the balanced chemical equation for the reaction, use and the values from to calculate the energy released by the combustion of 1 mol of palmitic acid.

B Divide this value by the molar mass of palmitic acid to find the energy released from the combustion of 1 g of palmitic acid. Compare this value with the value calculated infor the combustion of glucose to determine which is the better fuel.

Solution:

A To determine the energy released by the combustion of palmitic acid, we need to calculate it. As always, the first requirement is a balanced chemical equation:



Using (“products minus reactants”) with values from (and omitting the physical states of the reactants and products to save space) gives

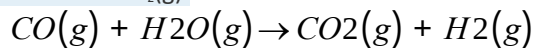
$$\begin{aligned} \Delta H_{\text{comb}} &= \sum m \Delta H_{\text{of}} (\text{products}) - \sum n \Delta H_{\text{of}} (\text{reactants}) \\ &= [16(-393.5 \text{ kJ/mol CO}_2) + 16(-285.8 \text{ kJ/mol H}_2\text{O})] \\ &\quad - [(-891.5 \text{ kJ/mol C}_{16}\text{H}_{32}\text{O}_2) + 23(0 \text{ kJ/mol O}_2)] \\ &= -9977.3 \text{ kJ/mol} \end{aligned}$$

This is the energy released by the combustion of 1 mol of palmitic acid.

The combustion of fats such as palmitic acid releases more than twice as much energy per gram as the combustion of sugars such as glucose. This is one reason many people try to minimize the fat content in their diets to lose weight.

Exercise

Use the data to calculate ΔH_{rxn} for the *water–gas shift reaction*, which is used industrially on an enormous scale to obtain $\text{H}_2(\text{g})$:



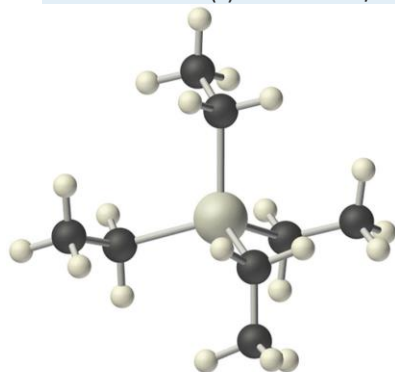
water – gas shift reaction

Answer: -41.2 kJ/mol

We can also measure the enthalpy change for another reaction, such as a combustion reaction, and then use it to calculate a compound's ΔH_o which we cannot obtain otherwise. This procedure is illustrated in Example 6.

EXAMPLE 6

Beginning in 1923, tetraethyllead $[(\text{C}_2\text{H}_5)_4\text{Pb}]$ was used as an antiknock additive in gasoline in the United States. Its use was completely phased out in 1986 because of the health risks associated with chronic lead exposure. Tetraethyllead is a highly poisonous, colorless liquid that burns in air to give an orange flame with a green halo. The combustion products are $\text{CO}_2(\text{g})$, $\text{H}_2\text{O}(\text{l})$, and red $\text{PbO}(\text{s})$. What is the standard enthalpy of formation of tetraethyllead, given that is -19.29 kJ/g for the combustion of tetraethyllead and of red $\text{PbO}(\text{s})$ is -219.0 kJ/mol ?



Tetraethyllead

Given: reactant, products, and ΔH_o

Asked for: ΔH_{of}

of reactant

Strategy:

A Write the balanced chemical equation for the combustion of tetraethyllead. Then insert the appropriate quantities

into to get the equation for ΔH_o of tetraethyllead.

B Convert ΔH_{comb} per gram given in the problem to ΔH_{comb} per mole by multiplying ΔH_{comb} per gram by the molar mass of tetraethyllead.

C Use to obtain values of ΔH_o for the other reactants and products. Insert these values into the equation

for **C** Use to obtain values of ΔH_o for the other reactants and products. Insert these values into the equation for of tetraethyllead and solve the equation.

Solution:

A The balanced chemical equation for the combustion reaction is as follows:



Using gives

$$\Delta H_{\text{comb}} = [2\Delta H_o(\text{PbO}) + 16\Delta H_o(\text{CO}_2) + 20\Delta H_o(\text{H}_2\text{O})] - \{2\Delta H_o[(\text{C}_2\text{H}_5)_4\text{Pb}] + 27\Delta H_o(\text{O}_2)\}$$

Solving for $\Delta H_o[(\text{C}_2\text{H}_5)_4\text{Pb}]$ gives

$$\Delta H_o[(\text{C}_2\text{H}_5)_4\text{Pb}] = \Delta H_o(\text{PbO}) + 8\Delta H_o(\text{CO}_2) + 10\Delta H_o(\text{H}_2\text{O}) - 27\Delta H_o(\text{O}_2) - \Delta H_{\text{comb}}/2$$

B The magnitude of ΔH_{comb} is given in the problem in kilojoules per gram of tetraethyllead. We must

therefore multiply this value by the molar mass of tetraethyllead (323.44 g/mol) to get ΔH_{comb} for 1 mol of tetraethyllead:

$$\Delta H_{\text{comb}} = (-19.29 \text{ kJ/g})(323.44 \text{ g/mol}) = -6329 \text{ kJ/mol}$$

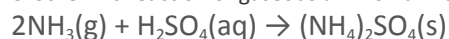
C Inserting the appropriate values into the equation for $\Delta H_o[(\text{C}_2\text{H}_5)_4\text{Pb}]$ gives

$$= -219.0 \text{ kJ} - 3148 \text{ kJ} - 2858 \text{ kJ} - 0 \text{ kJ} + 6240 \text{ kJ/mol}$$

$$= 15 \text{ kJ/mol}$$

Exercise

Ammonium sulfate $[(\text{NH}_4)_2\text{SO}_4]$ is used as a fire retardant and wood preservative; it is prepared industrially by the highly exothermic reaction of gaseous ammonia with sulfuric acid:



The value of ΔH_{rxn} is $-2805 \text{ kJ/g H}_2\text{SO}_4$. Use the data in to calculate the standard enthalpy of formation of ammonium sulfate (in kilojoules per mole).

Answer: -1181 kJ/mol

Enthalpies of Solution and Dilution

Physical changes, such as melting or vaporization, and chemical reactions, in which one substance is converted to another, are accompanied by changes in enthalpy. Two other kinds of changes that are accompanied by changes in enthalpy are the dissolution of solids and the dilution of concentrated solutions.

The dissolution of a solid can be described as follows:

Equation 5.32



The values of ΔH_{soln} for some common substances are given in . The sign and the magnitude of ΔH_{soln} depend on specific attractive and repulsive interactions between the solute and the solvent; these factors will be discussed in . When substances dissolve, the process can be either exothermic ($\Delta H_{\text{soln}} < 0$) or endothermic ($\Delta H_{\text{soln}} > 0$), as you can see from the data in .

Table 5.2 Enthalpies of Solution at 25°C of Selected Ionic Compounds in Water (in kJ/mol)

	Anion				
Cation	Fluoride	Chloride	Bromide	Iodide	Hydroxide
lithium	4.7	−37.0	−48.8	−63.3	−23.6
sodium	0.9	3.9	−0.6	−7.5	−44.5
potassium	−17.7	17.2	19.9	20.3	−57.6
ammonium	−1.2	14.8	16.8	13.7	—
silver	−22.5	65.5	84.4	112.2	—
magnesium	−17.7	−160.0	−185.6	−213.2	2.3
calcium	11.5	−81.3	−103.1	−119.7	−16.7
	Nitrate	Acetate	Carbonate	Sulfate	
lithium	−2.5	—	−18.2	−29.8	
sodium	20.5	−17.3	−26.7	2.4	
potassium	34.9	−15.3	−30.9	23.8	
ammonium	25.7	−2.4	—	6.6	
silver	22.6	—	22.6	17.8	
magnesium	−90.9	—	−25.3	−91.2	
calcium	−19.2	—	−13.1	−18.0	

Substances with large positive or negative enthalpies of solution have commercial applications as instant cold or hot packs. Single-use versions of these products are based on the dissolution of either calcium chloride (CaCl_2 , $\Delta H_{\text{soln}} = -81.3 \text{ kJ/mol}$) or ammonium nitrate (NH_4NO_3 , $\Delta H_{\text{soln}} = +25.7 \text{ kJ/mol}$). Both types consist of a plastic bag that contains about 100 mL of water plus a dry chemical (40 g of CaCl_2 or 30 g of NH_4NO_3) in a separate plastic pouch. When the pack is twisted or struck sharply, the inner plastic bag of water ruptures, and the salt dissolves in the water. If the salt is CaCl_2 , heat is released to produce a solution with a temperature of about 90°C ; hence the product is an “instant hot compress.” If the salt is NH_4NO_3 , heat is absorbed when it dissolves, and the temperature drops to about 0° for an “instant cold pack.”

A similar product based on the *precipitation* of sodium acetate, not its dissolution, is marketed as a reusable hand warmer (). At high temperatures, sodium acetate forms a highly concentrated aqueous solution. With cooling, an unstable *supersaturated* solution containing excess solute is formed. When the pack is agitated, sodium acetate trihydrate [$\text{CH}_3\text{CO}_2\text{Na} \cdot 3\text{H}_2\text{O}$] crystallizes, and heat is evolved:

$$\text{Na} + (\text{aq}) + \text{CH}_3\text{CO}_2 - (\text{aq}) + 3\text{H}_2\text{O}(\text{l}) \rightarrow \text{CH}_3\text{CO}_2\text{Na} \cdot 3\text{H}_2\text{O}(\text{s}) \quad \Delta H = - \Delta H_{\text{soln}} = - 19.7 \text{ kJ/mol}$$
A bag of concentrated sodium acetate solution can be carried until heat is needed, at which time vigorous agitation induces crystallization and heat is released. The pack can be reused after it is immersed in hot water until the sodium acetate redissolves.

The amount of heat released or absorbed when a substance is dissolved is not a constant; it depends on the final concentration of the solute. The ΔH_{soln} values given previously and in , for example, were obtained by measuring the enthalpy changes at various concentrations and extrapolating the data to infinite dilution.

Because ΔH_{soln} depends on the concentration of the solute, diluting a solution can produce a change in enthalpy. If the initial dissolution process is exothermic ($\Delta H < 0$), then the dilution process is also exothermic. This phenomenon is particularly relevant for strong acids and bases, which are often sold or stored as concentrated aqueous solutions. If water is added to a concentrated solution of sulfuric acid (which is 98% H_2SO_4 and 2% H_2O) or sodium hydroxide, the heat released by the large negative ΔH can cause the solution to boil. Dangerous spattering of strong acid or base can be avoided if the concentrated acid or base is slowly added to water, so that the heat liberated is largely dissipated by the water. Thus you should **never add water to a strong acid or base**; a useful way to avoid the danger is to remember: *Add water to acid and get blasted!*

KEY EQUATIONS

definition of enthalpy

$$: H = E + PV$$

pressure-volume work

$$: w = -P\Delta V$$

enthalpy change at constant pressure

$$: \Delta H = \Delta E + P\Delta V$$

$$: \Delta H = q_p$$

Summary

In chemistry, the small part of the universe that we are studying is the **system**, and the rest of the universe is the **surroundings**. **Open systems** can exchange both matter and energy with their surroundings, **closed systems** can exchange energy but not matter with their surroundings, and **isolated systems** can exchange neither matter nor energy with their surroundings. A **state function** is a property of a system that depends on only its present **state**, not its history. A reaction or process in which heat is transferred from a system to its surroundings is **exothermic**. A reaction or process in which heat is transferred to a system from its surroundings is **endothermic**.

Enthalpy is a state function used to measure the heat transferred from a system to its surroundings or vice versa at constant pressure. Only the **change in enthalpy** (ΔH) can be measured. A negative ΔH means that heat flows from a system to its surroundings; a positive ΔH means that heat flows into a system from its surroundings. For a chemical reaction, the **enthalpy of reaction** (ΔH_{rxn}) is the difference in enthalpy between products and reactants; the units of ΔH_{rxn} are kilojoules per mole. Reversing a chemical reaction reverses the sign of ΔH_{rxn} . The magnitude of ΔH_{rxn} also depends on the physical state of the reactants and the products because processes such as melting solids or vaporizing liquids are also accompanied by enthalpy changes: the **enthalpy of fusion** (ΔH_{fus}) and the **enthalpy of vaporization** (ΔH_{vap}), respectively. The overall enthalpy change for a series of reactions is the sum of the enthalpy changes for the individual reactions, which is **Hess's law**. The **enthalpy of combustion** (ΔH_{comb}) is the enthalpy change that occurs when a substance is burned in excess oxygen. The **enthalpy of formation** (ΔH_{f}) is the enthalpy change that accompanies the formation of a compound from its elements. **Standard enthalpies of formation** are determined under **standard conditions**: a pressure of 1 atm for gases and a concentration of 1 M for species in solution, with all pure substances

present in their **standard states** (their most stable forms at 1 atm pressure and the temperature of the measurement). The standard heat of formation of any element in its most stable form is defined to be zero. The **standard enthalpy of reaction** (can be calculated from the sum of the **standard enthalpies of formation** of the products (each multiplied by its stoichiometric coefficient) minus the sum of the standard enthalpies of formation of the reactants (each multiplied by its stoichiometric coefficient)—the “products minus reactants” rule. The **enthalpy of solution** (ΔH_{soln}) is the heat released or absorbed when a specified amount of a solute dissolves in a certain quantity of solvent at constant pressure.

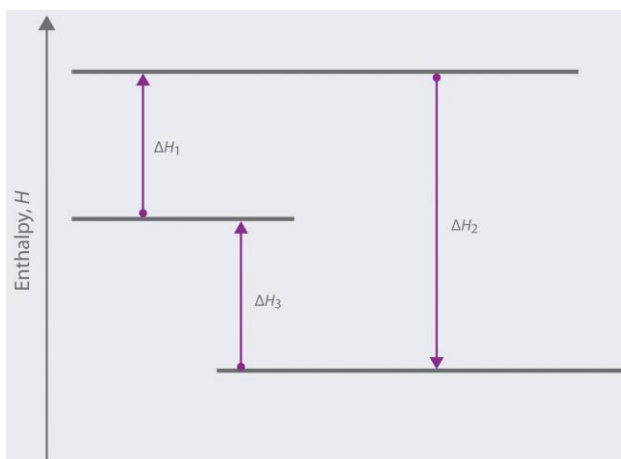
KEY TAKEAWAY

- Enthalpy is a state function whose change indicates the amount of heat transferred from a system to its surroundings or vice versa, at constant pressure.

CONCEPTUAL PROBLEMS

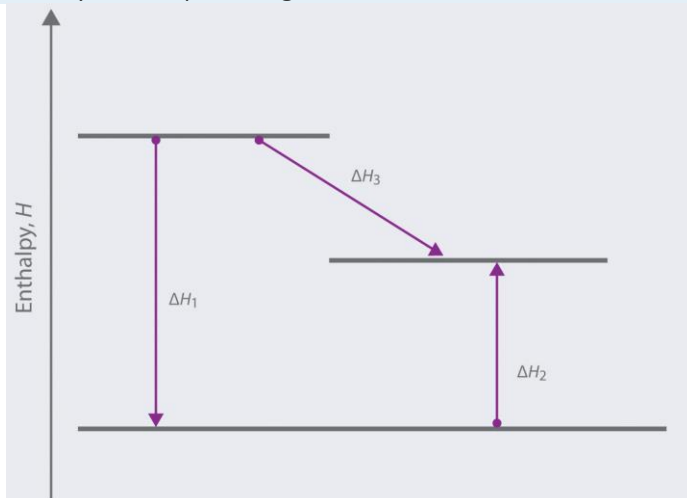
Please be sure you are familiar with the topics discussed in Essential Skills 4 () before proceeding to the Conceptual Problems.

1. Heat implies the flow of energy from one object to another. Describe the energy flow in an
 - a. exothermic reaction.
 - b. endothermic reaction.
2. Based on the following energy diagram,
 - a. write an equation showing how the value of ΔH_2 could be determined if the values of ΔH_1 and ΔH_3 are known.
 - b. identify each step as being exothermic or endothermic.



3. Based on the following energy diagram,

- write an equation showing how the value of ΔH_3 could be determined if the values of ΔH_1 and ΔH_2 are known.
- identify each step as being exothermic or endothermic.



- When a thermometer is suspended in an insulated thermos that contains a block of ice, the temperature recorded on the thermometer drops. Describe the direction of heat flow.
- In each scenario, the system is defined as the mixture of chemical substances that undergoes a reaction. State whether each process is endothermic or exothermic.
 - Water is added to sodium hydroxide pellets, and the flask becomes hot.
 - The body metabolizes glucose, producing carbon dioxide and water.
 - Ammonium nitrate crystals are dissolved in water, causing the solution to become cool.
- In each scenario, the system is defined as the mixture of chemical substances that undergoes a reaction. Determine whether each process is endothermic or exothermic.
 - Concentrated acid is added to water in a flask, and the flask becomes warm.

- b. Water evaporates from your skin, causing you to shiver.
- c. A container of ammonium nitrate detonates.
4. Is Earth's environment an isolated system, an open system, or a closed system? Explain your answer.
5. Why is it impossible to measure the absolute magnitude of the enthalpy of an object or a compound?
6. Determine whether energy is consumed or released in each scenario. Explain your reasoning.
 - a. A leaf falls from a tree.
 - b. A motorboat maneuvers against a current.
 - c. A child jumps rope.
 - d. Dynamite detonates.
 - e. A jogger sprints down a hill.
7. The chapter states that enthalpy is an extensive property. Why? Describe a situation that illustrates this fact.
8. The enthalpy of a system is affected by the physical states of the reactants and the products. Explain why.
9. Is the distance a person travels on a trip a state function? Why or why not?
10. Describe how Hess's law can be used to calculate the enthalpy change of a reaction that cannot be observed directly.
11. When you apply Hess's law, what enthalpy values do you need to account for each change in physical state?
 - a. the melting of a solid
 - b. the conversion of a gas to a liquid
 - c. the solidification of a liquid
 - d. the dissolution of a solid into water
12. In their elemental form, A_2 and B_2 exist as diatomic molecules. Given the following reactions, each
13. For the formation of each compound, write a balanced chemical equation corresponding to the standard enthalpy of formation of each compound.
 - a. HBr
 - b. CH_3OH
 - c. $NaHCO_3$
14. Describe the distinction between ΔH_{soln} and ΔH_f .
15. Does adding water to concentrated acid result in an endothermic or an exothermic process?

16. The following table lists values for some ionic compounds. If 1 mol of each solute is dissolved in 500 mL of water, rank the resulting solutions from warmest to coldest.

Compound	(kJ/mol)
KOH	-57.61
LiNO ₃	-2.51
KMnO ₄	43.56
NaC ₂ H ₃ O ₂	-17.32

NUMERICAL PROBLEMS

Please be sure you are familiar with the topics discussed in Essential Skills 4 () before proceeding to the Numerical Problems.

- Using ΔH_f° , calculate ΔH_{rxn}° for each chemical reaction.
 - $2\text{Mg(s)} + \text{O}_2\text{(g)} \rightarrow 2\text{MgO(s)}$
 - $\text{CaCO}_3\text{(s, calcite)} \rightarrow \text{CaO(s)} + \text{CO}_2\text{(g)}$
 - $\text{AgNO}_3\text{(s)} + \text{NaCl(s)} \rightarrow \text{AgCl(s)} + \text{NaNO}_3\text{(s)}$
 - $2\text{Na(s)} + \text{Pb(NO}_3)_2\text{(s)} \rightarrow 2\text{NaNO}_3\text{(s)} + \text{Pb(s)}$
 - $\text{Na}_2\text{CO}_3\text{(s)} + \text{H}_2\text{SO}_4\text{(l)} \rightarrow \text{Na}_2\text{SO}_4\text{(s)} + \text{CO}_2\text{(g)} + \text{H}_2\text{O(l)}$
 - $2\text{KClO}_3\text{(s)} \rightarrow 2\text{KCl(s)} + 3\text{O}_2\text{(g)}$
 - $\text{Fe(s)} + \text{CuCl}_2\text{(s)} \rightarrow \text{FeCl}_2\text{(s)} + \text{Cu(s)}$
 - $(\text{NH}_4)_2\text{SO}_4\text{(s)} + \text{Ca(OH)}_2\text{(s)} \rightarrow \text{CaSO}_4\text{(s)} + \text{NH}_3\text{(g)} + \text{H}_2\text{O(l)}$
 - $\text{Pb(s)} + \text{PbO}_2\text{(s)} + \text{H}_2\text{SO}_4\text{(l)} \rightarrow \text{PbSO}_4\text{(s)} + \text{H}_2\text{O(l)}$
 - $4\text{HBr(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{H}_2\text{O(l)} + 2\text{Br}_2\text{(l)}$
 - $2\text{KBr(s)} + \text{H}_2\text{SO}_4\text{(l)} \rightarrow \text{K}_2\text{SO}_4\text{(s)} + 2\text{HBr(g)}$
 - $4\text{Zn(s)} + 9\text{HNO}_3\text{(l)} \rightarrow 4\text{Zn(NO}_3)_2\text{(s)} + \text{NH}_3\text{(g)} + 3\text{H}_2\text{O(l)}$
- How much heat is released or required in the reaction of 0.50 mol of HBr(g) with 1.0 mol of chlorine gas to produce bromine gas?
- How much energy is released or consumed if 10.0 g of N₂O₅ is completely decomposed to produce gaseous nitrogen dioxide and oxygen?
- In the mid-1700s, a method was devised for preparing chlorine gas from the following reaction:

$$\text{NaCl(s)} + \text{H}_2\text{SO}_4\text{(l)} + \text{MnO}_2\text{(s)} \rightarrow \text{Na}_2\text{SO}_4\text{(s)} + \text{MnCl}_2\text{(s)} + \text{H}_2\text{O(l)} + \text{Cl}_2\text{(g)}$$

5. Would you expect heat to be evolved during each reaction?
 - a. solid sodium oxide with gaseous sulfur dioxide to give solid sodium sulfite
 - b. solid aluminum chloride reacting with water to give solid aluminum oxide and hydrogen chloride gas
6. How much heat is released in preparing an aqueous solution containing 6.3 g of calcium chloride, an aqueous solution containing 2.9 g of potassium carbonate, and then when the two solutions are mixed together to produce potassium chloride and calcium carbonate?
7. Methanol is used as a fuel in Indianapolis 500 race cars. Use the following table to determine whether methanol or 2,2,4-trimethylpentane (isooctane) releases more energy per liter during combustion.

Fuel	(kJ/mol)	Density (g/mL)
methanol	-726.1	0.791
2,2,4-trimethylpentane	-5461.4	0.692

8.
 - a. Use the enthalpies of combustion given in the following table to determine which organic compound releases the greatest amount of energy per gram during combustion.

Fuel	(kJ/mol)
methanol	-726.1
1-ethyl-2-methylbenzene	-5210.2
<i>n</i> -octane	-5470.5

- b. Calculate the standard enthalpy of formation of 1-ethyl-2-methylbenzene.
9. Given the enthalpies of combustion, which organic compound is the best fuel per gram?

Fuel	(kJ/mol)
ethanol	-1366.8
benzene	-3267.6
cyclooctane	-5434.7

ANSWERS

1.
 - a. -1203 kJ/mol O₂
 - b. 179.2 kJ
 - c. -59.3 kJ
2. -174.1 kJ/mol

3. -20.3 kJ
4. $-34.3 \text{ kJ/mol Cl}_2$; exothermic
5. $\Delta H = -2.86 \text{ kJ CaCl}_2$; -4.6 kJ ; K_2CO_3 , -0.65 kJ ; mixing, -0.28 kJ
6.
 - a. To one decimal place
 methanol: $\Delta H/\text{g} = -22.6 \text{ kJ}$; C_9H_{12} : $\Delta H/\text{g} = -43.3 \text{ kJ}$; octane: $\Delta H/\text{g} = -47.9 \text{ kJ}$
 Octane provides the largest amount of heat per gram upon combustion.
 - b.
 $\Delta H_f(\text{C}_9\text{H}_{17}) = -46.1 \text{ kJ/mol}$

5.3 Calorimetry

LEARNING OBJECTIVE

1. To use calorimetric data to calculate enthalpy changes.

Thermal energy itself cannot be measured easily, but the temperature change caused by the flow of thermal energy between objects or substances can be measured. Calorimetry describes a set of techniques employed to measure enthalpy changes in chemical processes using devices called *calorimeters*.

To have any meaning, the quantity that is actually measured in a calorimetric experiment, the change in the temperature of the device, must be related to the heat evolved or consumed in a chemical reaction. We begin this section by explaining how the flow of thermal energy affects the temperature of an object.

Heat Capacity

We have seen that the temperature of an object changes when it absorbs or loses thermal energy.

The *magnitude* of the temperature change depends on both the *amount* of thermal energy transferred (q) and the *heat capacity* of the object. Its heat capacity (C) is the amount of energy needed to raise the temperature of the object exactly 1°C ; the units of C are joules per degree Celsius ($\text{J}/^\circ\text{C}$). The change in temperature (ΔT) is

Equation 5.34

where q is the amount of heat (in joules), C is the heat capacity (in joules per degree Celsius), and ΔT is $T_{\text{final}} - T_{\text{initial}}$ (in degrees Celsius). Note that ΔT is *always* written as the final temperature minus the initial temperature. The value of C is intrinsically a positive number, but ΔT and q can be either positive or negative, and they both must have the *same* sign. If ΔT and q are positive, then *heat flows from the surroundings into an object*. If ΔT and q are negative, then *heat flows from an object into its surroundings*.

The heat capacity of an object depends on both its *mass* and its *composition*. For example, doubling the mass of an object doubles its heat capacity. Consequently, the amount of substance must be indicated when the heat capacity of the substance is reported. The molar heat capacity (C_p) is the amount of energy needed to increase the temperature of 1 mol of a substance by 1°C; the units of C_p are thus J/(mol·°C).^[1] The specific heat (C_s) is the amount of energy needed to increase the temperature of 1 g of a substance by 1°C; its units are thus J/(g·°C). We can relate the quantity of a substance, the amount of heat transferred, its heat capacity, and the temperature change in two ways:

Equation 5.35

$q = nC_p\Delta T$, where n = number of moles of substance

Equation 5.36

$q = mC_s\Delta T$, where m = mass of substance in grams

The specific heats of some common substances are given in Table 5.3 "Specific Heats of Selected Substances at 25°C". Note that the specific heat values of most solids are less than 1 J/(g·°C), whereas those of most liquids are about 2 J/(g·°C). Water in its solid and liquid states is an exception. The heat capacity of ice is twice as high as that of most solids; the heat capacity of liquid water, 4.184 J/(g·°C), is one of the highest known.

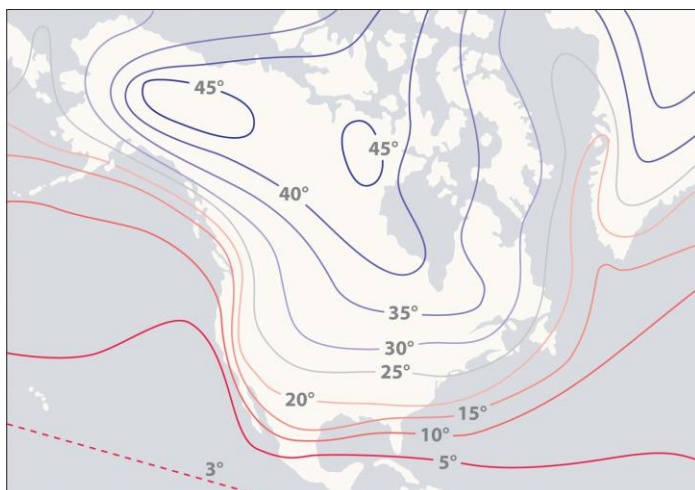
Table 5.3 Specific Heats of Selected Substances at 25°C

Compound	Specific Heat [J/(g·°C)]
H ₂ O(l)	4.184
H ₂ O(g)	2.062
CH ₃ OH (methanol)	2.531
CH ₃ CH ₂ OH (ethanol)	2.438
<i>n</i> -C ₆ H ₁₄ (<i>n</i> -hexane)	2.270
C ₆ H ₆ (benzene)	1.745

Compound	Specific Heat [J/(g·°C)]
C(s) (graphite)	0.709
C(s) (diamond)	0.509
Al(s)	0.897
Fe(s)	0.449
Cu(s)	0.385
Au(s)	0.129
Hg(l)	0.140
NaCl(s)	0.864
MgO(s)	0.921
SiO ₂ (s) (quartz)	0.742
CaCO ₃ (s) (calcite)	0.915

The high specific heat of liquid water has important implications for life on Earth. A given mass of water releases more than five times as much heat for a 1°C temperature change as does the same mass of limestone or granite. Consequently, coastal regions of our planet tend to have less variable climates than regions in the center of a continent. After absorbing large amounts of thermal energy from the sun in summer, the water slowly releases the energy during the winter, thus keeping coastal areas warmer than otherwise would be expected (Figure 5.13 "The High Specific Heat of Liquid Water Has Major Effects on Climate"). Water's capacity to absorb large amounts of energy without undergoing a large increase in temperature also explains why swimming pools and waterbeds are usually heated. Heat must be applied to raise the temperature of the water to a comfortable level for swimming or sleeping and to maintain that level as heat is exchanged with the surroundings. Moreover, because the human body is about 70% water by mass, a great deal of energy is required to change its temperature by even 1°C. Consequently, the mechanism for maintaining our body temperature at about 37°C does not have to be as finely tuned as would be necessary if our bodies were primarily composed of a substance with a lower specific heat.

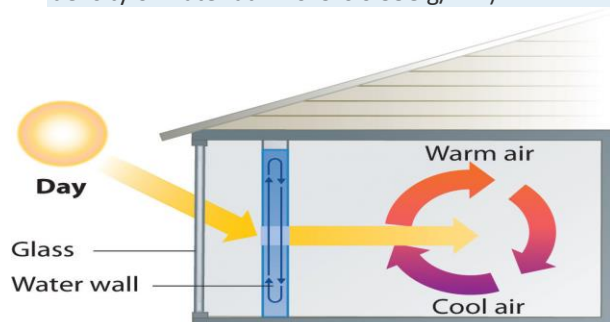
Figure 5.13 The High Specific Heat of Liquid Water Has Major Effects on Climate



Regions that are near very large bodies of water, such as oceans or lakes, tend to have smaller temperature differences between summer and winter months than regions in the center of a continent. The contours on this map show the difference between January and July monthly mean surface temperatures (in degrees Celsius).

EXAMPLE 7

A home solar energy storage unit uses 400 L of water for storing thermal energy. On a sunny day, the initial temperature of the water is 22.0°C. During the course of the day, the temperature of the water rises to 38.0°C as it circulates through the water wall. How much energy has been stored in the water? (The density of water at 22.0°C is 0.998 g/mL.)



Passive solar system. During the day (a), sunlight is absorbed by water circulating in the water wall. At night (b), heat stored in the water wall continues to warm the air inside the house.

Given: volume and density of water and initial and final temperatures

Asked for: amount of energy stored

Strategy:

A Use the density of water at 22.0°C to obtain the mass of water (m) that corresponds to 400 L of water. Then compute ΔT for the water.

B Determine the amount of heat absorbed by substituting values for m , C_s , and ΔT into Equation 5.36.

Solution:

A The mass of water is
 $\text{mass of } H_2O = 400 \text{ L} (1000 \text{ mL/L})$
 $(0.998 \text{ g/mL}) = 3.99 \times 10^5 \text{ g } H_2O$

The temperature change (ΔT) is $38.0^\circ\text{C} - 22.0^\circ\text{C} = +16.0^\circ\text{C}$.

B From Table 5.3 "Specific Heats of Selected Substances at 25°C", the specific heat of water is $4.184 \text{ J/(g}\cdot^\circ\text{C)}$.

From Equation 5.36, the heat absorbed by the water is thus
 $q = mC_s\Delta T = (3.99 \times 10^5 \text{ g}) (4.184 \text{ J/g}\cdot^\circ\text{C}) (16.0^\circ\text{C})$
 $= 2.67 \times 10^7 \text{ J} = 2.67 \times 10^4 \text{ kJ}$

Both q and ΔT are positive, consistent with the fact that the water has absorbed energy.

Exercise

Some solar energy devices used in homes circulate air over a bed of rocks that absorb thermal energy from the sun. If a house uses a solar heating system that contains 2500 kg of sandstone rocks, what amount of energy is stored if the temperature of the rocks increases from 20.0°C to 34.5°C during the day? Assume that the specific heat of sandstone is the same as that of quartz (SiO_2) in Table 5.3 "Specific Heats of Selected Substances at 25°C".

Answer: $2.7 \times 10^4 \text{ kJ}$ (Even though the mass of sandstone is more than six times the mass of the water in Example 7, the amount of thermal energy stored is the same to two significant figures.)

When two objects at different temperatures are placed in contact, heat flows from the warmer object to the cooler one until the temperature of both objects is the same. The law of conservation of energy says that the total energy cannot change during this process:

Equation 5.37

$$q_{\text{cold}} + q_{\text{hot}} = 0$$

The equation implies that the amount of heat that flows *from* a warmer object is the same as the amount of heat that flows *into* a cooler object. Because the direction of heat flow is opposite for the two objects, the sign of the heat flow values must be opposite:

Equation 5.38

$$q_{\text{cold}} = -q_{\text{hot}}$$

Thus heat is conserved in any such process, consistent with the law of conservation of energy.

Note the Pattern

The amount of heat lost by a warmer object equals the amount of heat gained by a cooler object.

Substituting for q from Equation 5.36 gives

Equation 5.39

$$[mC_s\Delta T]_{\text{hot}} + [mC_s\Delta T]_{\text{cold}} = 0$$

which can be rearranged to give

Equation 5.40

$$[mC_s\Delta T]_{\text{cold}} = -[mC_s\Delta T]_{\text{hot}}$$

When two objects initially at different temperatures are placed in contact, we can use Equation 5.40 to calculate the final temperature if we know the chemical composition and mass of the objects.

EXAMPLE 8

If a 30.0 g piece of copper pipe at 80.0°C is placed in 100.0 g of water at 27.0°C, what is the final temperature? Assume that no heat is transferred to the surroundings.

Given: mass and initial temperature of two objects

Asked for: final temperature

Strategy:

Using Equation 5.40 and writing ΔT as $T_{\text{final}} - T_{\text{initial}}$ for both the copper and the water, substitute the appropriate values of m , C_s , and T_{initial} into the equation and solve for T_{final} .

Solution:

We can adapt Equation 5.40 to solve this problem, remembering that ΔT is defined as $T_{\text{final}} - T_{\text{initial}}$:

$$[mC_s(T_{\text{final}} - T_{\text{initial}})]_{\text{Cu}} + [mC_s(T_{\text{final}} - T_{\text{initial}})]_{\text{H}_2\text{O}} = 0$$

Exercise (a)

If a 14.0 g chunk of gold at 20.0°C is dropped into 25.0 g of water at 80.0°C, what is the final temperature if no heat is transferred to the surroundings?

Answer: 80.0°C

Exercise (b)

A 28.0 g chunk of aluminum is dropped into 100.0 g of water with an initial temperature of 20.0°C. If the final temperature of the water is 24.0°C, what was the initial temperature of the aluminum? (Assume that no heat is transferred to the surroundings.)

Answer: 90.6°C

Measuring Heat Flow

In Example 7, radiant energy from the sun was used to raise the temperature of water. A calorimetric experiment uses essentially the same procedure, except that the thermal energy change accompanying a chemical reaction is responsible for the change in temperature that takes place in a calorimeter. If the reaction releases heat ($q_{\text{rxn}} < 0$), then heat is absorbed by the calorimeter ($q_{\text{calorimeter}} > 0$) and its temperature increases. Conversely, if the reaction absorbs heat ($q_{\text{rxn}} > 0$), then heat is transferred from the calorimeter to the system ($q_{\text{calorimeter}} < 0$) and the temperature of the calorimeter decreases. In both cases, *the amount of heat absorbed or released by the calorimeter is equal in magnitude and opposite in sign to the amount of heat produced or consumed by the reaction*. The heat capacity of the calorimeter or of the reaction mixture may be used to calculate the amount of heat released or absorbed by the chemical reaction. The amount of heat released or absorbed per gram or mole of reactant can then be calculated from the mass of the reactants.

Constant-Pressure Calorimetry

Because ΔH is defined as the heat flow at constant pressure, measurements made using a constant-pressure calorimeter give ΔH values directly. This device is particularly well suited to studying reactions carried out in solution at a constant atmospheric pressure. A “student” version, called a *coffee-cup calorimeter* (Figure 5.14 "A Coffee-Cup Calorimeter"), is often encountered in general chemistry laboratories. Commercial calorimeters operate on the same principle, but they can be used with smaller volumes of solution, have better thermal insulation, and can detect a change in temperature as small as

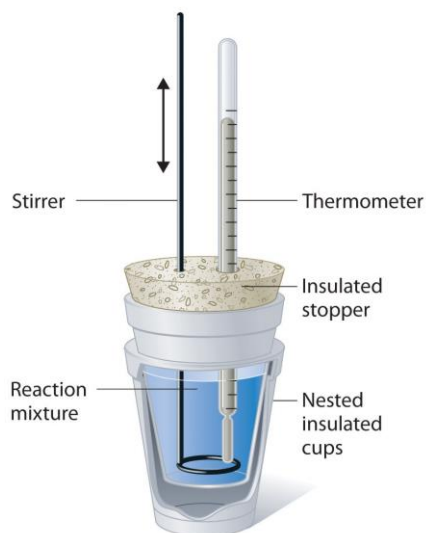
several millionths of a degree (10^{-6}°C). Because the heat released or absorbed at constant pressure is equal to ΔH , the relationship between heat and ΔH_{rxn} is

Equation 5.41

$$\Delta H_{\text{rxn}} = q_{\text{rxn}} = -q_{\text{calorimeter}} = -mC_s\Delta T$$

The use of a constant-pressure calorimeter is illustrated in Example 9.

Figure 5.14 A Coffee-Cup Calorimeter



This simplified version of a constant-pressure calorimeter consists of two Styrofoam cups nested and sealed with an insulated stopper to thermally isolate the system (the solution being studied) from the surroundings (the air and the laboratory bench). Two holes in the stopper allow the use of a thermometer to measure the temperature and a stirrer to mix the reactants.

EXAMPLE 9

When 5.03 g of solid potassium hydroxide are dissolved in 100.0 mL of distilled water in a coffee-cup calorimeter, the temperature of the liquid increases from 23.0°C to 34.7°C . The density of water in this temperature range averages 0.9969 g/cm^3 . What is ΔH_{soln} (in kilojoules per mole)? Assume that the calorimeter absorbs a negligible amount of heat and, because of the large volume of water, the specific heat of the solution is the same as the specific heat of pure water.

Given: mass of substance, volume of solvent, and initial and final temperatures

Asked for: ΔH_{soln}

Strategy:

A Calculate the mass of the solution from its volume and density and calculate the temperature change of the solution.

B Find the heat flow that accompanies the dissolution reaction by substituting the appropriate values into Equation 5.41.

C Use the molar mass of KOH to calculate ΔH_{soln} .

Solution:

A To calculate ΔH_{soln} we must first determine the amount of heat released in the calorimetry experiment.

The mass of the solution is

$$(100.0 \text{ mL } H_2O)(0.9969 \text{ g/mL}) + 5.03 \text{ g KOH} = 104.72 \text{ g}$$

The temperature change is $(34.7^\circ\text{C} - 23.0^\circ\text{C}) = +11.7^\circ\text{C}$.

B Because the solution is not very concentrated (approximately 0.9 M), we assume that the specific heat of the solution is the same as that of water. The heat flow that accompanies dissolution is thus $q_{\text{calorimeter}} = mCs\Delta T = (104.72 \text{ g})$

$$/4.184 \text{ Jg}^\circ\text{C} / (11.7^\circ\text{C}) = 5130 \text{ J} = 5.13 \text{ kJ}$$

The temperature of the solution increased because heat was absorbed by the solution ($q > 0$). Where did this heat come from? It was released by KOH dissolving in water. From Equation 5.41, we see that

$$\Delta H_{\text{rxn}} = -q_{\text{calorimeter}} = -5.13 \text{ kJ}$$

This experiment tells us that dissolving 5.03 g of KOH in water is accompanied by the release of 5.13 kJ of energy. Because the temperature of the solution increased, the dissolution of KOH in water must be exothermic.

C The last step is to use the molar mass of KOH to calculate ΔH_{soln} —the heat released when dissolving 1 mol of KOH:

$$\Delta H_{\text{soln}} = (-5.13 \text{ kJ}) / (5.03 \text{ g}) (56.11 \text{ g/mol}) = -57.2 \text{ kJ/mol}$$

Exercise

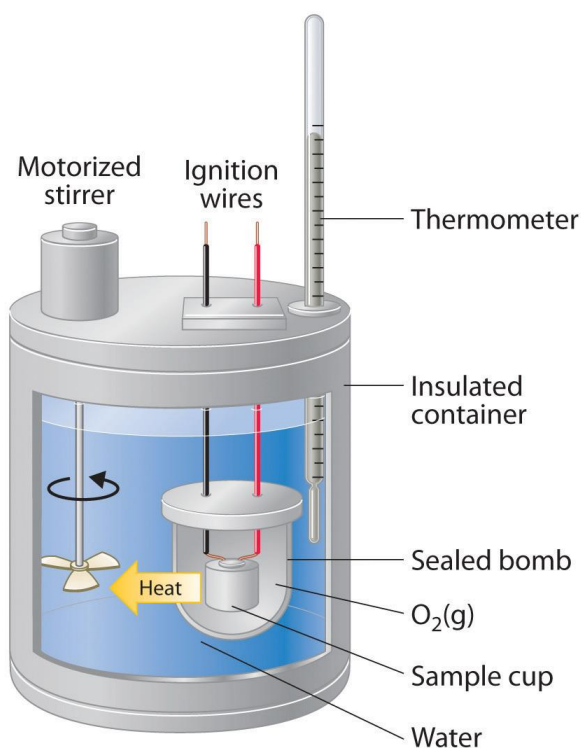
A coffee-cup calorimeter contains 50.0 mL of distilled water at 22.7°C . Solid ammonium bromide (3.14 g) is added and the solution is stirred, giving a final temperature of 20.3°C . Using the same assumptions as in Example 9, find ΔH_{soln} for NH_4Br (in kilojoules per mole).

Answer: 16.6 kJ/mol

Constant-Volume Calorimetry

Constant-pressure calorimeters are not very well suited for studying reactions in which one or more of the reactants is a gas, such as a combustion reaction. The enthalpy changes that accompany combustion reactions are therefore measured using a constant-volume calorimeter, such as the bomb calorimeter shown schematically in Figure 5.15 "A Bomb Calorimeter". The reactant is placed in a steel cup inside a steel vessel with a fixed volume (the "bomb"). The bomb is then sealed, filled with excess oxygen gas, and placed inside an insulated container that holds a known amount of water. Because combustion reactions are exothermic, the temperature of the bath and the calorimeter increases during combustion. If the heat capacity of the bomb and the mass of water are known, the heat released can be calculated.

Figure 5.15 A Bomb Calorimeter



After the temperature of the water in the insulated container has reached a constant value, the combustion reaction is initiated by passing an electric current through a wire embedded in the sample. Because this calorimeter operates at constant volume, the heat released is not precisely the same as the enthalpy change for the reaction.

Because the volume of the system (the inside of the bomb) is fixed, the combustion reaction occurs under conditions in which the volume, but not the pressure, is constant. As you will learn in Chapter 18 "Chemical Thermodynamics", the heat released by a reaction carried out at constant volume is identical to the change in *internal energy* (ΔE)

rather than the enthalpy change (ΔH); ΔE is related to ΔH by an expression that depends on the change in the number of moles of gas during the reaction. The difference between the heat flow measured at constant volume and the enthalpy change is usually quite small, however (on the order of a few percent). Assuming that $\Delta E < \Delta H$, the relationship between the measured temperature change and ΔH_{comb} is given in Equation 5.42, where C_{bomb} is the total heat capacity of the steel bomb and the water surrounding it:

Equation 5.42

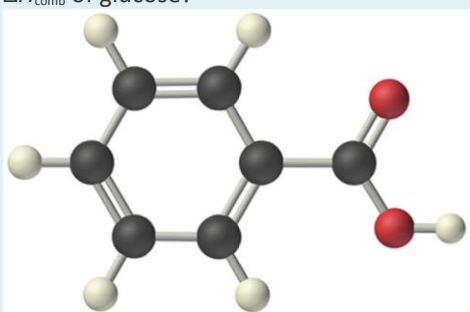
$$\Delta H_{\text{comb}} < q_{\text{comb}} = -q_{\text{calorimeter}} = -C_{\text{bomb}}\Delta T$$

To measure the heat capacity of the calorimeter, we first burn a carefully weighed mass of a standard compound whose enthalpy of combustion is accurately known. Benzoic acid ($\text{C}_6\text{H}_5\text{CO}_2\text{H}$) is often used for this purpose because it is a crystalline solid that can be obtained in high purity. The combustion of benzoic acid in a bomb calorimeter releases 26.38 kJ of heat per gram (i.e., its $\Delta H_{\text{comb}} = -26.38 \text{ kJ/g}$). This value and the measured increase in temperature of the calorimeter can be used in Equation 5.42 to determine C_{bomb} . The use of a bomb calorimeter to measure the ΔH_{comb} of a substance is illustrated in Example 10.

EXAMPLE 10

The combustion of 0.579 g of benzoic acid in a bomb calorimeter caused a 2.08°C increase in the temperature of the calorimeter. The chamber was then emptied and recharged with 1.732 g of glucose and excess oxygen. Ignition of the glucose resulted in a temperature increase of 3.64°C . What is the

ΔH_{comb} of glucose?



Benzoic acid

Given: mass and ΔT for combustion of standard and sample

Asked for: ΔH_{comb} of glucose

Strategy:

A Calculate the value of q_{rxn} for benzoic acid by multiplying the mass of benzoic acid by its ΔH_{comb} . Then use Equation 5.42 to determine the heat capacity of the calorimeter (C_{bomb}) from q_{comb} and ΔT .

B Calculate the amount of heat released during the combustion of glucose by multiplying the heat capacity of the bomb by the temperature change. Determine the ΔH_{comb} of glucose by multiplying the amount of heat released per gram by the molar mass of glucose.

Solution:

The first step is to use Equation 5.42 and the information obtained from the combustion of benzoic acid to calculate C_{bomb} . We are given ΔT , and we can calculate q_{comb} from the mass of benzoic acid:

$$q_{\text{comb}} = (0.579 \text{ g})(-26.38 \text{ kJ/g}) = -15.3 \text{ kJ}$$

$$-C_{\text{bomb}} = q_{\text{comb}}/\Delta T = -15.3 \text{ kJ}/2.08^\circ\text{C} = -7.34 \text{ kJ}/^\circ\text{C}$$

B According to the strategy, we can now use the heat capacity of the bomb to calculate the amount of heat released during the combustion of glucose:

$$q_{\text{comb}} = -C_{\text{bomb}}\Delta T = (-7.34 \text{ kJ}/^\circ\text{C})(3.64^\circ\text{C}) = -26.7 \text{ kJ}$$

Because the combustion of 1.732 g of glucose released 26.7 kJ of energy, the ΔH_{comb} of glucose is

$$\Delta H_{\text{comb}} = (-26.7 \text{ kJ}/1.732 \text{ g})(180.16 \text{ g/mol}) = -2780 \text{ kJ/mol} = -2.78 \times 10^3 \text{ kJ/mol}$$

This result is in good agreement (< 1% error) with the value of $\Delta H_{\text{c}} = -2803 \text{ kJ/mol}$ that we calculated in Section 5.2

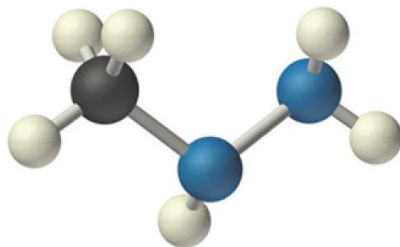
"Enthalpy" using enthalpies of formation.

Exercise

When 2.123 g of benzoic acid is ignited in a bomb calorimeter, a temperature increase of 4.75°C is observed. When

1.932 g of methylhydrazine (CH_3NHNH_2) is ignited in the same calorimeter, the temperature increase is 4.64°C .

Calculate the ΔH_{comb} of methylhydrazine, the fuel used in the maneuvering jets of the US space shuttle.



Methylhydrazine

Answer: $-1.30 \times 10^3 \text{ kJ/mol}$

KEY EQUATIONS

relationship of quantity of a substance, heat capacity, heat flow, and temperature change

Equation 5.35: $q = nC_p\Delta T$

Equation 5.36: $q = mC_s\Delta T$

constant-pressure calorimetry

Equation 5.41: $\Delta H_{\text{rxn}} = q_{\text{rxn}} = -q_{\text{calorimeter}} = -mC_s\Delta T$

constant-volume calorimetry

Equation 5.42: $\Delta H_{\text{comb}} < q_{\text{comb}} = -q_{\text{calorimeter}} = -C_{\text{bomb}}\Delta T$

Summary

Calorimetry is the set of techniques used to measure enthalpy changes during chemical processes. It uses devices called *calorimeters*, which measure the change in temperature when a chemical reaction is carried out. The magnitude of the temperature change depends on the amount of heat released or absorbed and on the heat capacity of the system. The **heat capacity (C)** of an object is the amount of energy needed to raise its temperature by 1°C; its units are joules per degree Celsius. The **specific heat (Cs)** of a substance is the amount of energy needed to raise the temperature of 1 g of the substance by 1°C, and the **molar heat capacity (Cp)** is the amount of energy needed to raise the temperature of 1 mol of a substance by 1°C. Liquid water has one of the highest specific heats known. Heat flow measurements can be made with either a **constant-pressure calorimeter**, which gives ΔH values directly, or a **bomb calorimeter**, which operates at constant volume and is particularly useful for measuring enthalpies of combustion.

KEY TAKEAWAY

- Calorimetry measures enthalpy changes during chemical processes, where the magnitude of the temperature change depends on the amount of heat released or absorbed and on the heat capacity of the system.

CONCEPTUAL PROBLEMS

1. Can an object have a negative heat capacity? Why or why not?
2. What two factors determine the heat capacity of an object? Does the specific heat also depend on these two factors? Explain your answer.
3. Explain why regions along seacoasts have a more moderate climate than inland regions do.

- Although soapstone is more expensive than brick, soapstone is frequently the building material of choice for fireplaces, particularly in northern climates with harsh winters. Propose an explanation for this.

NUMERICAL PROBLEMS

Please be sure you are familiar with the topics discussed in Essential Skills 4 (Section 5.6 "Essential Skills 4") before proceeding to the Numerical Problems.

- Using Equation 5.35 and Equation 5.36, derive a mathematical relationship between C_s and C_p .
- Complete the following table for 28.0 g of each element at an initial temperature of 22.0°C.

Element	q (J)	C_p [J/(mol·K)]	Final T (°C)
nickel	137	26.07	
silicon		19.789	3.0
zinc	603		77.5
mercury	137		57

- Using Table 5.3 "Specific Heats of Selected Substances at 25°C", how much heat is needed to raise the temperature of a 2.5 g piece of copper wire from 20°C to 80°C? How much heat is needed to increase the temperature of an equivalent mass of aluminum by the same amount? If you were using one of these metals to channel heat away from electrical components, which metal would you use? Once heated, which metal will cool faster? Give the specific heat for each metal.
- Gold has a molar heat capacity of 25.418 J/(mol·K), and silver has a molar heat capacity of 23.350 J/(mol·K).
 - If you put silver and gold spoons of equal mass into a cup of hot liquid and wait until the temperature of the liquid is constant, which spoon will take longer to cool down when removed from the hot liquid?
 - If 8.00 g spoons of each metal at 20.0°C are placed in an insulated mug with 50.0 g of water at 97.0°C, what will be the final temperature of the water after the system has equilibrated? (Assume that no heat is transferred to the surroundings.)
- In an exothermic reaction, how much heat would need to be evolved to raise the temperature of 150 mL of water 7.5°C? Explain how this process illustrates the law of conservation of energy.
- How much heat must be evolved by a reaction to raise the temperature of 8.0 oz of water 5.0°C? What mass of lithium iodide would need to be dissolved in this volume of water to produce this temperature change?

7. A solution is made by dissolving 3.35 g of an unknown salt in 150 mL of water, and the temperature of the water rises 3.0°C. The addition of a silver nitrate solution results in a precipitate. Assuming that the heat capacity of the solution is the same as that of pure water, use the information in Table 5.2 "Enthalpies of Solution at 25°C of Selected Ionic Compounds in Water (in kJ/mol)" and solubility rules to identify the salt.
8. Using the data in Table 5.8 "Enthalpies of Combustion of Common Fuels and Selected Organic Compounds", calculate the change in temperature of a calorimeter with a heat capacity of 1.78 kJ/°C when 3.0 g of charcoal is burned in the calorimeter. If the calorimeter is in a 2 L bath of water at an initial temperature of 21.5°C, what will be the final temperature of the water after the combustion reaction (assuming no heat is lost to the surroundings)?
9. A 3.00 g sample of TNT (trinitrotoluene, $C_7H_5N_3O_6$) is placed in a bomb calorimeter with a heat capacity of 1.93 kJ/°C; the ΔH_{comb} of TNT is -3403.5 kJ/mol. If the initial temperature of the calorimeter is 19.8°C, what will be the final temperature of the calorimeter after the combustion reaction (assuming no heat is lost to the surroundings)? What is the ΔH_f of TNT?

ANSWERS

1. $C_p = C_s \times (\text{molar mass})$
- 2.
3. For Cu: $q = 58$ J; For Al: $q = 130$ J; Even though the values of the molar heat capacities are very similar for the two metals, the specific heat of Cu is only about half as large as that of Al, due to the greater molar mass of Cu versus Al: $C_s = 0.385$ and 0.897 J/(g·K) for Cu and Al, respectively. Thus loss of one joule of heat will cause almost twice as large a decrease in temperature of Cu versus Al.
- 4.
5. 4.7 kJ
- 6.
7. $\Delta H_{\text{soln}} = -0.56$ kJ/g; based on reaction with AgNO_3 , salt contains halide; dividing ΔH_{soln} values in Table 5.2 "Enthalpies of Solution at 25°C of Selected Ionic Compounds in Water (in kJ/mol)" by molar mass of salts gives lithium bromide as best match, with -0.56 kJ/g.
- 8.
9. $T_{\text{final}} = 43.1^\circ\text{C}$; the combustion reaction is $4C_7H_5N_3O_6(s) + 21O_2(g) \rightarrow 28CO_2(g) + 10H_2O(g) + 6N_2(g)$; $DH_{\text{of}}(TNT) = -65.5 \text{ kJ/mol}$

[1] The subscript p indicates that the value was measured at constant pressure.

5.4 Thermochemistry and Nutrition

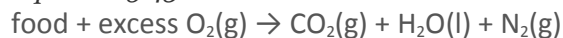
LEARNING OBJECTIVE

1. To understand the relationship between thermochemistry and nutrition.

The thermochemical quantities that you probably encounter most often are the caloric values of food. Food supplies the raw materials that your body needs to replace cells and the energy that keeps those cells functioning. About 80% of this energy is released as heat to maintain your body temperature at a sustainable level to keep you alive.

The nutritional Calorie (with a capital C) that you see on food labels is equal to 1 kcal (kilocalorie). The caloric content of food is determined from its enthalpy of combustion (ΔH_{comb}) per gram, as measured in a bomb calorimeter, using the general reaction

Equation 5.43



There are two important differences, however, between the caloric values reported for foods and the ΔH_{comb} of the same foods burned in a calorimeter. First, the ΔH_{comb} described in joules (or kilojoules) are negative for all substances that can be burned. In contrast, the caloric content of a food is always expressed as a *positive* number because it is *stored energy*. Therefore,

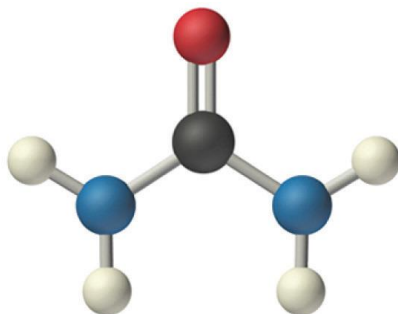
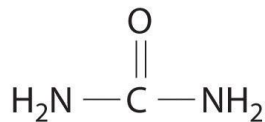
Equation 5.44

$$\text{caloric content} = -\Delta H_{\text{comb}}$$

Second, when foods are burned in a calorimeter, any nitrogen they contain (largely from proteins, which are rich in nitrogen) is transformed to N_2 . In the body, however, nitrogen from foods is converted to urea $[(\text{H}_2\text{N})_2\text{C}=\text{O}]$, rather than N_2 before it is excreted. The ΔH_{comb} of urea measured by bomb calorimetry is -632.0 kJ/mol . Consequently, the enthalpy change measured by calorimetry for any nitrogen-containing food is greater than the amount of energy the body would obtain from it. The difference in the values is equal to the ΔH_{comb} of urea multiplied by the number of moles of urea formed when the food is broken down. This point is illustrated schematically in the following equations:

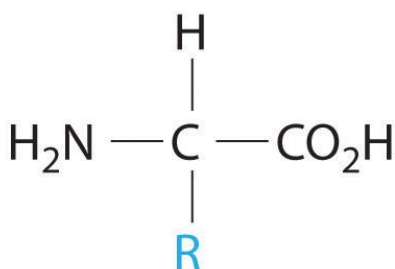
Equation 5.45

All three ΔH values are negative, and, by Hess's law, $\Delta H_3 = \Delta H_1 + \Delta H_2$. The magnitude of ΔH_1 must be less than ΔH_3 , the calorimetrically measured ΔH_{comb} for a food. By producing urea rather than N_2 , therefore, humans are excreting some of the energy that was stored in their food.



Urea

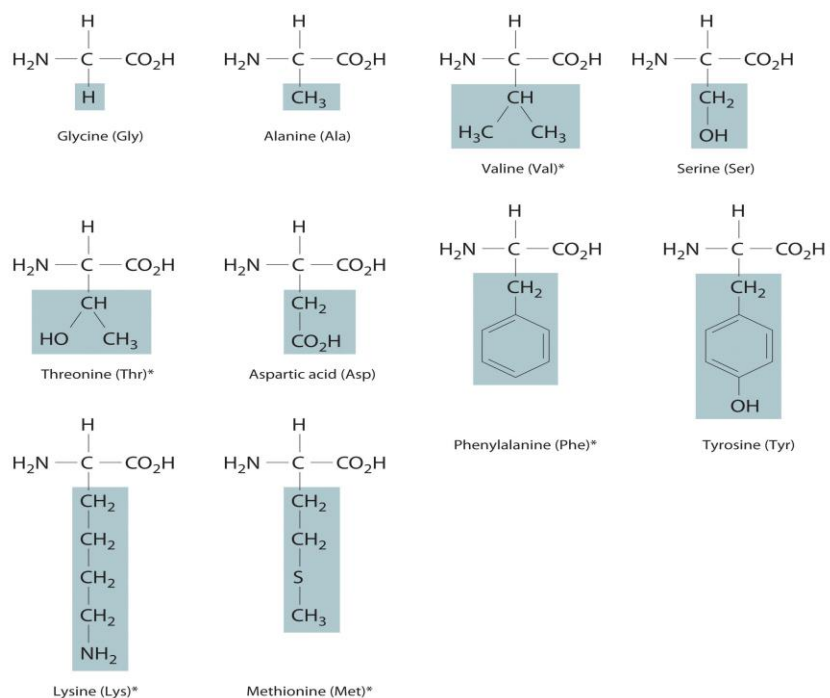
Because of their different chemical compositions, foods vary widely in caloric content. As we saw in Example 5, for instance, a fatty acid such as palmitic acid produces about 39 kJ/g during combustion, while a sugar such as glucose produces 15.6 kJ/g. Fatty acids and sugars are the building blocks of fats and carbohydrates, respectively, two of the major sources of energy in the diet. Nutritionists typically assign average values of 38 kJ/g (about 9 Cal/g) and 17 kJ/g (about 4 Cal/g) for fats and carbohydrates, respectively, although the actual values for specific foods vary because of differences in composition. Proteins, the third major source of calories in the diet, vary as well. Proteins are composed of amino acids, which have the following general structure:



General structure of an amino acid. An amino acid contains an amine group ($-\text{NH}_2$) and a carboxylic acid group ($-\text{CO}_2\text{H}$).

In addition to their amine and carboxylic acid components, amino acids may contain a wide range of other functional groups: R can be hydrogen ($-\text{H}$); an alkyl group (e.g., $-\text{CH}_3$); an aryl group (e.g., $-\text{CH}_2\text{C}_6\text{H}_5$); or a substituted alkyl group that contains an amine, an alcohol, or a carboxylic acid (Figure 5.16 "The Structures of 10 Amino Acids"). Of the 20 naturally occurring amino acids, 10 are required in the human diet; these 10 are called *essential amino acids* because our bodies are unable to synthesize them from other compounds. Because R can be any of several different groups, each amino acid has a different value of ΔH_{comb} . Proteins are usually estimated to have an average ΔH_{comb} of 17 kJ/g (about 4 Cal/g).

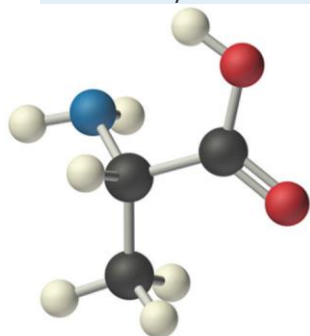
Figure 5.16 The Structures of 10 Amino Acids



Essential amino acids in this group are indicated with an asterisk.

EXAMPLE 11

Calculate the amount of available energy obtained from the biological oxidation of 1.000 g of alanine (an amino acid). Remember that the nitrogen-containing product is urea, not N_2 , so biological oxidation of alanine will yield *less* energy than will combustion. The value of ΔH_{comb} for alanine is -1577 kJ/mol .



Alanine

Given: amino acid and ΔH_{comb} per mole

Asked for: caloric content per gram

Strategy:

A Write balanced chemical equations for the oxidation of alanine to CO_2 , H_2O , and urea; the combustion of urea; and the combustion of alanine. Multiply both sides of the equations by appropriate factors and then rearrange them to cancel urea from both sides when the equations are added.

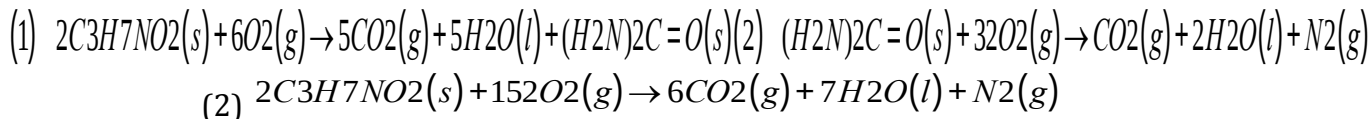
B Use Hess's law to obtain an expression for ΔH for the oxidation of alanine to urea in terms of the ΔH_{comb} of alanine and urea. Substitute the appropriate values of ΔH_{comb} into the equation and solve for ΔH for the oxidation of alanine to CO_2 , H_2O , and urea.

C Calculate the amount of energy released per gram by dividing the value of ΔH by the molar mass of alanine.

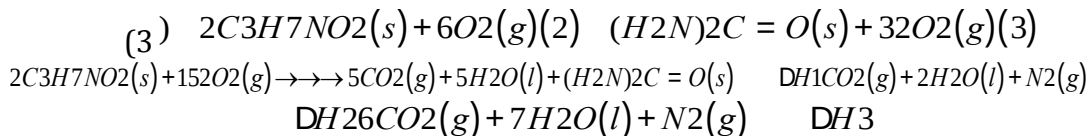
Solution:

The actual energy available biologically from alanine is less than its ΔH_{comb} because of the production of urea rather than N_2 . We know the ΔH_{comb} values for alanine and urea, so we can use Hess's law to calculate ΔH for the oxidation of alanine to CO_2 , H_2O , and urea.

A We begin by writing balanced chemical equations for (1) the oxidation of alanine to CO_2 , H_2O , and urea; (2) the combustion of urea; and (3) the combustion of alanine. Because alanine contains only a single nitrogen atom, whereas urea and N_2 each contain two nitrogen atoms, it is easier to balance Equations 1 and 3 if we write them for the oxidation of 2 mol of alanine:



Adding Equations 1 and 2 and canceling urea from both sides give the overall chemical equation directly:



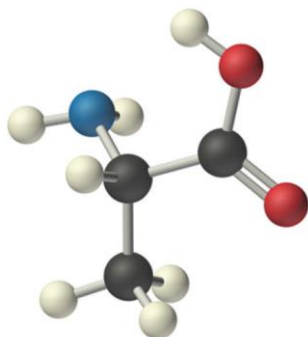
B By Hess's law, $\Delta H_3 = \Delta H_1 + \Delta H_2$. We know that $\Delta H_3 = 2\Delta H_{\text{comb}}(\text{alanine})$, $\Delta H_2 = \Delta H_{\text{comb}}(\text{urea})$, and $\Delta H_1 = 2\Delta H(\text{alanine} \rightarrow \text{urea})$. Rearranging and substituting the appropriate values gives

$$\Delta H_1 = \Delta H_3 - \Delta H_2 = 2\Delta H_{\text{comb}}(\text{alanine}) - \Delta H_{\text{comb}}(\text{urea}) = 2(-1577 \text{ kJ/mol}) - (-632.0 \text{ kJ/mol}) = -2522 \text{ kJ/(2 mol alanine)}$$

Thus $\Delta H(\text{alanine} \rightarrow \text{urea}) = -2522 \text{ kJ/(2 mol of alanine)} = -1261 \text{ kJ/mol of alanine}$. Oxidation of alanine to urea rather than to nitrogen therefore results in about a 20% decrease in the amount of energy released (-1261 kJ/mol versus -1577 kJ/mol).

C The energy released per gram by the biological oxidation of alanine is

$$-1261 \text{ kJ/mol} \div (1 \text{ mol} / 89.094 \text{ g}) = -14.15 \text{ kJ/g}$$

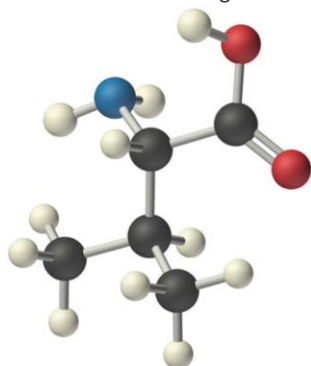


Alanine

This is equal to -3.382 Cal/g .

Exercise

Calculate the energy released per gram from the oxidation of valine (an amino acid) to CO_2 , H_2O , and urea. Report your answer to three significant figures. The value of ΔH_{comb} for valine is -2922 kJ/mol .



Valine

Answer: -22.2 kJ/g (-5.31 Cal/g)

The reported caloric content of foods does not include ΔH_{comb} for those components that are not digested, such as fiber. Moreover, meats and fruits are 50%–70% water, which cannot be oxidized by O_2 to obtain energy. So water contains no calories. Some foods contain large amounts of fiber, which is primarily composed of sugars. Although fiber can be burned in a calorimeter just like glucose to give carbon dioxide, water, and heat, humans lack the enzymes needed to break fiber down into smaller molecules that can be oxidized. Hence fiber also does not contribute to the caloric content of food.

We can determine the caloric content of foods in two ways. The most precise method is to dry a carefully weighed sample and carry out a combustion reaction in a bomb calorimeter. The more typical approach, however, is to analyze

the food for protein, carbohydrate, fat, water, and “minerals” (everything that doesn’t burn) and then calculate the caloric content using the average values for each component that produces energy (9 Cal/g for fats, 4 Cal/g for carbohydrates and proteins, and 0 Cal/g for water and minerals). An example of this approach is shown in Table 5.4 "Approximate Composition and Fuel Value of an 8 oz Slice of Roast Beef" for a slice of roast beef. The compositions and caloric contents of some common foods are given in Table 5.5 "Approximate Compositions and Fuel Values of Some Common Foods".

Table 5.4 Approximate Composition and Fuel Value of an 8 oz Slice of Roast Beef

Composition	Calories
97.5 g of water	$\times 0 \text{ Cal/g} = 0$
58.7 g of protein	$\times 4 \text{ Cal/g} = 235$
69.3 g of fat	$\times 9 \text{ Cal/g} = 624$
0 g of carbohydrates	$\times 4 \text{ Cal/g} = 0$
1.5 g of minerals	$\times 0 \text{ Cal/g} = 0$
Total mass: 227.0 g	Total calories: about 900 Cal

Table 5.5 Approximate Compositions and Fuel Values of Some Common Foods

Food (quantity)	Approximate Composition (%)				Food Value (Cal/g)	Calories
	Water	Carbohydrate	Protein	Fat		
beer (12 oz)	92	3.6	0.3	0	0.4	150
coffee (6 oz)	100	~0	~0	~0	~0	~0
milk (1 cup)	88	4.5	3.3	3.3	0.6	150
egg (1 large)	75	2	12	12	1.6	80
butter (1 tbsp)	16	~0	~0	79	7.1	100
apple (8 oz)	84	15	~0	0.5	0.6	125
bread, white (2 slices)	37	48	8	4	2.6	130
brownie (40 g)	10	55	5	30	4.8	190
hamburger (4 oz)	54	0	24	21	2.9	326
fried chicken (1 drumstick)	53	8.3	22	15	2.7	195
carrots (1 cup)	87	10	1.3	~0	0.4	70

Because the Calorie represents such a large amount of energy, a few of them go a long way. An average 73 kg (160 lb) person needs about 67 Cal/h (1600 Cal/day) to fuel the basic biochemical processes that keep that person alive. This

energy is required to maintain body temperature, keep the heart beating, power the muscles used for breathing, carry out chemical reactions in cells, and send the nerve impulses that control those automatic functions. Physical activity increases the amount of energy required but not by as much as many of us hope (Table 5.6 "Approximate Energy Expenditure by a 160 lb Person Engaged in Various Activities"). A moderately active individual requires about 2500–3000 Cal/day; athletes or others engaged in strenuous activity can burn 4000 Cal/day. Any excess caloric intake is stored by the body for future use, usually in the form of fat, which is the most compact way to store energy. When more energy is needed than the diet supplies, stored fuels are mobilized and oxidized. We usually exhaust the supply of stored carbohydrates before turning to fats, which accounts in part for the popularity of low-carbohydrate diets.

Table 5.6 Approximate Energy Expenditure by a 160 lb Person Engaged in Various Activities

Activity	Cal/h
sleeping	80
driving a car	120
standing	140
eating	150
walking 2.5 mph	210
mowing lawn	250
swimming 0.25 mph	300
roller skating	350
tennis	420
bicycling 13 mph	660
running 10 mph	900

EXAMPLE 12

What is the minimum number of Calories expended by a 160 lb person who climbs a 30-story building? (Assume each flight of stairs is 14 ft high.) How many grams of glucose are required to supply this amount of energy? (The energy released during the combustion of glucose was calculated in Example 5.)

Given: mass, height, and energy released by combustion of glucose

Asked for: calories expended and mass of glucose needed

Strategy:

A Convert mass and height to SI units and then substitute these values into Equation 5.6 to calculate the change in potential energy (in kilojoules). Divide the calculated energy by 4.184 Cal/kJ to convert the potential energy change to Calories.

B Use the value obtained in Example 5 for the combustion of glucose to calculate the mass of glucose needed to supply this amount of energy.

Solution:

The energy needed to climb the stairs equals the difference between the person's potential energy (PE) at the top of the building and at ground level.

A Recall from Section 5.1 "Energy and Work" that $PE = mgh$. Because m and h are given in non-SI units, we must convert them to kilograms and meters, respectively:

$$m(100\text{ cm}) = 128\text{ m}$$

Thus

$$PE = (72.6\text{ kg})(9.81\text{ m/s}^2)(128\text{ m}) = 8.55 \times 10^4\text{ (kg}\cdot\text{m}^2)/\text{s}^2 = 91.2\text{ kJ}$$

To convert to Calories, we divide by 4.184 kJ/kcal:

$$PE = (91.2\text{ kJ}) \left(\frac{1\text{ kcal}}{4.184\text{ kJ}} \right) = 21.8\text{ kcal} = 21.8\text{ Cal}$$

B Because the combustion of glucose produces 15.6 kJ/g (Example 5), the mass of glucose needed to supply 91.2 kJ of energy is

$$(91.2\text{ kJ}) / 15.6\text{ kJ/g} = 5.85\text{ g glucose}$$

This mass corresponds to only about a teaspoonful of sugar! Because the body is only about 30% efficient in using the energy in glucose, the actual amount of glucose required would be higher: $(100\%/30\%) \times 5.85\text{ g} = 19.5\text{ g}$. Nonetheless, this calculation illustrates the difficulty many people have in trying to lose weight by exercise alone.

Exercise

Calculate how many times a 160 lb person would have to climb the tallest building in the United States, the 110-story Willis Tower in Chicago, to burn off 1.0 lb of stored fat. Assume that each story of the building is 14 ft high and use a calorie content of 9.0 kcal/g of fat.

Answer: About 55 times

The calculations in Example 12 ignore various factors, such as how fast the person is climbing. Although the rate is irrelevant in calculating the change in potential energy, it is very relevant to the amount of energy actually required to ascend the stairs. The calculations also ignore the fact that the body's conversion of chemical energy to mechanical work is significantly less than 100% efficient. According to the average energy expended for various activities listed in Table 5.6 "Approximate Energy Expenditure by a 160 lb Person Engaged in Various Activities", a person must run more than 4.5 h at 10 mph or bicycle for 6 h at 13 mph to burn off 1 lb of fat ($1.0 \text{ lb} \times 454 \text{ g/lb} \times 9.0 \text{ Cal/g} = 4100 \text{ Cal}$). But if a person rides a bicycle at 13 mph for only 1 h per day 6 days a week, that person will burn off 50 lb of fat in the course of a year (assuming, of course, the cyclist doesn't increase his or her intake of calories to compensate for the exercise).

Summary

The nutritional **Calorie** is equivalent to 1 kcal (4.184 kJ). The caloric content of a food is its ΔH_{comb} per gram. The combustion of nitrogen-containing substances produces $\text{N}_2(\text{g})$, but the biological oxidation of such substances produces urea. Hence the actual energy available from nitrogen-containing substances, such as proteins, is less than the ΔH_{comb} of urea multiplied by the number of moles of urea produced. The typical caloric contents for food are 9 Cal/g for fats, 4 Cal/g for carbohydrates and proteins, and 0 Cal/g for water and minerals.

KEY TAKEAWAY

- Thermochemical concepts can be applied to determine the actual energy available in food.

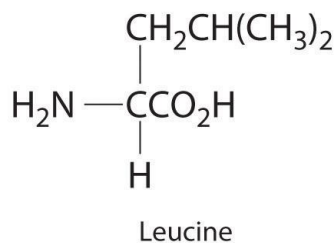
CONCEPTUAL PROBLEMS

- Can water be considered a food? Explain your answer.
- Describe how you would determine the caloric content of a bag of popcorn using a calorimeter.
- Why do some people initially feel cold after eating a meal and then begin to feel warm?
- In humans, one of the biochemical products of the combustion/digestion of amino acids is urea. What effect does this have on the energy available from these reactions? Speculate why conversion to urea is preferable to the generation of N_2 .

NUMERICAL PROBLEMS

Please be sure you are familiar with the topics discussed in Essential Skills 4 (Section 5.6 "Essential Skills 4") before proceeding to the Numerical Problems.

1. Determine the amount of energy available from the biological oxidation of 1.50 g of leucine (an amino acid, $\Delta H_{\text{comb}} = -3581.7 \text{ kJ/mol}$).



2. Calculate the energy released (in kilojoules) from the metabolism of 1.5 oz of vodka that is 62% water and 38% ethanol by volume, assuming that the total volume is equal to the sum of the volume of the two components. The density of ethanol is 0.824 g/mL. What is this enthalpy change in nutritional Calories?
3. While exercising, a person lifts an 80 lb barbell 7 ft off the ground. Assuming that the transformation of chemical energy to mechanical energy is only 35% efficient, how many Calories would the person use to accomplish this task? From Figure 5.11 "A Thermochemical Cycle for the Combustion of Glucose", how many grams of glucose would be needed to provide the energy to accomplish this task?
4. A 30 g sample of potato chips is placed in a bomb calorimeter with a heat capacity of 1.80 kJ/°C, and the bomb calorimeter is immersed in 1.5 L of water. Calculate the energy contained in the food per gram if, after combustion of the chips, the temperature of the calorimeter increases to 58.6°C from an initial temperature of 22.1°C.

5.5 Energy Sources and the Environment

LEARNING OBJECTIVE

1. To use thermochemical concepts to solve environmental issues.

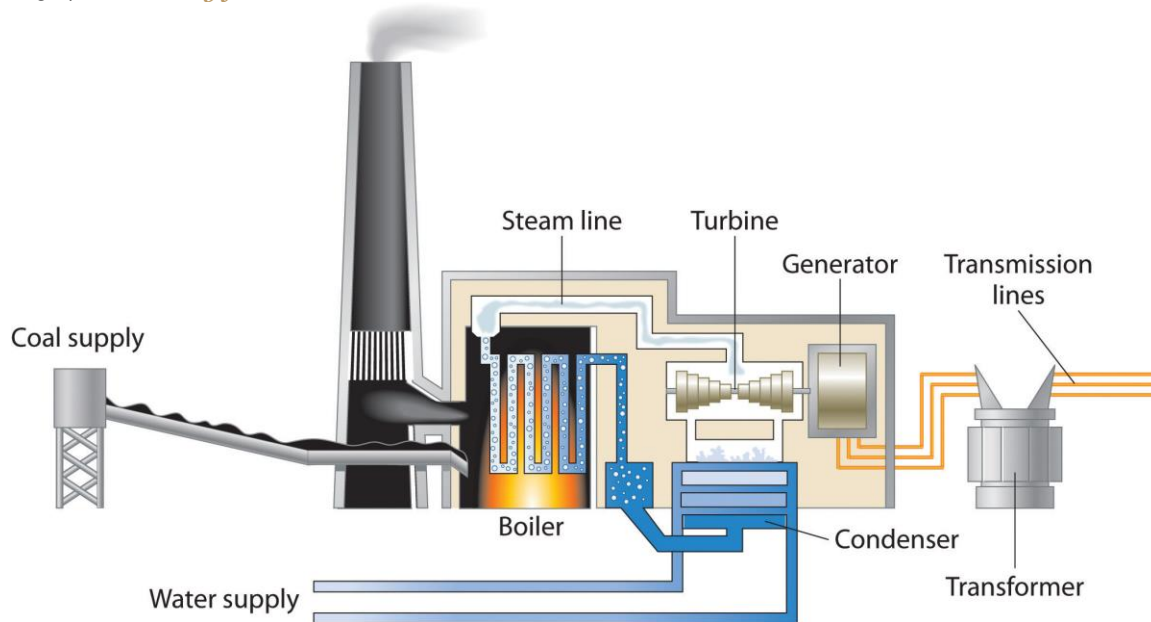
Our contemporary society requires the constant expenditure of huge amounts of energy to heat our homes, provide telephone and cable service, transport us from one location to another, provide light when it is dark outside, and run the machinery that manufactures material goods. The United States alone consumes almost 10^6 kJ per person per day, which is about 100 times the normal required energy content of the human diet. This figure is about 30% of the world's total energy usage, although only about 5% of the total population of the world lives in the United States. In contrast, the average energy consumption elsewhere in the world is about 10^5 kJ per person per day, although actual values vary widely depending on a country's level of industrialization. In this section, we describe various sources of energy and their impact on the environment.

Fuels

According to the law of conservation of energy, energy can never actually be “consumed”; it can only be changed from one form to another. What is consumed on a huge scale, however, are resources that can be readily converted to a form of energy that is useful for doing work. As you will see in Chapter 18 "Chemical Thermodynamics", energy that is not used to perform work is either stored as potential energy for future use or transferred to the surroundings as heat.

A major reason for the huge consumption of energy by our society is the low *efficiency* of most machines in transforming stored energy into work. Efficiency can be defined as the ratio of useful work accomplished to energy expended. Automobiles, for example, are only about 20% efficient in converting the energy stored in gasoline to mechanical work; the rest of the energy is released as heat, either emitted in the exhaust or produced by friction in bearings and tires. The production of electricity by coal- or oil-powered steam turbines is significantly more efficient (Figure 5.17 "Electricity from Coal"): about 38% of the energy released from combustion is converted to electricity. In comparison, modern nuclear power plants can be more than 50% efficient.

Figure 5.17 *Electricity from Coal*

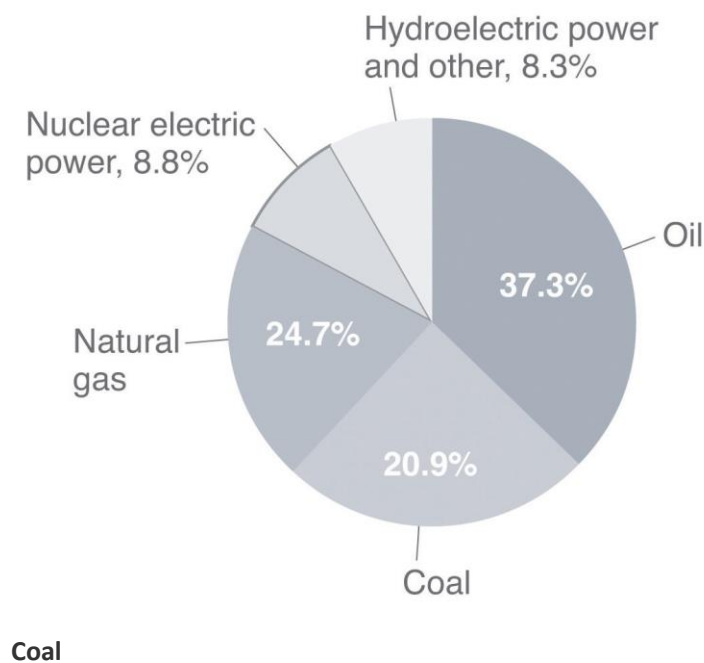


A coal-powered electric power plant uses the combustion of coal to produce steam, which drives a turbine to produce electricity.

In general, it is more efficient to use primary sources of energy directly (such as natural gas or oil) than to transform them to a secondary source such as electricity prior to their use. For example, if a furnace is well maintained, heating a house with natural gas is about 70% efficient. In contrast, burning the natural gas in a remote power plant, converting it to electricity, transmitting it long distances through wires, and heating the house by electric baseboard heaters have an overall efficiency of less than 35%.

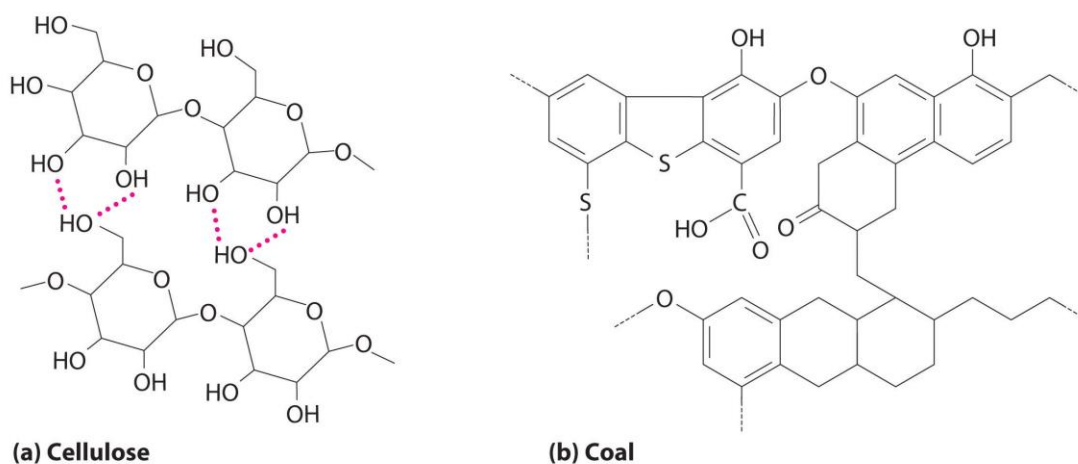
The total expenditure of energy in the world each year is about 3×10^{17} kJ. More than 80% of this energy is provided by the combustion of fossil fuels: oil, coal, and natural gas. (The sources of the energy consumed in the United States in 2009 are shown in Figure 5.18 "Energy Consumption in the United States by Source, 2009".) Natural gas and petroleum, whose compositions were described in Chapter 2 "Molecules, Ions, and Chemical Formulas", are the preferred fuels because they or products derived from them are gases or liquids that are readily transported, stored, and burned. Natural gas and petroleum are derived from the remains of marine creatures that died hundreds of millions of years ago and were buried beneath layers of sediment. As the sediment turned to rock, the tremendous heat and pressure inside Earth transformed the organic components of the buried sea creatures to petroleum and natural gas.

Figure 5.18 Energy Consumption in the United States by Source, 2009



Coal is a complex solid material derived primarily from plants that died and were buried hundreds of millions of years ago and were subsequently subjected to high temperatures and pressures. Because plants contain large amounts of *cellulose*, derived from linked glucose units, the structure of coal is more complex than that of petroleum (Figure 5.19 "The Structures of Cellulose and Coal"). In particular, coal contains a large number of oxygen atoms that link parts of the structure together, in addition to the basic framework of carbon–carbon bonds. It is impossible to draw a single structure for coal; however, because of the prevalence of rings of carbon atoms (due to the original high cellulose content), coal is more similar to an aromatic hydrocarbon than an aliphatic one.

Figure 5.19 *The Structures of Cellulose and Coal*



(a) Cellulose consists of long chains of cyclic glucose molecules linked by hydrogen bonds. (b) When cellulose is subjected to high pressures and temperatures for long periods of time, water is eliminated, and bonds are formed between the rings, eventually producing coal. This drawing shows some of the common structural features of coal; note the presence of many different kinds of ring structures.

There are four distinct classes of coal (Table 5.7 "Properties of Different Types of Coal"); their hydrogen and oxygen contents depend on the length of time the coal has been buried and the pressures and temperatures to which it has been subjected. Lignite, with a hydrogen:carbon ratio of about 1.0 and a high oxygen content, has the lowest ΔH_{comb} . Anthracite, in contrast, with a hydrogen:carbon ratio of about 0.5 and the lowest oxygen content, has the highest ΔH_{comb} and is the highest grade of coal. The most abundant form in the United States is bituminous coal, which has a high sulfur content because of the presence of small particles of pyrite (FeS_2). As discussed in Chapter 4 "Reactions in Aqueous Solution", the combustion of coal releases the sulfur in FeS_2 as SO_2 , which is a major contributor to acid rain. Table 5.8 "Enthalpies of Combustion of Common Fuels and Selected Organic Compounds" compares the ΔH_{comb} per gram of oil, natural gas, and coal with those of selected organic compounds.

Table 5.7 Properties of Different Types of Coal

Type	% Carbon	Hydrogen:Carbon Mole Ratio	% Oxygen	% Sulfur	Heat Content	US Deposits
anthracite	92	0.5	3	1	high	Pennsylvania, New York
bituminous	80	0.6	8	5	medium	Appalachia, Midwest, Utah
subbituminous	77	0.9	16	1	medium	Rocky Mountains
lignite	71	1.0	23	1	low	Montana

Table 5.8 Enthalpies of Combustion of Common Fuels and Selected Organic Compounds

Fuel	ΔH_{comb} (kJ/g)
dry wood	-15
peat	-20.8
bituminous coal	-28.3
charcoal	-35
kerosene	-37
C ₆ H ₆ (benzene)	-41.8
crude oil	-43
natural gas	-50
C ₂ H ₂ (acetylene)	-50.0
CH ₄ (methane)	-55.5
gasoline	-84
hydrogen	-143

Peat, a precursor to coal, is the partially decayed remains of plants that grow in swampy areas. It is removed from the ground in the form of soggy bricks of mud that will not burn until they have been dried. Even though peat is a smoky, poor-burning fuel that gives off relatively little heat, humans have burned it since ancient times (Figure 5.20 "A Peat Bog"). If a peat bog were buried under many layers of sediment for a few million years, the peat could eventually be compressed and heated enough to become lignite, the lowest grade of coal; given enough time and heat, lignite would eventually become anthracite, a much better fuel.

Converting Coal to Gaseous and Liquid Fuels

Oil and natural gas resources are limited. Current estimates suggest that the known reserves of petroleum will be exhausted in about 60 years, and supplies of natural gas are estimated to run out in about 120 years. Coal, on the other hand, is relatively abundant, making up more than 90% of the world's fossil fuel reserves. As a solid, coal is much more difficult to mine and ship than petroleum (a liquid) or natural gas. Consequently, more than 75% of the coal produced each year is simply burned in power plants to produce electricity. A great deal of current research focuses on developing methods to convert coal to gaseous fuels (*coal gasification*) or liquid fuels (*coal liquefaction*). In the most common approach to coal gasification, coal reacts with steam to produce a mixture of CO and H₂ known as *synthesis gas*, or *syngas*:^[1]

Converting coal to syngas removes any sulfur present and produces a clean-burning mixture of gases.

Syngas is also used as a reactant to produce methane and methanol. A promising approach is to convert coal directly to methane through a series of reactions.

Similarly, the techniques available for converting coal to liquid fuels are not yet economically competitive with the production of liquid fuels from petroleum. Current approaches to coal liquefaction use a catalyst to break the complex network structure of coal into more manageable fragments. The products are then treated with hydrogen (from syngas or other sources) under high pressure to produce a liquid more like petroleum. Subsequent distillation, cracking, and reforming can be used to create products similar to those obtained from petroleum. (For more information about cracking, see Chapter 2 "Molecules, Ions, and Chemical Formulas", Section 2.6 "Industrially Important Chemicals".) The total yield of liquid fuels is about 5.5 bbl of crude liquid per ton of coal (1 bbl is 42 gal or 160 L). Although the economics of coal liquefaction are currently even less attractive than for coal gasification, liquid fuels based on coal are likely to become economically competitive as supplies of petroleum are consumed.

EXAMPLE 13

If bituminous coal is converted to methane by the process in Equation 5.46, what is the ratio of the ΔH_{comb} of the methane produced to the enthalpy of the coal consumed to produce the methane? (Note that 1 mol of CH₄ is produced for every 2 mol of carbon in coal.)

Given: chemical reaction and ΔH_{comb} (Table 5.8 "Enthalpies of Combustion of Common Fuels and Selected Organic Compounds")

Asked for: ratio of ΔH_{comb} of methane produced to coal consumed

Strategy:

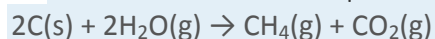
A Write a balanced chemical equation for the conversion of coal to methane. Referring to Table 5.8

"Enthalpies of Combustion of Common Fuels and Selected Organic Compounds", calculate the ΔH_{comb} of methane and carbon.

B Calculate the ratio of the energy released by combustion of the methane to the energy released by combustion of the carbon.

Solution:

A The balanced chemical equation for the conversion of coal to methane is as follows:



Thus 1 mol of methane is produced for every 2 mol of carbon consumed. The ΔH_{comb} of 1 mol of methane is

= -890 kJ

The ΔH_{comb} of 2 mol of carbon (as coal) is

= -680 kJ

B The ratio of the energy released from the combustion of methane to the energy released from the combustion of carbon is

= 1.31

The energy released from the combustion of the product (methane) is 131% of that of the reactant (coal).

The fuel value of coal is actually *increased* by the process!

How is this possible when the law of conservation of energy states that energy cannot be created? The

reaction consumes 2 mol of water ($\Delta H_{\text{of}} = -285.8 \text{ kJ/mol}$) but produces only 1 mol of CO_2 ($\Delta H_{\text{of}} = -393.5 \text{ kJ/mol}$). Part of the difference in potential energy between the two

(approximately 180 kJ/mol) is stored in CH_4 and can be released during combustion.

Exercise

Using the data in Table 5.8 "Enthalpies of Combustion of Common Fuels and Selected Organic

Compounds", calculate the mass of hydrogen necessary to provide as much energy during combustion as 1 bbl of crude oil (density approximately 0.75 g/mL).

Answer: 36 kg

The Carbon Cycle and the Greenhouse Effect

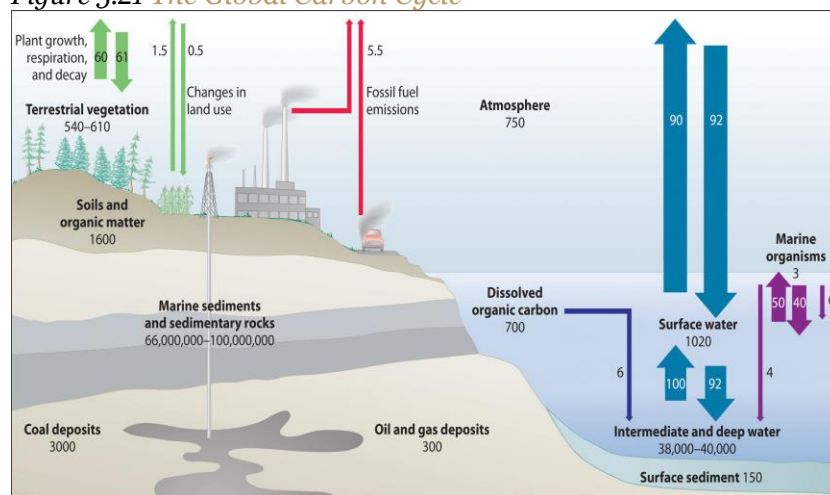
Even if carbon-based fuels could be burned with 100% efficiency, producing only $\text{CO}_2\text{(g)}$ and $\text{H}_2\text{O(g)}$, doing so could still potentially damage the environment when carried out on the vast scale required by an industrial society. The amount of CO_2 released is so large and is increasing so rapidly that it is apparently

overwhelming the natural ability of the planet to remove CO₂ from the atmosphere. In turn, the elevated levels of CO₂ are thought to be affecting the temperature of the planet through a mechanism known as the greenhouse effect. As you will see, there is little doubt that atmospheric CO₂ levels are increasing, and the major reason for this increase is the combustion of fossil fuels. There is substantially less agreement, however, on whether the increased CO₂ levels are responsible for a significant increase in temperature.

The Global Carbon Cycle

Figure 5.21 "The Global Carbon Cycle" illustrates the global carbon cycle, the distribution and flow of carbon on Earth. Normally, the fate of atmospheric CO₂ is to either (1) dissolve in the oceans and eventually precipitate as carbonate rocks or (2) be taken up by plants. The rate of uptake of CO₂ by the ocean is limited by its surface area and the rate at which gases dissolve, which are approximately constant. The rate of uptake of CO₂ by plants, representing about 60 billion metric tons of carbon per year, partly depends on how much of Earth's surface is covered by vegetation. Unfortunately, the rapid deforestation for agriculture is reducing the overall amount of vegetation, and about 60 billion metric tons of carbon are released annually as CO₂ from animal respiration and plant decay. The amount of carbon released as CO₂ every year by fossil fuel combustion is estimated to be about 5.5 billion metric tons. The net result is a system that is slightly out of balance, experiencing a slow but steady increase in atmospheric CO₂ levels (Figure 5.22 "Changes in Atmospheric CO"). As a result, average CO₂ levels have increased by about 30% since 1850.

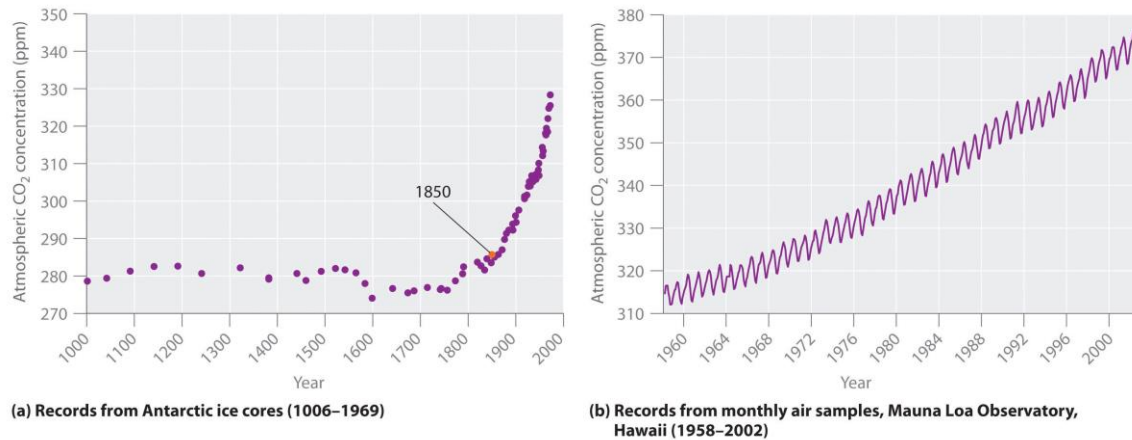
Figure 5.21 *The Global Carbon Cycle*



Volumes and exchanges in billions of metric tons

Most of Earth's carbon is found in the crust, where it is stored as calcium and magnesium carbonate in sedimentary rocks. The oceans also contain a large reservoir of carbon, primarily as the bicarbonate ion (HCO_3^-). Green plants consume about 60 billion metric tons of carbon per year as CO_2 during photosynthesis, and about the same amount of carbon is released as CO_2 annually from animal and plant respiration and decay. The combustion of fossil fuels releases about 5.5 billion metric tons of carbon per year as CO_2 .

Figure 5.22 *Changes in Atmospheric CO_2 Levels*

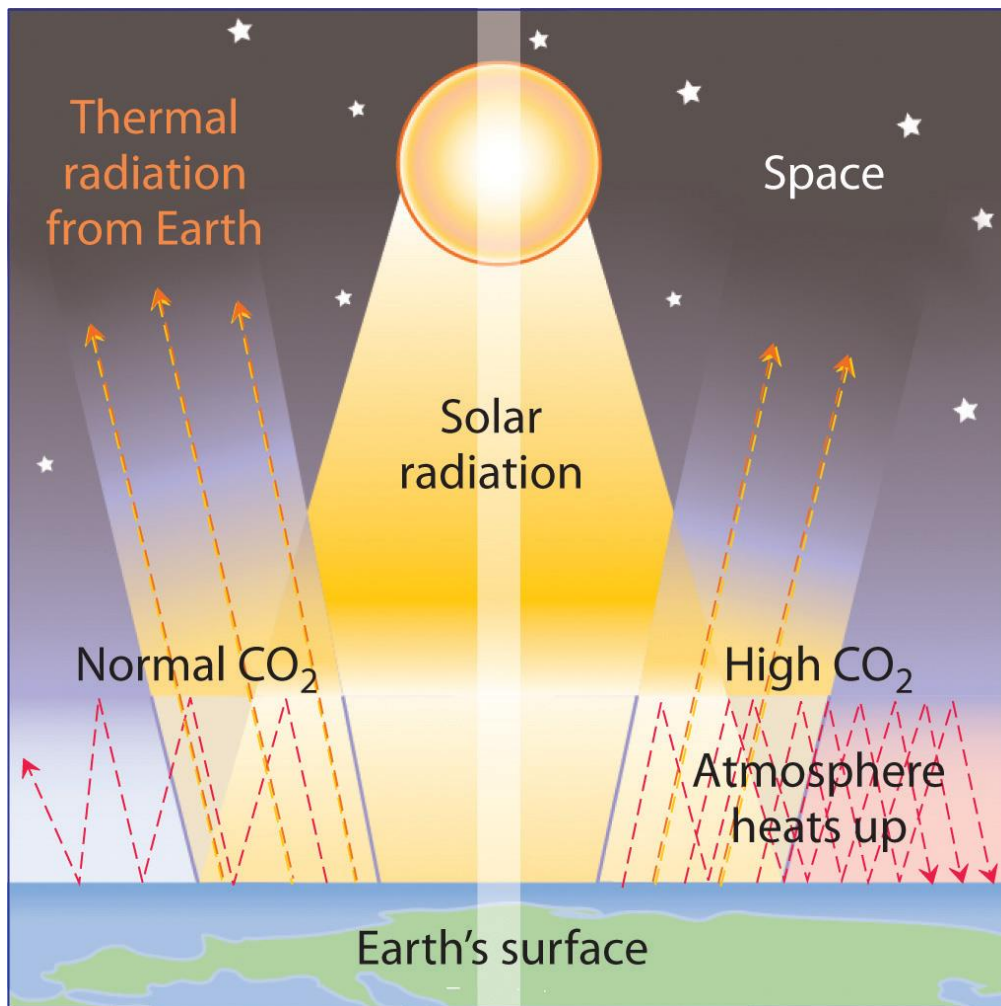


(a) Average worldwide CO_2 levels have increased by about 30% since 1850. (b) Atmospheric CO_2 concentrations measured at Mauna Loa in Hawaii show seasonal variations caused by the removal of CO_2 from the atmosphere by green plants during the growing season along with a general increase in CO_2 levels.

The Atmospheric Greenhouse Effect

The increasing levels of atmospheric CO_2 are of concern because CO_2 absorbs thermal energy radiated by the Earth, as do other gases such as water vapor, methane, and chlorofluorocarbons. Collectively, these substances are called greenhouse gases; they mimic the effect of a greenhouse by trapping thermal energy in the Earth's atmosphere, a phenomenon known as the greenhouse effect (Figure 5.23 "The Greenhouse Effect").

Figure 5.23 *The Greenhouse Effect*



Thermal energy can be trapped in Earth's atmosphere by gases such as CO₂, water vapor, methane, and chlorofluorocarbons before it can be radiated into space—like the effect of a greenhouse. It is not yet clear how large an increase in the temperature of Earth's surface can be attributed to this phenomenon.

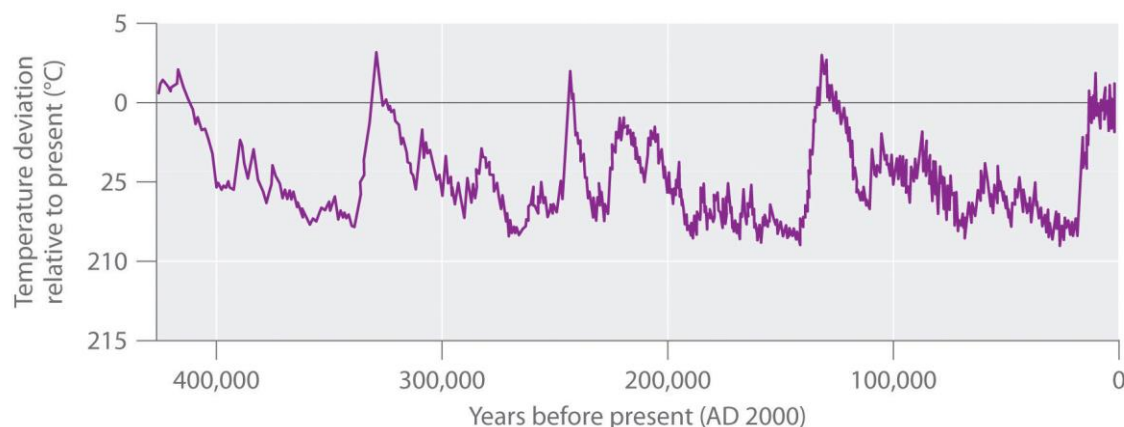
Venus is an example of a planet that has a runaway greenhouse effect. The atmosphere of Venus is about 95 times denser than that of Earth and contains about 95% CO₂. Because Venus is closer to the sun, it also receives more solar radiation than Earth does. The result of increased solar radiation and high CO₂ levels is an average surface temperature of about 450°C, which is hot enough to melt lead.

Data such as those in Figure 5.22 "Changes in Atmospheric CO" indicate that atmospheric levels of greenhouse gases have increased dramatically over the past 100 years, and it seems clear that the heavy use of fossil fuels by industry is largely responsible. It is not clear, however, how large an increase in temperature (*global warming*) may result from a continued increase in the levels of these gases. Estimates of the effects of doubling the preindustrial levels of CO₂ range from a 0°C to a 4.5°C increase in the average temperature of Earth's surface, which is currently about

14.4°C. Even small increases, however, could cause major perturbations in our planet's delicately balanced systems. For example, an increase of 5°C in Earth's average surface temperature could cause extensive melting of glaciers and the Antarctic ice cap. It has been suggested that the resulting rise in sea levels could flood highly populated coastal areas, such as New York City, Calcutta, Tokyo, Rio de Janeiro, and Sydney. An analysis conducted in 2009 by leading climate researchers from the US National Oceanic and Atmospheric Administration, Switzerland, and France shows that CO₂ in the atmosphere will remain near peak levels far longer than other greenhouse gases, which dissipate more quickly. The study predicts a rise in sea levels of approximately 3 ft by the year 3000, excluding the rise from melting glaciers and polar ice caps. According to the analysis, southwestern North America, the Mediterranean, and southern Africa are projected to face droughts comparable to that of the Dust Bowl of the 1930s as a result of global climate changes.

The increase in CO₂ levels is only one of many trends that can affect Earth's temperature. In fact, geologic evidence shows that the average temperature of Earth has fluctuated significantly over the past 400,000 years, with a series of glacial periods (during which the temperature was 10°C–15°C *lower* than it is now and large glaciers covered much of the globe) interspersed with relatively short, warm interglacial periods (Figure 5.24 "Average Surface Temperature of Earth over the Past 400,000 Years"). Although average temperatures appear to have increased by 0.5°C in the last century, the statistical significance of this increase is open to question, as is the existence of a cause-and-effect relationship between the temperature change and CO₂ levels. Despite the lack of incontrovertible scientific evidence, however, many people believe that we should take steps now to limit CO₂ emissions and explore alternative sources of energy, such as solar energy, geothermal energy from volcanic steam, and nuclear energy, to avoid even the possibility of creating major perturbations in Earth's environment. In 2010, international delegates met in Cancún, Mexico, and agreed on a broad array of measures that would advance climate protection. These included the development of low-carbon technologies, providing a framework to reduce deforestation, and aiding countries in assessing their own vulnerabilities. They avoided, however, contentious issues of assigning emissions reductions commitments.

Figure 5.24 Average Surface Temperature of Earth over the Past 400,000 Years



Summary

More than 80% of the energy used by modern society (about 3×10^{17} kJ/yr) is from the combustion of fossil fuels. Because of their availability, ease of transport, and facile conversion to convenient fuels, natural gas and petroleum are currently the preferred fuels. Supplies of **coal**, a complex solid material derived from plants that lived long ago, are much greater, but the difficulty in transporting and burning a solid makes it less attractive as a fuel. Coal releases the smallest amount of energy per gram of any fossil fuel, and natural gas the greatest amount. The combustion of fossil fuels releases large amounts of CO_2 that upset the balance of the **carbon cycle** and result in a steady increase in atmospheric CO_2 levels. Because CO_2 is a **greenhouse gas**, which absorbs heat before it can be radiated from Earth into space, CO_2 in the atmosphere can result in increased surface temperatures (the **greenhouse effect**). The temperature increases caused by increased CO_2 levels because of human activities are, however, superimposed on much larger variations in Earth's temperature that have produced phenomena such as the ice ages and are still poorly understood.

KEY TAKEAWAY

- Thermochemical concepts can be used to calculate the efficiency of various forms of fuel, which can then be applied to environmental issues.

CONCEPTUAL PROBLEMS

1. Why is it preferable to convert coal to syngas before use rather than burning coal as a solid fuel?
2. What is meant by the term *greenhouse gases*? List three greenhouse gases that have been implicated in global warming.
3. Name three factors that determine the rate of planetary CO_2 uptake.

4. The structure of coal is quite different from the structure of gasoline. How do their structural differences affect their enthalpies of combustion? Explain your answer.

NUMERICAL PROBLEMS

Please be sure you are familiar with the topics discussed in Essential Skills 4 (Section 5.6 "Essential Skills 4") before proceeding to the Numerical Problems.

- One of the side reactions that occurs during the burning of fossil fuels is
$$4\text{FeS}_2(\text{s}) + 11\text{O}_2(\text{g}) \rightarrow 2\text{Fe}_2\text{O}_3(\text{s}) + 8\text{SO}_2(\text{g})$$
 - How many kilojoules of energy are released during the combustion of 10 lb of FeS_2 ?
 - How many pounds of SO_2 are released into the atmosphere?
 - Discuss the potential environmental impacts of this combustion reaction.
- How many kilograms of CO_2 are released during the combustion of 16 gal of gasoline? Assume that gasoline is pure isooctane with a density of 0.6919 g/mL. If this combustion was used to heat 4.5×10^3 L of water from an initial temperature of 11.0°C , what would be the final temperature of the water assuming 42% efficiency in the energy transfer?
- A 60 W light bulb is burned for 6 hours. If we assume an efficiency of 38% in the conversion of energy from oil to electricity, how much oil must be consumed to supply the electrical energy needed to light the bulb? ($1 \text{ W} = 1 \text{ J/s}$)
- How many liters of cyclohexane must be burned to release as much energy as burning 10.0 lb of pine logs? The density of cyclohexane is 0.7785 g/mL, and its $\Delta H_{\text{comb}} = -46.6 \text{ kJ/g}$.

[1] Because coal is 70%–90% carbon by mass, it is approximated as C in Equation 5.46.

5.6 Essential Skills 4

TOPICS

- Temperature
- Unit Conversions: Dimensional Analysis

The previous Essential Skills sections introduced some fundamental operations that you need to successfully manipulate mathematical equations in chemistry. This section describes how to convert between temperature scales and further develops the topic of unit conversions started in Essential Skills 2 in Chapter 3 "Chemical Reactions", Section 3.7 "Essential Skills 2".

Temperature

The concept of temperature may seem familiar to you, but many people confuse temperature with heat. **Temperature** is a measure of how hot or cold an object is relative to another object (its thermal energy content), whereas **heat** is the flow of thermal energy between objects with different temperatures. Three different scales are commonly used to measure temperature: Fahrenheit (expressed as °F), Celsius (°C), and Kelvin (K). Thermometers measure temperature by using materials that expand or contract when heated or cooled. Mercury or alcohol thermometers, for example, have a reservoir of liquid that expands when heated and contracts when cooled, so the liquid column lengthens or shortens as the temperature of the liquid changes.

The Fahrenheit Scale

The Fahrenheit temperature scale was developed in 1717 by the German physicist Gabriel Fahrenheit, who designated the temperature of a bath of ice melting in a solution of salt as the zero point on his scale. Such a solution was commonly used in the 18th century to carry out low-temperature reactions in the laboratory. The scale was measured in increments of 12; its upper end, designated as 96°, was based on the armpit temperature of a healthy person—in this case, Fahrenheit's wife. Later, the number of increments shown on a thermometer increased as measurements became more precise. The upper point is based on the boiling point of water, designated as 212° to maintain the original magnitude of a Fahrenheit degree, whereas the melting point of ice is designated as 32°.

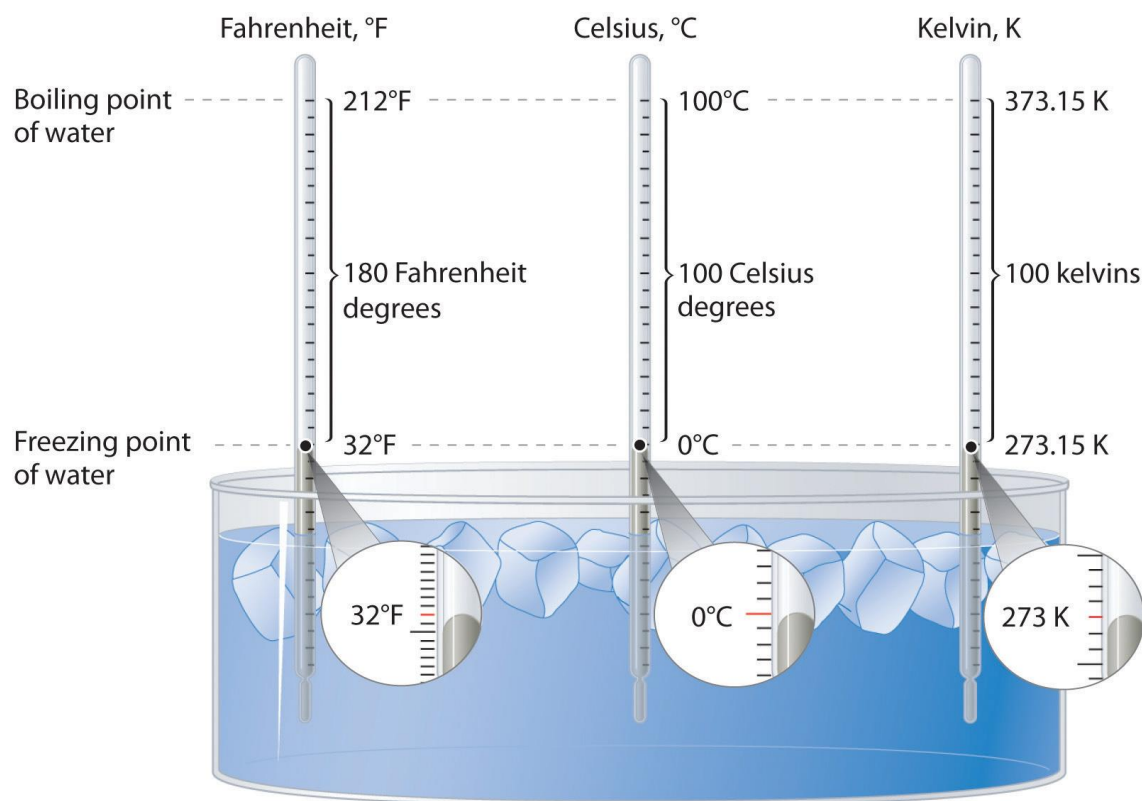
The Celsius Scale

The Celsius scale was developed in 1742 by the Swedish astronomer Anders Celsius. It is based on the melting and boiling points of water under normal atmospheric conditions. The current scale is an inverted form of the original scale, which was divided into 100 increments. Because of these 100 divisions, the Celsius scale is also called the *centigrade scale*.

The Kelvin Scale

Lord Kelvin, working in Scotland, developed the Kelvin scale in 1848. His scale uses molecular energy to define the extremes of hot and cold. Absolute zero, or 0 K, corresponds to the point at which molecular energy is at a minimum. The Kelvin scale is preferred in scientific work, although the Celsius scale is also commonly used. Temperatures measured on the Kelvin scale are reported simply as K, not °K. Figure 5.25 "A Comparison of the Fahrenheit, Celsius, and Kelvin Temperature Scales" compares the three scales.

Figure 5.25 A Comparison of the Fahrenheit, Celsius, and Kelvin Temperature Scales



Because the difference between the freezing point of water and the boiling point of water is 100° on both the Celsius and Kelvin scales, the size of a degree Celsius ($^\circ\text{C}$) and a kelvin (K) are precisely the same. In contrast, both a degree Celsius and a kelvin are $9/5$ the size of a degree Fahrenheit ($^\circ\text{F}$).

Converting between Scales

The kelvin is the same size as the Celsius degree, so measurements are easily converted from one to the other. The freezing point of water is $0^\circ\text{C} = 273.15\text{ K}$; the boiling point of water is $100^\circ\text{C} = 373.15\text{ K}$. The

Kelvin and Celsius scales are related as follows:

$$T (\text{in } ^\circ\text{C}) + 273.15 = T (\text{in K}) \quad T (\text{in K}) - 273.15 = T (\text{in } ^\circ\text{C})$$

Degrees on the Fahrenheit scale, however, are based on an English tradition of using 12 divisions, just as 1 ft = 12 in. The relationship between degrees Fahrenheit and degrees Celsius is as follows:

$$T (\text{in } ^\circ\text{F}) = 9/5 T (^\circ\text{C}) + 32^\circ\text{F} \quad T (\text{in } ^\circ\text{C}) = 5/9 [T (^\circ\text{F}) - 32^\circ\text{F}]$$

where the coefficient for degrees Fahrenheit is exact. (Some calculators have a function that allows you to convert directly between $^\circ\text{F}$ and $^\circ\text{C}$.) There is only one temperature for which the numerical value is the same on both the

Fahrenheit and Celsius scales: $-40^\circ\text{C} = -40^\circ\text{F}$.

SKILL BUILDER ES1

- a. Convert the temperature of the surface of the sun (5800 K) and the boiling points of gold (3080 K) and liquid nitrogen (77.36 K) to °C and °F.
- b. A student is ill with a temperature of 103.5°F. What is her temperature in °C and K?

Solution:

a.

Sun: Gold: N₂:

$$\begin{aligned}
 5800 \text{ K} &= (5800 - 273.15)^\circ\text{C} \\
 &= 5527^\circ\text{C} = 9981^\circ\text{F} \\
 3080 \text{ K} &= (3080 - 273.15)^\circ\text{C} = 2807^\circ\text{C}
 \end{aligned}$$

b.

$$103.5^\circ\text{F} = 5^\circ\text{C} \quad 9^\circ\text{F}(103.5^\circ\text{F} - 32^\circ\text{F}) = 40^\circ\text{C} = 40^\circ\text{C} + 273.15 = 313 \text{ K}$$

c.

Unit Conversions: Dimensional Analysis

In Essential Skills 2, you learned a convenient way of converting between units of measure, such as from grams to kilograms or seconds to hours. The use of units in a calculation to ensure that we obtain the final proper units is called *dimensional analysis*. For example, if we observe experimentally that an object's potential energy is related to its mass, its height from the ground, and to a gravitational force, then when multiplied, the units of mass, height, and the force of gravity must give us units corresponding to those of energy.

Energy is typically measured in joules, calories, or electron volts (eV), defined by the following expressions:

$$1 \text{ J} = 1 (\text{kg}\cdot\text{m}^2)/\text{s}^2 = 1 \text{ coulomb}\cdot\text{volt} \quad 1 \text{ cal} = 4.184 \text{ J} \quad 1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$$

To illustrate the use of dimensional analysis to solve energy problems, let us calculate the kinetic energy in joules of a 320 g object traveling at 123 cm/s. To obtain an answer in joules, we must convert grams to kilograms and centimeters to meters. Using Equation 5.4, the calculation may be set up as follows:

$$\begin{aligned}
 KE &= \frac{1}{2}mv^2 = \frac{1}{2}(g)(kgg)[(cms)(mcm)]^2 \\
 &= (g)(kgg)(cm^2s^2 / m^2cm^2) = kg \cancel{m}^2s^2 \\
 &= 12320 \text{ g} (1 \text{ kg} / 1000 \text{ g}) [(123 \text{ cm} / 100 \text{ cm}) (1 \text{ s} / 1000 \text{ s})]^2 \\
 &= 0.320 \text{ kg} [123 \text{ ms} (100)]^2 \\
 &= 120.320 \text{ kg} [(123)^2 m^2s^2 (100)^2] = 0.242 (kg \cancel{m}^2) / s^2 = 0.242 \text{ J}
 \end{aligned}$$

Now suppose you wish to report the number of kilocalories of energy contained in a 7.00 oz piece of chocolate in units of kilojoules per gram. To obtain an answer in kilojoules, we must convert 7.00 oz to grams and kilocalories to kilojoules. Food reported to contain a value in Calories actually contains that same value in kilocalories. If the chocolate wrapper lists the caloric content as 120 Calories, the chocolate contains 120 kcal of energy. If we choose to use multiple steps to obtain our answer, we can begin with the conversion of kilocalories to kilojoules:

$$120 \text{ kcal} \left(\frac{1000 \text{ cal}}{1 \text{ kcal}} \right) \left(\frac{4.184 \text{ J}}{1 \text{ cal}} \right) \left(\frac{1 \text{ kJ}}{1000 \text{ J}} \right) = 502 \text{ kJ}$$

We next convert the 7.00 oz of chocolate to grams:

$$7.00 \text{ oz} \left(\frac{28.35 \text{ g}}{1 \text{ oz}} \right) = 199 \text{ g}$$

The number of kilojoules per gram is therefore

$$502 \text{ kJ} / 199 \text{ g} = 2.52 \text{ kJ/g}$$

The discrepancy between the two answers is attributable to rounding to the correct number of significant figures for each step when carrying out the calculation in a stepwise manner. Recall that all digits in the calculator should be carried forward when carrying out a calculation using multiple steps. In this problem, we first converted kilocalories to kilojoules and then converted ounces to grams. Skill Builder ES2 allows you to practice making multiple conversions between units in a single step.

SKILL BUILDER ES2

- Write a single equation to show how to convert cm/min to km/h; cal/oz to J/g; lb/in.² to kg/m²; and °C/s to K/h.
- How many Calories are contained in an 8.0 oz serving of green beans if their fuel value is 1.5 kJ/g?
- Gasoline has a fuel value of 48 kJ/g. How much energy in joules can be obtained by filling an automobile's 16.3 gal tank with gasoline, assuming gasoline has a density of 0.70 g/mL?

Solution:

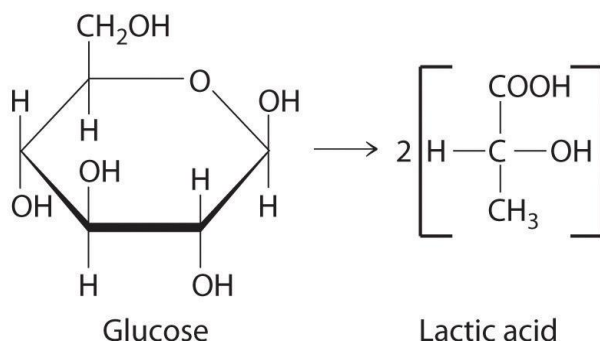
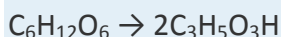
- Our goal is to convert 1.5 kJ/g to Calories in 8 oz:
- Our goal is to use the energy content, 48 kJ/g, and the density, 0.70 g/mL, to obtain the number of joules in 16.3 gal of gasoline:

5.7 End-of-Chapter Material

APPLICATION PROBLEMS

Please be sure you are familiar with the topics discussed in Essential Skills 4 (Section 5.6 "Essential Skills 4") before proceeding to the Application Problems. Problems marked with a ♦ involve multiple concepts.

1. Palm trees grow on the coast of southern England even though the latitude is the same as that of Winnipeg, Canada. What is a plausible explanation for this phenomenon? (Hint: the Gulf Stream current is a factor.)
2. During intense exercise, your body cannot provide enough oxygen to allow the complete combustion of glucose to carbon dioxide. Under these conditions, an alternative means of obtaining energy from glucose is used in which glucose ($C_6H_{12}O_6$) is converted to lactic acid ($C_3H_5O_3H$). The equation for this reaction is as follows:



1.
 - a. Calculate the energy yield for this reaction per mole of glucose.
 - b. How does this energy yield compare with that obtained per mole of glucose for the combustion reaction?
 - c. Muscles become sore after intense exercise. Propose a chemical explanation for this.
2. ♦ During the late spring, icebergs in the North Atlantic pose a hazard to shipping. To avoid them, ships travel routes that are about 30% longer. Many attempts have been made to destroy icebergs, including using explosives, torpedoes, and bombs. How much heat must be generated to melt 15% of a 1.9×10^8 kg iceberg? How many kilograms of TNT (trinitrotoluene, $C_7H_5N_3O_6$) would be needed to provide enough energy to melt the ice? (The ΔH for explosive decomposition of TNT is -1035.8 kJ/mol.)

3. Many biochemical processes occur through sequences of reactions called *pathways*. The total energy released by many of these pathways is much more than the energy a cell could handle if it were all released in a single step. For example, the combustion of glucose in a single step would release enough energy to kill a cell. By using a series of smaller steps that release less energy per reaction, however, the cell can extract the maximum energy from glucose without being destroyed. Referring to Equation 5.30, calculate how many grams of glucose would need to be metabolized to raise the temperature of a liver cell from an average body temperature of 37°C to 100°C, if the cell has a volume of 5000 μm^3 . Although the cell is only 69% water, assume that the density of the cell is 1.00 and that its C_s is the same as that of water.
4. ♦ During smelting, naturally occurring metal oxides are reduced by carbon at high temperature. For copper(II) oxide, this process includes the following series of chemical equations:

$$\text{CuO(s)} + \text{C(s)} \rightarrow \text{Cu(l)} + \text{CO(g)} \quad 2\text{C(s)} + \text{O}_2\text{(g)} \rightarrow 2\text{CO(g)} \quad \text{CuO(l)} + \text{CO(g)} \rightarrow \text{Cu(s)} + \text{CO}_2\text{(g)}$$

The final products are CO_2 and Cu. The discovery of this process led to the increasing use of ores as sources of metals in ancient cultures. In fact, between 3000 BC and 2000 BC, the smelting of copper was well established, and beads made from copper are some of the earliest known metal artifacts.

 - a. Write a balanced chemical equation for the overall reaction of CuO, C, and O_2 to give *only* CO_2 and Cu.
 - b. Using Hess's law and the data in Chapter 25 "Appendix A: Standard Thermodynamic Quantities for Chemical Substances at 25°C", calculate ΔH_{rxn} for the smelting of CuO ore to give Cu and CO_2 .
 - c. Assuming complete reaction, how much heat was released if 23 g of Cu metal was produced from its ore?
5. ♦ The earliest known Egyptian artifacts made from tin metal date back to approximately 1400 BC. If the smelting process for SnO_2 occurs via the reaction sequence

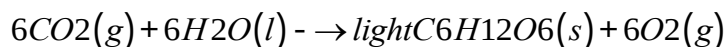
$$\text{SnO}_2\text{(s)} + 2\text{C(s)} \rightarrow \text{Sn(s)} + 2\text{CO(g)} \quad \text{SnO}_2\text{(s)} + 2\text{CO(g)} \rightarrow \text{Sn(s)} + 2\text{CO}_2\text{(g)}$$

what is ΔH_{rxn} for the conversion of SnO_2 to Sn (s, white) by this smelting process? How much heat was released or required if 28 g of Sn metal was produced from its ore, assuming complete reaction?
6. ♦ An average American consumes approximately 10^6 kJ of energy per day. The average life expectancy of an American is 77.9 years.

- a. How much coal would need to be burned to provide enough energy to meet a person's energy demands if the efficiency of energy production from coal is 38%?
 - b. If the coal contains 0.6% by mass FeS_2 , how many kilograms of sulfuric acid are produced during the time in part (a)?
7. Several theories propose that life on Earth evolved in the absence of oxygen. One theory is that primitive organisms used fermentation processes, in which sugars are decomposed in an oxygen-free environment, to obtain energy. Many kinds of fermentation processes are possible, including the conversion of glucose to lactic acid (a), to CO_2 and ethanol (b), and to ethanol and acetic acid (c):
- a. $\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) \rightarrow 2\text{C}_3\text{H}_6\text{O}_3(\text{s})$
 - b. $\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) \rightarrow 2\text{C}_2\text{H}_5\text{OH}(\text{l}) + 2\text{CO}_2(\text{g})$
 - c. $\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{C}_2\text{H}_5\text{OH}(\text{l}) + \text{CH}_3\text{CO}_2\text{H}(\text{l}) + 2\text{H}_2(\text{g}) + 2\text{CO}_2(\text{g})$

Reaction (a) occurs in rapidly exercising muscle cells, reaction (b) occurs in yeast, and reaction (c) occurs in intestinal bacteria. Using Chapter 25 "Appendix A: Standard Thermodynamic Quantities for Chemical Substances at 25°C", calculate which reaction gives the greatest energy yield per mole of glucose.

8. A 70 kg person expends 85 Cal/h watching television. If the person eats 8 cups of popcorn that contains 55 Cal per cup, how many kilojoules of energy from the popcorn will have been burned during a 2 h movie? After the movie, the person goes outside to play tennis and burns approximately 500 Cal/h. How long will that person have to play tennis to work off all the residual energy from the popcorn?
9. ♦ Photosynthesis in higher plants is a complex process in which glucose is synthesized from atmospheric carbon dioxide and water in a sequence of reactions that uses light as an energy source. The overall reaction is as follows:



Glucose may then be used to produce the complex carbohydrates, such as cellulose, that constitute plant tissues.

- a. Is the reaction endothermic or exothermic?
- b. How many grams of glucose are produced per kilogram of carbon dioxide?
- c. A 2.5 lb sweet potato is approximately 73% water by mass. If the remaining mass is made up of carbohydrates derived from glucose, how much carbon dioxide was needed to grow this sweet potato?

- d. How many kilojoules of energy are stored in the potato?
- e. Which releases more energy—digestion of the potato or combustion of the potato?
10. Adipose (fat) tissue consists of cellular protoplasm, which is mostly water, and fat globules. Nearly all the energy stored in adipose tissue comes from the chemical energy of its fat globules, totaling approximately 3500 Cal per pound of tissue. How many kilojoules of energy are stored in 10 g of adipose tissue? How many 50 g brownies would you need to consume to generate 10 lb of fat? (Refer to Table 5.5 "Approximate Compositions and Fuel Values of Some Common Foods" for the necessary caloric data.)
11. If a moderate running pace of 5 min/km expends energy at a rate of about 400 kJ/km, how many 8 oz apples would a person have to eat to have enough energy to run 5 mi? How many 4 oz hamburgers? (Refer to Table 5.5 "Approximate Compositions and Fuel Values of Some Common Foods" for the necessary caloric data.)
12. Proteins contain approximately 4 Cal/g, carbohydrates approximately 4 Cal/g, and fat approximately 9 Cal/g. How many kilojoules of energy are available from the consumption of one serving (8 oz) of each food in the table? (Data are shown per serving.)

Food	Protein (g)	Fat (g)	Carbohydrates (g)
sour cream	7	48	10
banana	2	1	35
cheeseburger	60	31	40
green peas	8	1	21

13. When you eat a bowl of cereal with 500 g of milk, how many Calories must your body burn to warm the milk from 4°C to a normal body temperature of 37°C? (Assume milk has the same specific heat as water.) How many Calories are burned warming the same amount of milk in a 32°C bowl of oatmeal from 32°C to normal body temperature? In some countries that experience starvation conditions, it has been found that infants don't starve even though the milk from their mothers doesn't contain the number of Calories thought necessary to sustain them. Propose an explanation for this.
14. If a person's fever is caused by an increase in the temperature of water inside the body, how much additional energy is needed if a 70 kg person with a normal body temperature of 37°C runs a temperature of 39.5°C? (A person's body is approximately 79% water.) The old adage "feed a fever" may contain some truth in this case. How many 4 oz hamburgers would the person need to consume to cause this change? (Refer to Table 5.5 "Approximate Compositions and Fuel Values of Some Common Foods" for the necessary caloric data.)

15. Approximately 810 kJ of energy is needed to evaporate water from the leaves of a 9.2 m tree in one day.

What mass of water is evaporated from the tree?

Chapter 6

The Structure of Atoms

Chapter 1 "Introduction to Chemistry" through Chapter 5 "Energy Changes in Chemical Reactions" introduced you to a wide variety of chemical substances and some of the most fundamental concepts in chemistry, including general descriptions of chemical bonding, mass relationships in chemical equations, and the energy changes associated with chemical reactions. You learned that the atoms of each element contain a unique number of positively charged protons in the nucleus and that a neutral atom has the same number of electrons as protons. You also learned that protons and neutrons constitute most of the mass of the atom and that electrons occupy most of the volume of an atom. These facts do not, however, explain the stoichiometries and the structures of chemical compounds; a deeper understanding of the electronic structure of atoms is required.

The noble gases. Helium, neon, argon, krypton, and xenon, all monatomic elements, are five of the six known noble gases. When atoms of these gases are excited by the flow of electrons in the discharge tubes, they emit photons of visible light in their characteristic spectral colors. All noble gases have the maximum number of electrons possible in their outer shell (2 for helium, 8 for all others), so they do not form chemical compounds easily.

In this chapter, we describe how electrons are arranged in atoms and how the spatial arrangements of electrons are related to their energies. We also explain how knowing the arrangement of electrons in an atom enables chemists to predict and explain the chemistry of an element. As you study the material presented in this chapter, you will discover how the shape of the periodic table reflects the electronic arrangements of elements. In this and subsequent chapters, we build on this information to explain why certain chemical changes occur and others do not.

After reading this chapter, you will know enough about the theory of the electronic structure of atoms to explain what causes the characteristic colors of neon signs, how laser beams are created, and why gemstones and fireworks have such brilliant colors. In later chapters, we will develop the concepts introduced here to explain why the only compound formed by sodium and chlorine is NaCl, an ionic compound, whereas neon and argon do not form any

stable compounds, and why carbon and hydrogen combine to form an almost endless array of covalent compounds, such as CH_4 , C_2H_2 , C_2H_4 , and C_2H_6 . You will discover that knowing how to use the periodic table is the single most important skill you can acquire to understand the incredible chemical diversity of the elements.

6.1 Waves and Electromagnetic Radiation

LEARNING OBJECTIVE

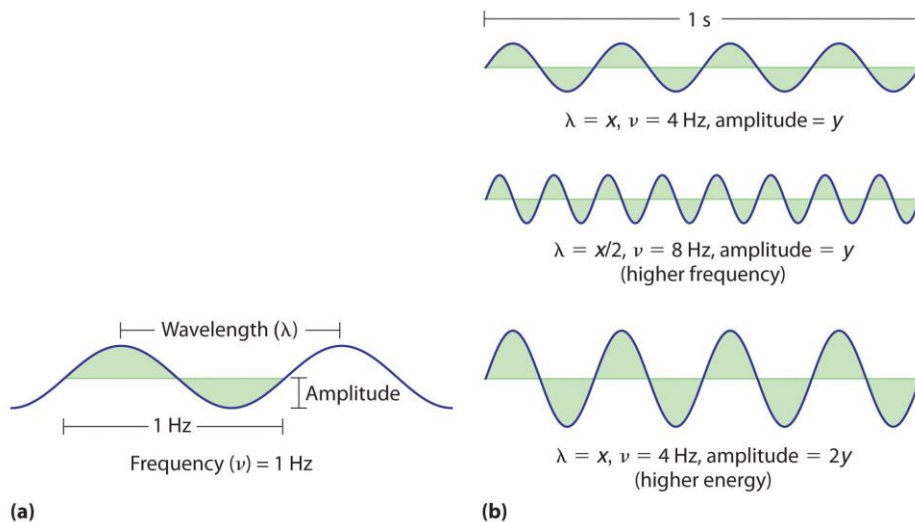
1. To know the characteristics of electromagnetic energy.

Scientists discovered much of what we know about the structure of the atom by observing the interaction of atoms with various forms of radiant, or transmitted, energy, such as the energy associated with the visible light we detect with our eyes, the infrared radiation we feel as heat, the ultraviolet light that causes sunburn, and the x-rays that produce images of our teeth or bones. All these forms of radiant energy should be familiar to you. We begin our discussion of the development of our current atomic model by describing the properties of waves and the various forms of electromagnetic radiation.

Properties of Waves

A wave is a periodic oscillation that transmits energy through space. Anyone who has visited a beach or dropped a stone into a puddle has observed waves traveling through water (Figure 6.1 "A Wave in Water"). These waves are produced when wind, a stone, or some other disturbance, such as a passing boat, transfers energy to the water, causing the surface to oscillate up and down as the energy travels outward from its point of origin. As a wave passes a particular point on the surface of the water, anything floating there moves up and down.

Figure 6.2 Important Properties of Waves



(a) Wavelength (λ), frequency (ν , labeled in Hz), and amplitude are indicated on this drawing of a wave. (b) The wave with the shortest wavelength has the greatest number of wavelengths per unit time (i.e., the highest frequency). If two waves have the same frequency and speed, the one with the greater amplitude has the higher energy.

Waves have characteristic properties (Figure 6.2 "Important Properties of Waves"). As you may have noticed in Figure 6.1 "A Wave in Water", waves are periodic; that is, they repeat regularly in both space and time. The distance between two corresponding points in a wave—between the midpoints of two peaks, for example, or two troughs—is the wavelength (λ).^[1] Wavelengths are described by a unit of distance, typically meters.

The frequency (ν) of a wave is the number of oscillations that pass a particular point in a given period of time. The usual units are oscillations per second ($1/\text{s} = \text{s}^{-1}$), which in the SI system is called the hertz (Hz).^[2] The amplitude, or vertical height, of a wave is defined as half the peak-to-trough height; as the amplitude of a wave with a given frequency increases, so does its energy. As you can see in Figure 6.2 "Important Properties of Waves", two waves can have the same amplitude but different wavelengths and vice versa. The distance traveled by a wave per unit time is its speed (v), which is typically measured in meters per second (m/s). The speed of a wave is equal to the product of its wavelength and frequency:

Equation 6.1

$$(\text{wavelength}) (\text{frequency}) = \text{speed}$$

Water waves are slow compared to sound waves, which can travel through solids, liquids, and gases.

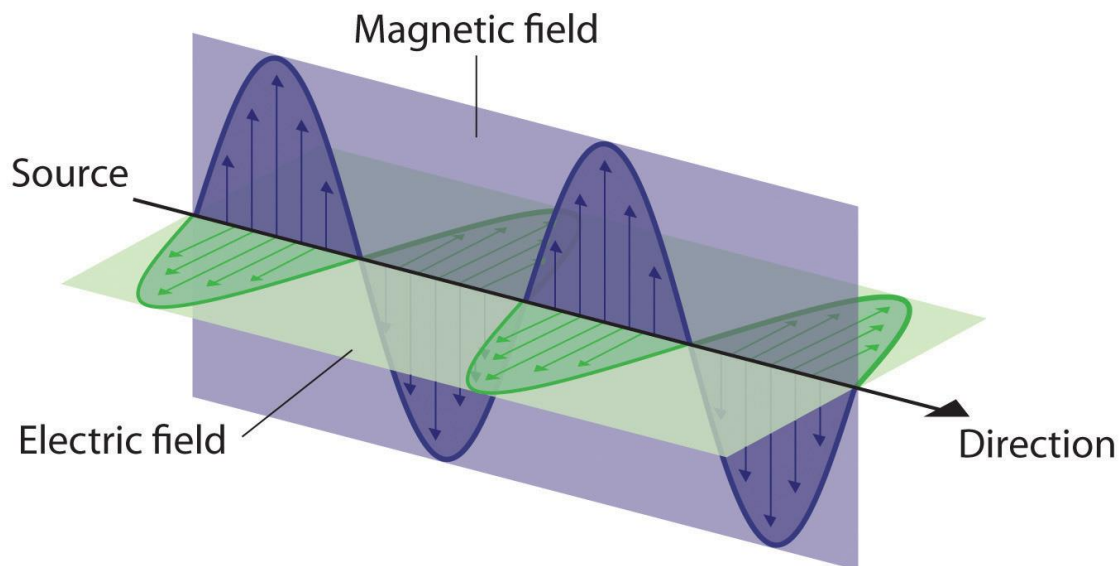
Whereas water waves may travel a few meters per second, the speed of sound in dry air at 20°C is 343.5 m/s. Ultrasonic waves, which travel at an even higher speed ($>1500 \text{ m/s}$) and have a greater frequency,

are used in such diverse applications as locating underwater objects and the medical imaging of internal organs.

Electromagnetic Radiation

Water waves transmit energy through space by the periodic oscillation of matter (the water). In contrast, energy that is transmitted, or radiated, through space in the form of periodic oscillations of electric and magnetic fields is known as electromagnetic radiation (Figure 6.3 "The Nature of Electromagnetic Radiation"). Some forms of electromagnetic radiation are shown in Figure 6.4 "The Electromagnetic Spectrum". In a vacuum, all forms of electromagnetic radiation—whether microwaves, visible light, or gamma rays—travel at the speed of light (c), a fundamental physical constant with a value of 2.99792458×10^8 m/s (which is about 3.00×10^8 m/s or 1.86×10^5 mi/s). This is about a million times faster than the speed of sound.

Figure 6.3 *The Nature of Electromagnetic Radiation*



All forms of electromagnetic radiation consist of perpendicular oscillating electric and magnetic fields.

Because the various kinds of electromagnetic radiation all have the same speed (c), they differ in only wavelength and frequency. As shown in Figure 6.4 "The Electromagnetic Spectrum" and Table 6.1 "Common Wavelength Units for Electromagnetic Radiation", the wavelengths of familiar electromagnetic radiation range from 10^1 m for radio waves to 10^{-12} m for gamma rays, which are emitted by nuclear reactions. By replacing v with c in Equation 6.1, we can show that the frequency of electromagnetic radiation is inversely proportional to its wavelength:

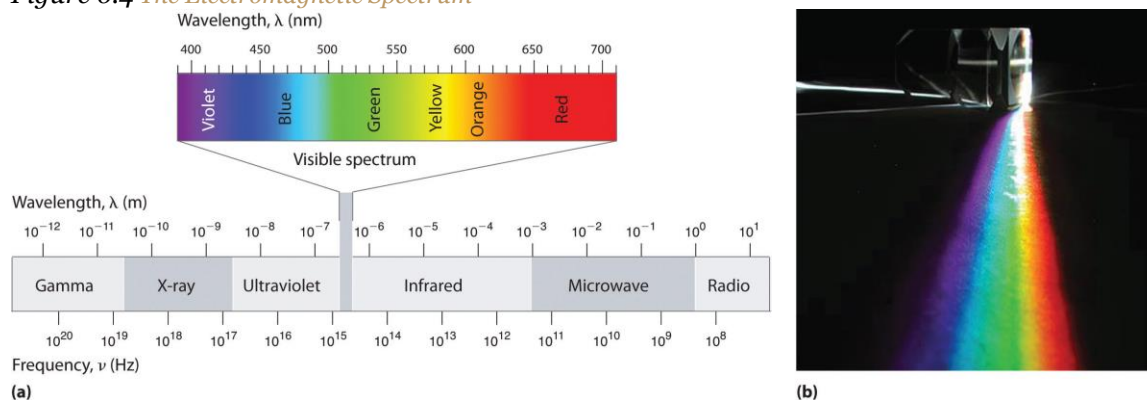
Equation 6.2

$$c = \lambda \nu = c/\lambda$$

For example, the frequency of radio waves is about 10^8 Hz, whereas the frequency of gamma rays is about 10^{20} Hz.

Visible light, which is electromagnetic radiation that can be detected by the human eye, has wavelengths between about 7×10^{-7} m (700 nm, or 4.3×10^{14} Hz) and 4×10^{-7} m (400 nm, or 7.5×10^{14} Hz). Within this range, the eye perceives radiation of different wavelengths (or frequencies) as light of different colors, ranging from red to violet in order of decreasing wavelength. The components of white light—a mixture of all the frequencies of visible light—can be separated by a prism, as shown in part (b) in Figure 6.4 "The Electromagnetic Spectrum". A similar phenomenon creates a rainbow, where water droplets suspended in the air act as tiny prisms.

Figure 6.4 *The Electromagnetic Spectrum*



(a) This diagram shows the wavelength and frequency ranges of electromagnetic radiation. The visible portion of the electromagnetic spectrum is the narrow region with wavelengths between about 400 and 700 nm. (b) When white light is passed through a prism, it is split into light of different wavelengths, whose colors correspond to the visible spectrum.

Table 6.1 Common Wavelength Units for Electromagnetic Radiation

Unit	Symbol	Wavelength (m)	Type of Radiation
picometer	pm	10^{-12}	gamma ray
angstrom	Å	10^{-10}	x-ray
nanometer	nm	10^{-9}	x-ray
micrometer	μm	10^{-6}	infrared
millimeter	mm	10^{-3}	infrared
centimeter	cm	10^{-2}	microwave
meter	m	10^0	radio

As you will soon see, the energy of electromagnetic radiation is directly proportional to its frequency and inversely proportional to its wavelength:

Equation 6.3

$$E \propto \nu$$

Equation 6.4

$$E \propto 1/\lambda$$

Whereas visible light is essentially harmless to our skin, ultraviolet light, with wavelengths of ≤ 400 nm, has enough energy to cause severe damage to our skin in the form of sunburn. Because the ozone layer described in Chapter 3 "Chemical Reactions" absorbs sunlight with wavelengths less than 350 nm, it protects us from the damaging effects of highly energetic ultraviolet radiation.

Note the Pattern

The energy of electromagnetic radiation increases with increasing frequency and decreasing wavelength.

EXAMPLE 1

Your favorite FM radio station, WXYZ, broadcasts at a frequency of 101.1 MHz. What is the wavelength of this radiation?

Given: frequency

Asked for: wavelength

Strategy:

Substitute the value for the speed of light in meters per second into Equation 6.2 to calculate the wavelength in meters.

Solution:

From Equation 6.2, we know that the product of the wavelength and the frequency is the speed of the wave, which for electromagnetic radiation is 2.998×10^8 m/s:

$$\lambda \nu = c = 2.998 \times 10^8 \text{ m/s}$$

Thus the wavelength λ is given by

$$\lambda = c/\nu = ((2.998 \times 10^8 \text{ m/s}) / (101.1 \text{ MHz}))$$

$$((1 \text{ MHz} = 10^6 \text{ s}^{-1})) = 2.965 \text{ m}$$

Exercise

As the police officer was writing up your speeding ticket, she mentioned that she was using a state-of-the-art radar gun operating at 35.5 GHz. What is the wavelength of the radiation emitted by the radar gun?

Answer: 8.45 mm

In Section 6.2 "The Quantization of Energy" and Section 6.3 "Atomic Spectra and Models of the Atom", we describe how scientists developed our current understanding of the structure of atoms using the scientific method described in Chapter 1 "Introduction to Chemistry". You will discover why scientists had to rethink their classical understanding of the nature of electromagnetic energy, which clearly distinguished between the particulate behavior of matter and the wavelike nature of energy.

KEY EQUATIONS

The relationship between wavelength, frequency, and speed of a wave

Equation 6.1: $\lambda\nu = v$

The relationship between wavelength, frequency, and speed of electromagnetic radiation

Equation 6.2: $c = \lambda\nu$

Summary

A basic knowledge of the electronic structure of atoms requires an understanding of the properties of waves and electromagnetic radiation. A **wave** is a periodic oscillation by which energy is transmitted through space. All waves are **periodic**, repeating regularly in both space and time. Waves are characterized by several interrelated properties: **wavelength (λ)**, the distance between successive waves; **frequency (ν)**, the number of waves that pass a fixed point per unit time; **speed (v)**, the rate at which the wave propagates through space; and **amplitude**, the magnitude of the oscillation about the mean position. The speed of a wave is equal to the product of its wavelength and frequency. **Electromagnetic radiation** consists of two perpendicular waves, one electric and one magnetic, propagating at the **speed of light (c)**. Electromagnetic radiation is radiant energy that includes radio waves, microwaves, visible light, x-rays, and gamma rays, which differ only in their frequencies and wavelengths.

KEY TAKEAWAY

- Understanding the electronic structure of atoms requires an understanding of the properties of waves and electromagnetic radiation.

CONCEPTUAL PROBLEMS

1. What are the characteristics of a wave? What is the relationship between electromagnetic radiation and wave energy?
2. At constant wavelength, what effect does increasing the frequency of a wave have on its speed? its amplitude?
3. List the following forms of electromagnetic radiation in order of increasing wavelength: x-rays, radio waves, infrared waves, microwaves, ultraviolet waves, visible waves, and gamma rays. List them in order of increasing frequency. Which has the highest energy?
4. A large industry is centered on developing skin-care products, such as suntan lotions and cosmetics, that cannot be penetrated by ultraviolet radiation. How does the wavelength of visible light compare with the wavelength of ultraviolet light? How does the energy of visible light compare with the energy of ultraviolet light? Why is this industry focused on blocking ultraviolet light rather than visible light?

NUMERICAL PROBLEMS

1. The human eye is sensitive to what fraction of the electromagnetic spectrum, assuming a typical spectral range of 10^4 to 10^{20} Hz? If we came from the planet Krypton and had x-ray vision (i.e., if our eyes were sensitive to x-rays in addition to visible light), how would this fraction be changed?
2. What is the frequency in megahertz corresponding to each wavelength?
 - a. 755 m
 - b. 6.73 nm
 - c. 1.77×10^3 km
 - d. $9.88 \text{ \AA}$
 - e. 3.7×10^{-10} m
3. What is the frequency in megahertz corresponding to each wavelength?
 - a. 5.8×10^{-7} m
 - b. $2.3 \text{ \AA}$
 - c. 8.6×10^7 m
 - d. 6.2 mm
 - e. 3.7 nm
4. Line spectra are also observed for molecular species. Given the following characteristic wavelengths for each species, identify the spectral region (ultraviolet, visible, etc.) in which the following line spectra will occur.

Given 1.00 mol of each compound and the wavelength of absorbed or emitted light, how much energy does this correspond to?

- a. NH_3 , $1.0 \times 10^{-2} \text{ m}$
- b. $\text{CH}_3\text{CH}_2\text{OH}$, $9.0 \mu\text{m}$
- c. Mo atom, $7.1 \text{ \AA}$
5. What is the speed of a wave in meters per second that has a wavelength of 1250 m and a frequency of $2.36 \times 10^5 \text{ s}^{-1}$?
6. A wave travels at 3.70 m/s with a frequency of $4.599 \times 10^7 \text{ Hz}$ and an amplitude of 1.0 m. What is its wavelength in nanometers?
7. An AM radio station broadcasts with a wavelength of 248.0 m. What is the broadcast frequency of the station in kilohertz? An AM station has a broadcast range of 92.6 MHz. What is the corresponding wavelength range in meters for this reception?
8. An FM radio station broadcasts with a wavelength of 3.21 m. What is the broadcast frequency of the station in megahertz? An FM radio typically has a broadcast range of 82–112 MHz. What is the corresponding wavelength range in meters for this reception?
9. A microwave oven operates at a frequency of approximately 2450 MHz. What is the corresponding wavelength? Water, with its polar molecules, absorbs electromagnetic radiation primarily in the infrared portion of the spectrum. Given this fact, why are microwave ovens used for cooking food?
10. [1] λ is the lowercase Greek lambda, and ν is the lowercase Greek nu.
11. [2] Named after German physicist Heinrich Hertz (1857–1894), a pioneer in the field of electromagnetic radiation.

6.2 The Quantization of Energy

LEARNING OBJECTIVE

1. To understand how energy is quantized.

By the late 19th century, many physicists thought their discipline was well on the way to explaining most natural phenomena. They could calculate the motions of material objects using Newton's laws of classical mechanics, and they could describe the properties of radiant energy using mathematical relationships known as Maxwell's equations,

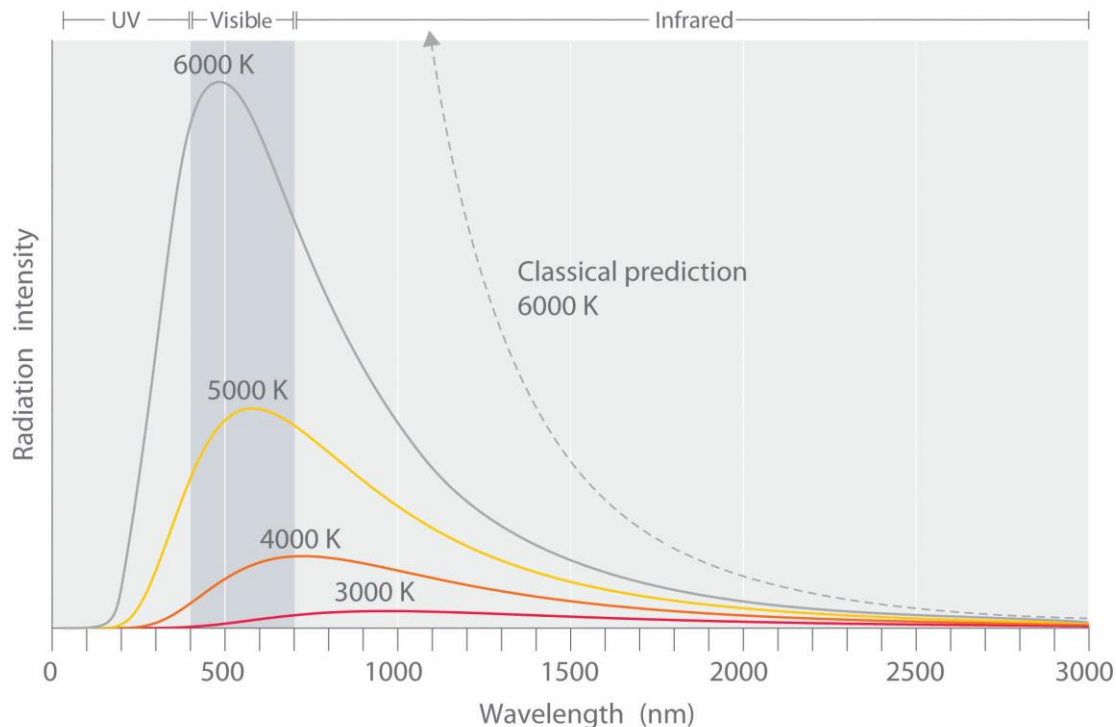
developed in 1873 by James Clerk Maxwell, a Scottish physicist. The universe appeared to be a simple and orderly place, containing matter, which consisted of particles that had mass and whose location and motion could be accurately described, and electromagnetic radiation, which was viewed as having no mass and whose exact position in space could not be fixed. Thus matter and energy were considered distinct and unrelated phenomena. Soon, however, scientists began to look more closely at a few inconvenient phenomena that could *not* be explained by the theories available at the time.

Blackbody Radiation

One phenomenon that seemed to contradict the theories of classical physics was blackbody radiation, the energy emitted by an object when it is heated. The wavelength of energy emitted by an object depends on only its temperature, not its surface or composition. Hence an electric stove burner or the filament of a space heater glows dull red or orange when heated, whereas the much hotter tungsten wire in an incandescent light bulb gives off a yellowish light (Figure 6.5 "Blackbody Radiation").

The *intensity* of radiation is a measure of the energy emitted per unit area. A plot of the intensity of blackbody radiation as a function of wavelength for an object at various temperatures is shown in Figure 6.6 "Relationship between the Temperature of an Object and the Spectrum of Blackbody Radiation It Emits". One of the major assumptions of classical physics was that energy increased or decreased in a smooth, continuous manner. For example, classical physics predicted that as wavelength decreased, the intensity of the radiation an object emits should increase in a smooth curve without limit at *all* temperatures, as shown by the broken line for 6000 K in Figure 6.6 "Relationship between the Temperature of an Object and the Spectrum of Blackbody Radiation It Emits". Thus classical physics could not explain the sharp *decrease* in the intensity of radiation emitted at shorter wavelengths (primarily in the ultraviolet region of the spectrum), which we now refer to as the "ultraviolet catastrophe." In 1900, however, the German physicist Max Planck (1858–1947) explained the ultraviolet catastrophe by proposing that the energy of electromagnetic waves is *quantized* rather than continuous. This means that for each temperature, there is a maximum intensity of radiation that is emitted in a blackbody object, corresponding to the peaks in Figure 6.6 "Relationship between the Temperature of an Object and the Spectrum of Blackbody Radiation It Emits", so the intensity does not follow a smooth curve as the temperature increases, as predicted by classical physics. Thus energy could be gained or lost only in integral multiples of some smallest unit of energy, a quantum.

Figure 6.6 Relationship between the Temperature of an Object and the Spectrum of Blackbody Radiation It Emits



At relatively low temperatures, most radiation is emitted at wavelengths longer than 700 nm, which is in the infrared portion of the spectrum. The dull red glow of the electric stove element in Figure 6.5 "Blackbody Radiation" is due to the small amount of radiation emitted at wavelengths less than 700 nm, which the eye can detect. As the temperature of the object increases, the maximum intensity shifts to shorter wavelengths, successively resulting in orange, yellow, and finally white light. At high temperatures, all wavelengths of visible light are emitted with approximately equal intensities. The white light spectrum shown for an object at 6000 K closely approximates the spectrum of light emitted by the sun (Figure 6.14 "The Visible Spectrum of Sunlight"). Note the sharp decrease in the intensity of radiation emitted at wavelengths below 400 nm, which constituted the ultraviolet catastrophe. The classical prediction fails to fit the experimental curves entirely and does not have a maximum intensity.

Max Planck (1858–1947)

In addition to being a physicist, Planck was a gifted pianist, who at one time considered music as a career. During the 1930s, Planck felt it was his duty to remain in Germany, despite his open opposition to the policies of the Nazi government. One of his sons was executed in 1944 for his part in an unsuccessful

attempt to assassinate Hitler, and bombing during the last weeks of World War II destroyed Planck's home.

Although quantization may seem to be an unfamiliar concept, we encounter it frequently. For example, US money is integral multiples of pennies. Similarly, musical instruments like a piano or a trumpet can produce only certain musical notes, such as C or F sharp. Because these instruments cannot produce a continuous range of frequencies, their frequencies are quantized. Even electrical charge is quantized: an ion may have a charge of -1 or -2 but *not* -1.33 .

Planck postulated that the energy of a particular quantum of radiant energy could be described explicitly by the equation

Equation 6.5

$$E = h\nu$$

where the proportionality constant h is called Planck's constant, one of the most accurately known fundamental constants in science. For our purposes, its value to four significant figures is generally sufficient:

$$h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s (joule-seconds)}$$

As the frequency of electromagnetic radiation increases, the magnitude of the associated quantum of radiant energy increases. By assuming that energy can be emitted by an object only in integral multiples of $h\nu$, Planck devised an equation that fit the experimental data shown in Figure 6.6 "Relationship between the Temperature of an Object and the Spectrum of Blackbody Radiation It Emits". We can understand Planck's explanation of the ultraviolet catastrophe qualitatively as follows: At low temperatures, radiation with only relatively low frequencies is emitted, corresponding to low-energy quanta. As the temperature of an object increases, there is an increased probability of emitting radiation with higher frequencies, corresponding to higher-energy quanta. At any temperature, however, it is simply more probable for an object to lose energy by emitting n lower-energy quanta than a single very high-energy quantum that corresponds to ultraviolet radiation. The result is a maximum in the plot of intensity of emitted radiation versus wavelength, as shown in Figure 6.6 "Relationship between the Temperature of an Object and the Spectrum of Blackbody Radiation It Emits", and a shift in the position of the maximum to lower wavelength (higher frequency) with increasing temperature.

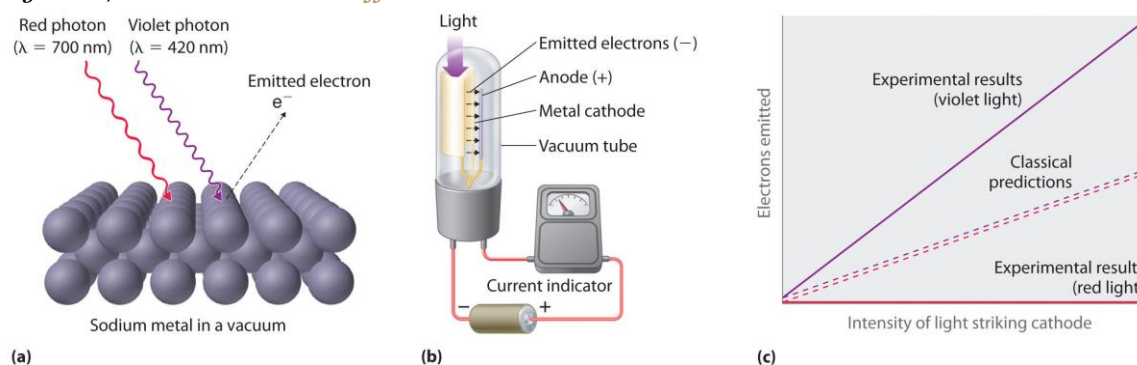
At the time he proposed his radical hypothesis, Planck could not explain *why* energies should be quantized. Initially, his hypothesis explained only one set of experimental data—blackbody radiation. If

quantization were observed for a large number of different phenomena, then quantization would become a law (as defined in Chapter 1 "Introduction to Chemistry"). In time, a theory might be developed to explain that law. As things turned out, Planck's hypothesis was the seed from which modern physics grew.

The Photoelectric Effect

Only five years after he proposed it, Planck's quantization hypothesis was used to explain a second phenomenon that conflicted with the accepted laws of classical physics. When certain metals are exposed to light, electrons are ejected from their surface (Figure 6.7 "The Photoelectric Effect"). Classical physics predicted that the number of electrons emitted and their kinetic energy should depend on only the intensity of the light, *not* its frequency. In fact, however, each metal was found to have a characteristic threshold frequency of light; below that frequency, *no* electrons are emitted regardless of the light's intensity. Above the threshold frequency, the number of electrons emitted was found to be proportional to the intensity of the light, and their kinetic energy was proportional to the frequency. This phenomenon was called the photoelectric effect.

Figure 6.7 The Photoelectric Effect



(a) Irradiating a metal surface with photons of sufficiently high energy causes electrons to be ejected from the metal. (b) A photocell that uses the photoelectric effect, similar to those found in automatic door openers. When light strikes the metal cathode, electrons are emitted and attracted to the anode, resulting in a flow of electrical current. If the incoming light is interrupted by, for example, a passing person, the current drops to zero. (c) In contrast to predictions using classical physics, no electrons are emitted when photons of light with energy less than E_0 , such as red light, strike the cathode. The energy of violet light is above the threshold frequency, so the number of emitted photons is proportional to the light's intensity.

Albert Einstein (1879–1955; Nobel Prize in Physics, 1921) quickly realized that Planck's hypothesis about the quantization of radiant energy could also explain the photoelectric effect. The key feature of Einstein's hypothesis was

the assumption that radiant energy arrives at the metal surface in particles that we now call photons, each possessing a particular energy E given by Equation 6.5. Einstein postulated that each metal has a particular electrostatic attraction for its electrons that must be overcome before an electron can be emitted from its surface ($E_o = h\nu_o$). If photons of light with energy less than E_o strike a metal surface, no single photon has enough energy to eject an electron, so no electrons are emitted regardless of the intensity of the light. If a photon with energy greater than E_o strikes the metal, then part of its energy is used to overcome the forces that hold the electron to the metal surface, and the excess energy appears as the kinetic energy of the ejected electron:

Equation 6.6

$$\text{kinetic energy of ejected electron} = E - E_o = h\nu - h\nu_o = h(\nu - \nu_o)$$

When a metal is struck by light with energy above the threshold energy E_o , the *number* of emitted electrons is proportional to the *intensity* of the light beam, which corresponds to the number of photons per square centimeter, but the *kinetic energy* of the emitted electrons is proportional to the *frequency* of the light. Thus Einstein showed that the energy of the emitted electrons depended on the frequency of the light, contrary to the prediction of classical physics.

Albert Einstein (1879–1955)

In 1900, Einstein was working in the Swiss patent office in Bern. He was born in Germany and throughout his childhood his parents and teachers had worried that he might be developmentally disabled. The patent office job was a low-level civil service position that was not very demanding, but it did allow Einstein to spend a great deal of time reading and thinking about physics. In 1905, he published his paper on the photoelectric effect, for which he received the Nobel Prize in 1921.

Planck's and Einstein's postulate that energy is quantized is in many ways similar to Dalton's description of atoms. Both theories are based on the existence of simple building blocks, atoms in one case and quanta of energy in the other. The work of Planck and Einstein thus suggested a connection between the quantized nature of energy and the properties of individual atoms. In fact, Einstein's Nobel Prize was awarded for his work on the photoelectric effect (*not* for his more famous equation $E = mc^2$), demonstrating its fundamental importance.

Recently, scientists have theorized that even our sense of smell has its basis in quantum physics. Preliminary research indicates that odorant molecules absorb a quantum of energy that causes their bonds to vibrate at a specific frequency. Because different assemblages of molecules have different characteristic frequencies, these vibrations seem to act as a molecular signature that can be detected as an odor. Studies with flies show that they can distinguish

between similar molecules with different vibrational frequencies. This vibrational theory of smell could serve as a discriminatory process in nature in other ways and is an active area of research.

EXAMPLE 2

A ruby laser, a device that produces light in a narrow range of wavelengths (Section 6.3 "Atomic Spectra and Models of the Atom"), emits red light at a wavelength of 694.3 nm (Figure 6.8 "A Beam of Red Light Emitted by a Ruby Laser"). What is the energy in joules of a

- single photon?
- mole of photons?

Given: wavelength

Asked for: energy of single photon and mole of photons

Strategy:

A Use Equation 6.2 and Equation 6.5 to calculate the energy in joules.

B Multiply the energy of a single photon by Avogadro's number to obtain the energy in a mole of photons.

Solution:

The energy of a single photon is given by $E = h\nu = hc/\lambda$.

$$E = (6.626 \times 10^{-34} \text{ J}\cdot\text{s})(2.998 \times 10^8 \text{ m}\cdot\text{s}^{-1})/694.3 \times 10^{-9} \text{ m} = 2.861 \times 10^{-19} \text{ J}_{\text{photon}}$$

calculate the energy in a mole of photons, we multiply the energy of a single photon by the number of photons in a mole (Avogadro's number). If we write the energy of a photon as $2.861 \times 10^{-19} \text{ J/photon}$, we obtain the energy of a mole of photons with wavelength 694.3 nm:

This energy is of the same magnitude as some of the enthalpies of reaction in Chapter 5 "Energy Changes in Chemical Reactions", and, as you will see in Chapter 8 "Ionic versus Covalent Bonding", it is comparable to the strength of many chemical bonds. As a result, light can be used to initiate chemical reactions. In fact, an entire area of chemistry called *photochemistry* is devoted to studying such processes. In the phenomenon of *photosynthesis*, green plants use the energy of visible light to convert carbon dioxide and water into sugars such as glucose.

Exercise

An x-ray generator, such as those used in hospitals, emits radiation with a wavelength of 1.544 Å.

- What is the energy in joules of a single photon?

- b. What is the energy in joules of a mole of photons?
- c. How many times more energetic is a single x-ray photon of this wavelength than a photon emitted by a ruby laser?

Answer:

- a. $1.287 \times 10^{-15} \text{ J/photon}$
- b. $7.748 \times 10^8 \text{ J/mol} = 7.748 \times 10^5 \text{ kJ/mol}$
- c. 4497 times

KEY EQUATION

quantization of energy

Equation 6.5: $E = h\nu$

Summary

The properties of **blackbody radiation**, the radiation emitted by hot objects, could not be explained with classical physics. Max Planck postulated that energy was quantized and could be emitted or absorbed only in integral multiples of a small unit of energy, known as a **quantum**. The energy of a quantum is proportional to the frequency of the radiation; the proportionality constant h is a fundamental constant (Planck's constant). Albert Einstein used Planck's concept of the quantization of energy to explain the **photoelectric effect**, the ejection of electrons from certain metals when exposed to light. Einstein postulated the existence of what today we call **photons**, particles of light with a particular energy, $E = h\nu$. Both energy and matter have fundamental building blocks: quanta and atoms, respectively.

KEY TAKEAWAY

- The fundamental building blocks of energy are quanta and of matter are atoms.

CONCEPTUAL PROBLEMS

1. Describe the relationship between the energy of a photon and its frequency.
2. How was the ultraviolet catastrophe explained?
3. If electromagnetic radiation with a continuous range of frequencies above the threshold frequency of a metal is allowed to strike a metal surface, is the kinetic energy of the ejected electrons continuous or quantized? Explain your answer.
4. The vibrational energy of a plucked guitar string is said to be *quantized*. What do we mean by this? Are the sounds emitted from the 88 keys on a piano also quantized?

5. Which of the following exhibit quantized behavior: a human voice, the speed of a car, a harp, the colors of light, automobile tire sizes, waves from a speedboat?

ANSWERS

1. The energy of a photon is directly proportional to the frequency of the electromagnetic radiation.
- 2.
- 3.
- 4.
5. Quantized: harp, tire size, speedboat waves; continuous: human voice, colors of light, car speed.

NUMERICAL PROBLEMS

1. What is the energy of a photon of light with each wavelength? To which region of the electromagnetic spectrum does each wavelength belong?
 - a. 4.33×10^5 m
 - b. 0.065 nm
 - c. 786 pm
2. How much energy is contained in each of the following? To which region of the electromagnetic spectrum does each wavelength belong?
 - a. 250 photons with a wavelength of 3.0 m
 - b. 4.2×10^6 photons with a wavelength of 92 μm
 - c. 1.78×10^{22} photons with a wavelength of 2.1 $\text{\AA}$
3. A mole of photons is found to have an energy of 225 kJ. What is the wavelength of the radiation?
4. Use the data in Table 6.1 "Common Wavelength Units for Electromagnetic Radiation" to calculate how much more energetic a single gamma-ray photon is than a radio-wave photon. How many photons from a radio source operating at a frequency of 8×10^5 Hz would be required to provide the same amount of energy as a single gamma-ray photon with a frequency of 3×10^{19} Hz?
5. Use the data in Table 6.1 "Common Wavelength Units for Electromagnetic Radiation" to calculate how much more energetic a single x-ray photon is than a photon of ultraviolet light.
6. A radio station has a transmitter that broadcasts at a frequency of 100.7 MHz with a power output of 50 kW. Given that $1 \text{ W} = 1 \text{ J/s}$, how many photons are emitted by the transmitter each second?

ANSWERS

1.
 - a. 4.59×10^{-31} J/photon, radio
 - b. 3.1×10^{-15} J/photon, gamma ray
 - c. 2.53×10^{-16} J/photon, gamma ray
- 2.
3. 532 nm

6.3 Atomic Spectra and Models of the Atom

LEARNING OBJECTIVE

1. To know the relationship between atomic spectra and the electronic structure of atoms.

The photoelectric effect provided indisputable evidence for the existence of the photon and thus the particle-like behavior of electromagnetic radiation. The concept of the photon, however, emerged from experimentation with *thermal radiation*, electromagnetic radiation emitted as the result of a source's temperature, which produces a continuous spectrum of energies. More direct evidence was needed to verify the quantized nature of electromagnetic radiation. In this section, we describe how experimentation with visible light provided this evidence.

Line Spectra

Although objects at high temperature emit a continuous spectrum of electromagnetic radiation (Figure 6.6 "Relationship between the Temperature of an Object and the Spectrum of Blackbody Radiation It Emits"), a different kind of spectrum is observed when pure samples of individual elements are heated. For example, when a high-voltage electrical discharge is passed through a sample of hydrogen gas at low pressure, the resulting individual isolated hydrogen atoms caused by the dissociation of H_2 emit a red light. Unlike blackbody radiation, the color of the light emitted by the hydrogen atoms does not depend greatly on the temperature of the gas in the tube. When the emitted light is passed through a prism, only a few narrow lines, called a line spectrum, are seen (Figure 6.9 "The Emission of Light by Hydrogen Atoms"), rather than a continuous range of colors. The light emitted by hydrogen atoms is red because, of its four characteristic lines, the most intense line in its spectrum is in the red portion of the visible spectrum, at 656 nm. With sodium, however, we observe a yellow color because the most intense lines in its spectrum are in the yellow portion of the spectrum, at about 589 nm.

Such *emission spectra* were observed for many other elements in the late 19th century, which presented a major challenge because classical physics was unable to explain them. Part of the explanation is provided by Planck's equation (Equation 6.5): the observation of only a few values of λ (or ν) in the line spectrum meant that only a few values of E were possible. Thus *the energy levels of a hydrogen atom had to be quantized*; in other words, only states that had certain values of energy were possible, or *allowed*. If a hydrogen atom could have *any* value of energy, then a continuous spectrum would have been observed, similar to blackbody radiation.

In 1885, a Swiss mathematics teacher, Johann Balmer (1825–1898), showed that the frequencies of the lines observed in the visible region of the spectrum of hydrogen fit a simple equation that can be expressed as follows:

Equation 6.7

$$n = \text{constant}(122 - 1n^2)$$

where $n = 3, 4, 5, 6$. As a result, these lines are known as the *Balmer series*. The Swedish physicist Johannes Rydberg (1854–1919) subsequently restated and expanded Balmer's result in the *Rydberg equation*:

Equation 6.8

$$1/\lambda = R(1/n_1^2 - 1/n_2^2)$$

where n_1 and n_2 are positive integers, $n_2 > n_1$, and the *Rydberg constant*, has a value of $1.09737 \times 10^7 \text{ m}^{-1}$.

Johann Balmer (1825–1898)

A mathematics teacher at a secondary school for girls in Switzerland, Balmer was 60 years old when he wrote the paper on the spectral lines of hydrogen that made him famous. He published only one other paper on the topic, which appeared when he was 72 years old.

Like Balmer's equation, Rydberg's simple equation described the wavelengths of the visible lines in the emission spectrum of hydrogen (with $n_1 = 2$, $n_2 = 3, 4, 5, \dots$). More important, Rydberg's equation also described the wavelengths of other series of lines that would be observed in the emission spectrum of hydrogen: one in the ultraviolet ($n_1 = 1$, $n_2 = 2, 3, 4, \dots$) and one in the infrared ($n_1 = 3$, $n_2 = 4, 5, 6$).

Unfortunately, scientists had not yet developed any theoretical justification for an equation of this form.

The Bohr Model

In 1913, a Danish physicist, Niels Bohr (1885–1962; Nobel Prize in Physics, 1922), proposed a theoretical model for the hydrogen atom that explained its emission spectrum. Bohr's model required only one assumption: *The electron moves around the nucleus in circular orbits that can have only certain allowed radii.* As discussed in Chapter 1 "Introduction to Chemistry", Rutherford's earlier model of the atom had also assumed that electrons moved in circular orbits around the nucleus and that the atom was held together by the electrostatic attraction between the positively charged nucleus and the negatively charged electron. Although we now know that the assumption of circular orbits was incorrect, Bohr's insight was to propose that *the electron could occupy only certain regions of space.*

Niels Bohr (1885–1962)

During the Nazi occupation of Denmark in World War II, Bohr escaped to the United States, where he became associated with the Atomic Energy Project. In his final years, he devoted himself to the peaceful application of atomic physics and to resolving political problems arising from the development of atomic weapons.

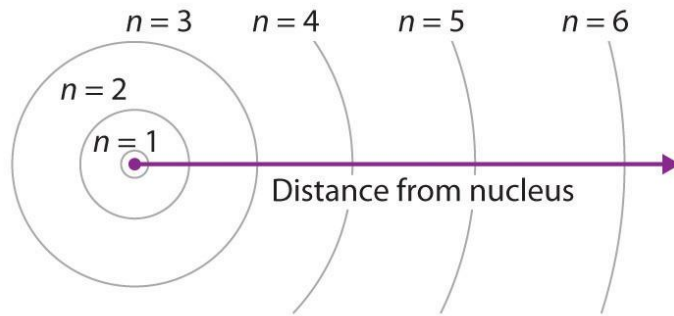
Using classical physics, Bohr showed that the energy of an electron in a particular orbit is given by

Equation 6.9

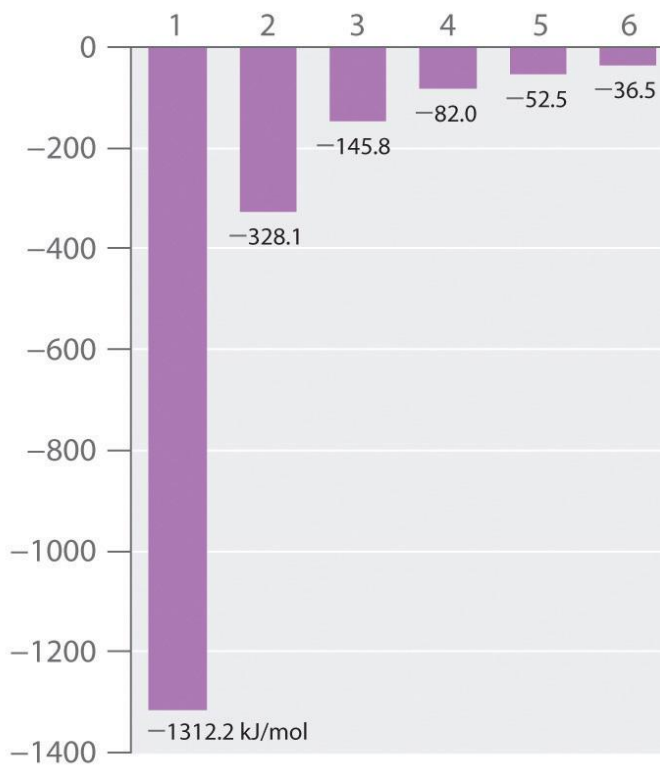
$$E_n = -Rhc/n^2$$

where R is the Rydberg constant, h is Planck's constant, c is the speed of light, and n is a positive integer corresponding to the number assigned to the orbit, with $n = 1$ corresponding to the orbit closest to the nucleus.^[1] Thus the orbit with $n = 1$ is the lowest in energy. Because a hydrogen atom with its one electron in this orbit has the lowest possible energy, this is the ground state, the most stable arrangement for a hydrogen atom. As n increases, the radius of the orbit increases; the electron is farther from the proton, which results in a less stable arrangement with higher potential energy (Figure 6.10 "The Bohr Model of the Hydrogen Atom"). A hydrogen atom with an electron in an orbit with $n > 1$ is therefore in an excited state: its energy is higher than the energy of the ground state. When an atom in an excited state undergoes a transition to the ground state in a process called *decay*, it loses energy by emitting a photon whose energy corresponds to the difference in energy between the two states (Figure 6.11 "The Emission of Light by a Hydrogen Atom in an Excited State").

Figure 6.10 *The Bohr Model of the Hydrogen Atom*



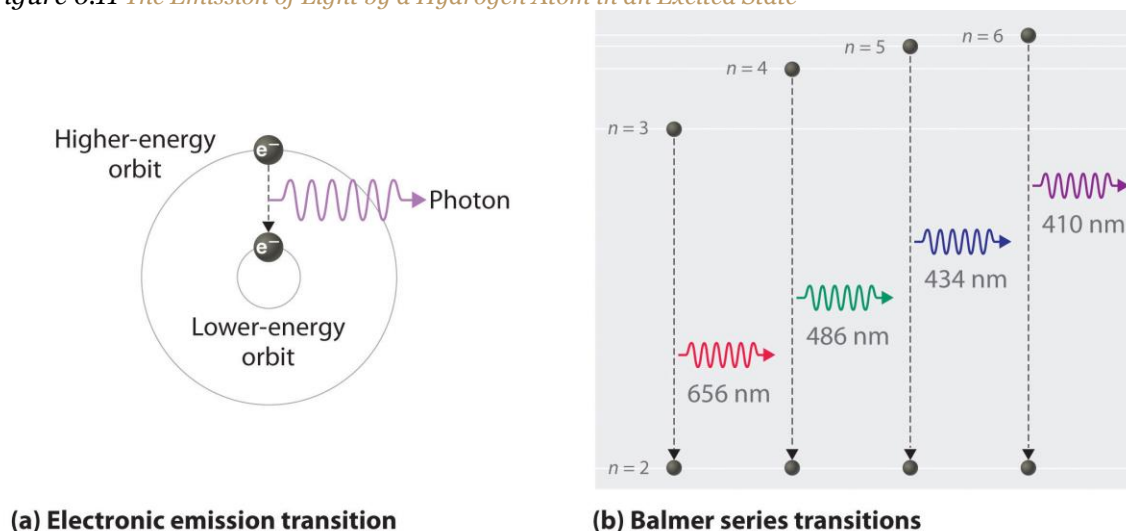
(a) Hydrogen orbits (Bohr model). Orbits are not drawn to scale.



(b) Hydrogen orbit energy (kJ/mol) vs. n

(a) The distance of the orbit from the nucleus increases with increasing n . (b) The energy of the orbit becomes increasingly less negative with increasing n .

Figure 6.11 The Emission of Light by a Hydrogen Atom in an Excited State



(a) Light is emitted when the electron undergoes a transition from an orbit with a higher value of n (at a higher energy) to an orbit with a lower value of n (at lower energy). (b) The Balmer series of emission lines is due to transitions from orbits with $n \geq 3$ to the orbit with $n = 2$. The differences in energy between these levels corresponds to light in the visible portion of the electromagnetic spectrum.

So the difference in energy (ΔE) between any two orbits or energy levels is given by $\Delta E = E_{n_1} - E_{n_2}$ where n_1 is the final orbit and n_2 the initial orbit. Substituting from Bohr's equation (Equation 6.9) for each energy value gives

Equation 6.10

$$\Delta E = E_{\text{final}} - E_{\text{initial}} = -Rhc/n_1^2 - (-Rhc/n_2^2) = -Rhc(1/n_1^2 - 1/n_2^2)$$

If $n_2 > n_1$, the transition is from a higher energy state (larger-radius orbit) to a lower energy state (smaller-radius orbit), as shown by the dashed arrow in part (a) in Figure 6.11 "The Emission of Light by a Hydrogen Atom in an Excited State". Substituting hc/λ for ΔE gives

Equation 6.11

$$\Delta E = hc/\lambda = -Rhc(1/n_1^2 - 1/n_2^2)$$

Canceling hc on both sides gives

Equation 6.12

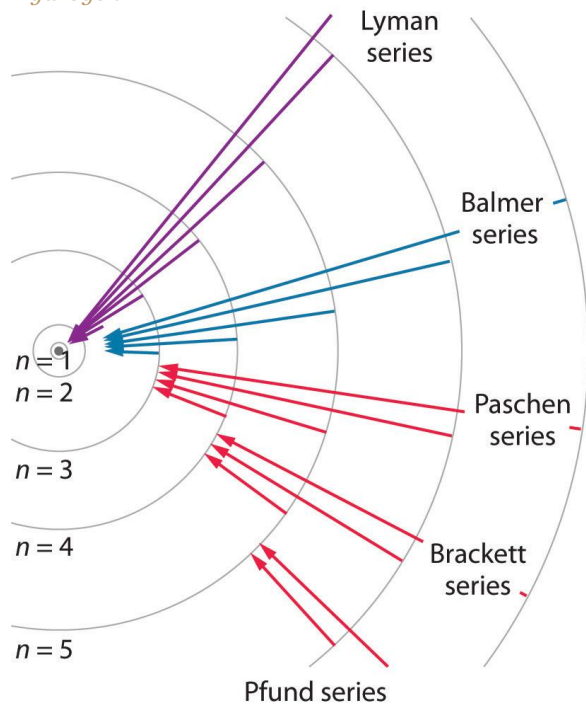
$$1/\lambda = -R(1/n_1^2 - 1/n_2^2)$$

Except for the negative sign, this is the same equation that Rydberg obtained

experimentally. The negative sign in Equation 6.11 and Equation 6.12 indicates that energy is released as the electron moves from orbit n_2 to orbit n_1 because orbit n_2 is at a higher energy than orbit n_1 . Bohr calculated the value of R independently and obtained a value of $1.0974 \times 10^7 \text{ m}^{-1}$, the same number Rydberg had obtained by analyzing the emission spectra.

We can now understand the physical basis for the Balmer series of lines in the emission spectrum of hydrogen (part (b) in Figure 6.9 "The Emission of Light by Hydrogen Atoms"). As shown in part (b) in Figure 6.11 "The Emission of Light by a Hydrogen Atom in an Excited State", the lines in this series correspond to transitions from higher-energy orbits ($n > 2$) to the *second* orbit ($n = 2$). Thus the hydrogen atoms in the sample have absorbed energy from the electrical discharge and decayed from a higher-energy excited state ($n > 2$) to a lower-energy state ($n = 2$) by emitting a photon of electromagnetic radiation whose energy corresponds exactly to the *difference* in energy between the two states (part (a) in Figure 6.11 "The Emission of Light by a Hydrogen Atom in an Excited State"). The $n = 3$ to $n = 2$ transition gives rise to the line at 656 nm (red), the $n = 4$ to $n = 2$ transition to the line at 486 nm (green), the $n = 5$ to $n = 2$ transition to the line at 434 nm (blue), and the $n = 6$ to $n = 2$ transition to the line at 410 nm (violet). Because a sample of hydrogen contains a large number of atoms, the intensity of the various lines in a line spectrum depends on the number of atoms in each excited state. At the temperature in the gas discharge tube, more atoms are in the $n = 3$ than the $n \geq 4$ levels. Consequently, the $n = 3$ to $n = 2$ transition is the most intense line, producing the characteristic red color of a hydrogen discharge (part (a) in Figure 6.9 "The Emission of Light by Hydrogen Atoms"). Other families of lines are produced by transitions from excited states with $n > 1$ to the orbit with $n = 1$ or to orbits with $n \geq 3$. These transitions are shown schematically in Figure 6.12 "Electron Transitions Responsible for the Various Series of Lines Observed in the Emission Spectrum of Hydrogen".

Figure 6.12 *Electron Transitions Responsible for the Various Series of Lines Observed in the Emission Spectrum of Hydrogen*



The Lyman series of lines is due to transitions from higher-energy orbits to the lowest-energy orbit ($n = 1$); these transitions release a great deal of energy, corresponding to radiation in the ultraviolet portion of the electromagnetic spectrum. The Paschen, Brackett, and Pfund series of lines are due to transitions from higher-energy orbits to orbits with $n = 3, 4$, and 5 , respectively; these transitions release substantially less energy, corresponding to infrared radiation. (Orbits are not drawn to scale.)

In contemporary applications, electron transitions are used in timekeeping that needs to be exact.

Telecommunications systems, such as cell phones, depend on timing signals that are accurate to within a millionth of a second per day, as are the devices that control the US power grid. Global positioning system (GPS) signals must be accurate to within a billionth of a second per day, which is equivalent to gaining or losing no more than one second in 1,400,000 years. Quantifying time requires finding an event with an interval that repeats on a regular basis. To achieve the accuracy required for modern purposes, physicists have turned to the atom. The current standard used to calibrate clocks is the cesium atom. Supercooled cesium atoms are placed in a vacuum chamber and bombarded with microwaves whose frequencies are carefully controlled. When the frequency is exactly right, the atoms absorb enough energy to undergo an electronic transition to a higher-energy state. Decay to a lower-energy state emits radiation. The microwave frequency is continually adjusted, serving as the clock's pendulum. In 1967, the second was defined as the

duration of 9,192,631,770 oscillations of the resonant frequency of a cesium atom, called the *cesium clock*. Research is currently under way to develop the next generation of atomic clocks that promise to be even more accurate. Such devices would allow scientists to monitor vanishingly faint electromagnetic signals produced by nerve pathways in the brain and geologists to measure variations in gravitational fields, which cause fluctuations in time, that would aid in the discovery of oil or minerals.

EXAMPLE 3

The so-called Lyman series of lines in the emission spectrum of hydrogen corresponds to transitions from various excited states to the $n = 1$ orbit. Calculate the wavelength of the lowest-energy line in the Lyman series to three significant figures. In what region of the electromagnetic spectrum does it occur?

Given: lowest-energy orbit in the Lyman series

Asked for: wavelength of the lowest-energy Lyman line and corresponding region of the spectrum

Strategy:

A Substitute the appropriate values into Equation 6.8 (the Rydberg equation) and solve for λ .

B Use Figure 6.4 "The Electromagnetic Spectrum" to locate the region of the electromagnetic spectrum corresponding to the calculated wavelength.

Solution:

We can use the Rydberg equation to calculate the wavelength:

$$1/\lambda = R(1/n_1^2 - 1/n_2^2)$$

A For the Lyman series, $n_1 = 1$. The lowest-energy line is due to a transition from the $n = 2$ to $n = 1$ orbit because they are the closest in energy.

$$1/\lambda = R(1/n_1^2 - 1/n_2^2) = 1.097 \times 10^7 \text{ m}^{-1}(1/1^2 - 1/2^2) = 8.228 \times 10^6 \text{ m}^{-1} \text{ and}$$

$$\lambda = 1.215 \times 10^{-7} \text{ m} = 122 \text{ nm}$$

B This wavelength is in the ultraviolet region of the spectrum.

Exercise

The Pfund series of lines in the emission spectrum of hydrogen corresponds to transitions from higher excited states to the $n = 5$ orbit. Calculate the wavelength of the *second* line in the Pfund series to three significant figures. In which region of the spectrum does it lie?

Answer: $4.65 \times 10^3 \text{ nm}$; infrared

Bohr's model of the hydrogen atom gave an exact explanation for its observed emission spectrum. The following are his key contributions to our understanding of atomic structure:

- Electrons can occupy only certain regions of space, called *orbits*.
- Orbits closer to the nucleus are lower in energy.
- Electrons can move from one orbit to another by absorbing or emitting energy, giving rise to characteristic spectra.

Unfortunately, Bohr could not explain *why* the electron should be restricted to particular orbits. Also, despite a great deal of tinkering, such as assuming that orbits could be ellipses rather than circles, his model could not quantitatively explain the emission spectra of any element other than hydrogen (Figure 6.13 "The Emission Spectra of Elements Compared with Hydrogen"). In fact, Bohr's model worked only for species that contained just one electron: H, He⁺, Li²⁺, and so forth. Scientists needed a fundamental change in their way of thinking about the electronic structure of atoms to advance beyond the Bohr model.

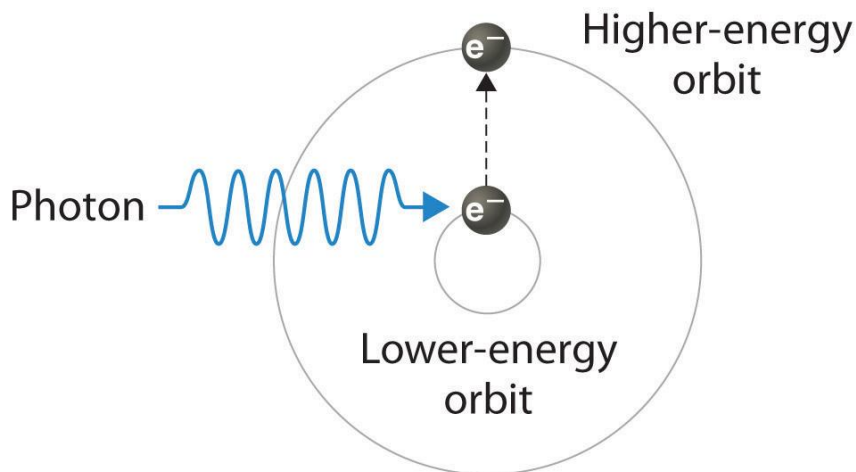
Thus far we have explicitly considered only the emission of light by atoms in excited states, which produces an emission spectrum. The converse, absorption of light by ground-state atoms to produce an excited state, can also occur, producing an absorption spectrum. Because each element has characteristic emission and absorption spectra, scientists can use such spectra to analyze the composition of matter, as we describe in Section 6.4 "The Relationship between Energy and Mass".

Note the Pattern

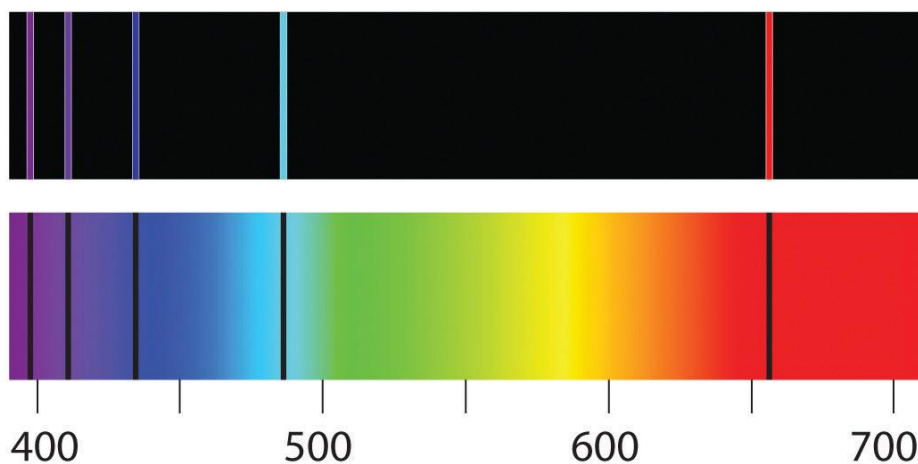
When an atom emits light, it decays to a lower energy state; when an atom absorbs light, it is excited to a higher energy state.

Applications of Emission and Absorption Spectra

If white light is passed through a sample of hydrogen, hydrogen atoms absorb energy as an electron is excited to higher energy levels (orbits with $n \geq 2$). If the light that emerges is passed through a prism, it forms a continuous spectrum with *black* lines (corresponding to no light passing through the sample) at 656, 486, 434, and 410 nm. These wavelengths correspond to the $n = 2$ to $n = 3$, $n = 2$ to $n = 4$, $n = 2$ to $n = 5$, and $n = 2$ to $n = 6$ transitions. Any given element therefore has both a characteristic emission spectrum and a characteristic absorption spectrum, which are essentially complementary images.



(a) Electronic absorption transition



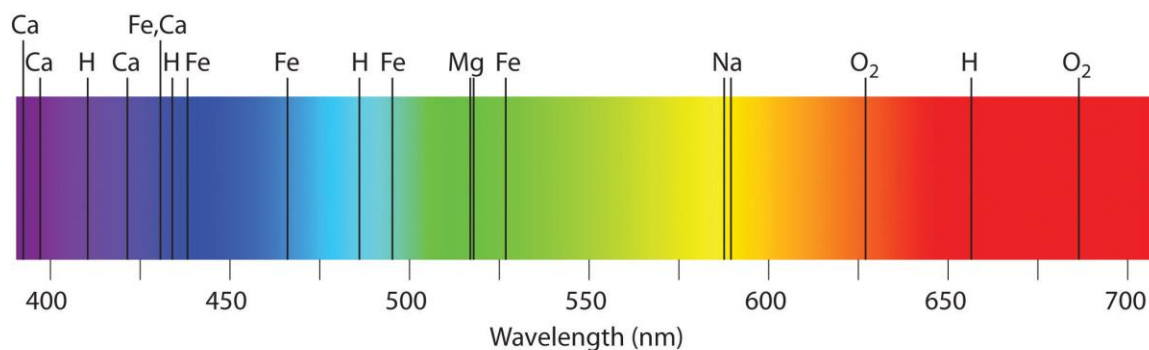
(b) H₂ emission spectrum (top), H₂ absorption spectrum (bottom)

Absorption of light by a hydrogen atom. (a) When a hydrogen atom absorbs a photon of light, an electron is excited to an orbit that has a higher energy and larger value of n . (b) Images of the emission and absorption spectra of hydrogen are shown here.

Emission and absorption spectra form the basis of *spectroscopy*, which uses spectra to provide information about the structure and the composition of a substance or an object. In particular, astronomers use emission and absorption spectra to determine the composition of stars and interstellar matter. As an example, consider the spectrum of sunlight shown in Figure 6.14 "The Visible Spectrum of Sunlight". Because the sun is very hot, the light it emits is in

the form of a continuous emission spectrum. Superimposed on it, however, is a series of dark lines due primarily to the absorption of specific frequencies of light by cooler atoms in the outer atmosphere of the sun. By comparing these lines with the spectra of elements measured on Earth, we now know that the sun contains large amounts of hydrogen, iron, and carbon, along with smaller amounts of other elements. During the solar eclipse of 1868, the French astronomer Pierre Janssen (1824–1907) observed a set of lines that did not match those of any known element. He suggested that they were due to the presence of a new element, which he named *helium*, from the Greek *helios*, meaning “sun.” Helium was finally discovered in uranium ores on Earth in 1895.

Figure 6.14 *The Visible Spectrum of Sunlight*



The characteristic dark lines are mostly due to the absorption of light by elements that are present in the cooler outer part of the sun’s atmosphere; specific elements are indicated by the labels. The lines at 628 and 687 nm, however, are due to the absorption of light by oxygen molecules in Earth’s atmosphere.

The familiar red color of “neon” signs used in advertising is due to the emission spectrum of neon shown in part (b) in Figure 6.13 “The Emission Spectra of Elements Compared with Hydrogen”. Similarly, the blue and yellow colors of certain street lights are caused, respectively, by mercury and sodium discharges. In all these cases, an electrical discharge excites neutral atoms to a higher energy state, and light is emitted when the atoms decay to the ground state. In the case of mercury, most of the emission lines are below 450 nm, which produces a blue light (part (c) in Figure 6.13 “The Emission Spectra of Elements Compared with Hydrogen”). In the case of sodium, the most intense emission lines are at 589 nm, which produces an intense yellow light.



Hg vapor spectrum (350-700 nm)



Low-pressure Na spectrum
(350-700 nm)



High-pressure Na spectrum
(350-700 nm)

Sodium and mercury spectra. Many street lights use bulbs that contain sodium or mercury vapor. Due to the very different emission spectra of these elements, they emit light of different colors.

The Chemistry of Fireworks

Figure 6.15 *The Chemistry of Fireworks*



(a) In the "multibreak" shell used for fireworks, the chambers contain mixtures of fuels and oxidizers plus compounds for special effects ("stars") connected by time-delay fuses so that the

chambers explode in stages. (b) The finale of a fireworks display usually consists of many shells fired simultaneously to give a dazzling multicolor display. The labels indicate the substances that are responsible for the colors of some of the fireworks shown.

The colors of fireworks are also due to atomic emission spectra. As shown in part (a) in Figure 6.15 "The Chemistry of Fireworks", a typical shell used in a fireworks display contains gunpowder to propel the shell into the air and a fuse to initiate a variety of redox reactions that produce heat and small explosions.

Thermal energy excites the atoms to higher energy states; as they decay to lower energy states, the atoms emit light that gives the familiar colors. When oxidant/reductant mixtures listed in Table 6.2 "Common Chemicals Used in the Manufacture of Fireworks*" are ignited, a flash of white or yellow light is produced along with a loud bang. Achieving the colors shown in part (b) in Figure 6.15 "The Chemistry of Fireworks" requires adding a small amount of a substance that has an emission spectrum in the desired portion of the visible spectrum. For example, sodium is used for yellow because of its 589 nm emission lines. The intense yellow color of sodium would mask most other colors, so potassium and ammonium salts, rather than sodium salts, are usually used as oxidants to produce other colors, which explains the preponderance of such salts in Table 6.2 "Common Chemicals Used in the Manufacture of Fireworks*". Strontium salts, which are also used in highway flares, emit red light, whereas barium gives a green color. Blue is one of the most difficult colors to achieve. Copper(II) salts emit a pale blue light, but copper is dangerous to use because it forms highly unstable explosive compounds with anions such as chlorate. As you might guess, preparing fireworks with the desired properties is a complex, challenging, and potentially hazardous process.

Table 6.2 Common Chemicals Used in the Manufacture of Fireworks*

Oxidizers	Fuels (reductants)	Special effects
ammonium perchlorate	aluminum	<i>blue flame:</i> copper carbonate, copper sulfate, or copper oxide
barium chlorate	antimony sulfide	<i>red flame:</i> strontium nitrate or strontium carbonate
barium nitrate	charcoal	<i>white flame:</i> magnesium or aluminum
potassium chlorate	magnesium	<i>yellow flame:</i> sodium oxalate or cryolite (Na_3AlF_6)
potassium nitrate	sulfur	<i>green flame:</i> barium nitrate or barium chlorate
potassium perchlorate	titanium	<i>white smoke:</i> potassium nitrate plus sulfur
strontium nitrate		<i>colored smoke:</i> potassium chlorate and sulfur, plus

Oxidizers	Fuels (reductants)	Special effects
		organic dye
		<i>whistling noise</i> : potassium benzoate or sodium salicylate
		<i>white sparks</i> : aluminum, magnesium, or titanium
		<i>gold sparks</i> : iron fillings or charcoal
*Almost any combination of an oxidizer and a fuel may be used along with the compounds needed to produce a desired special effect.		

Lasers

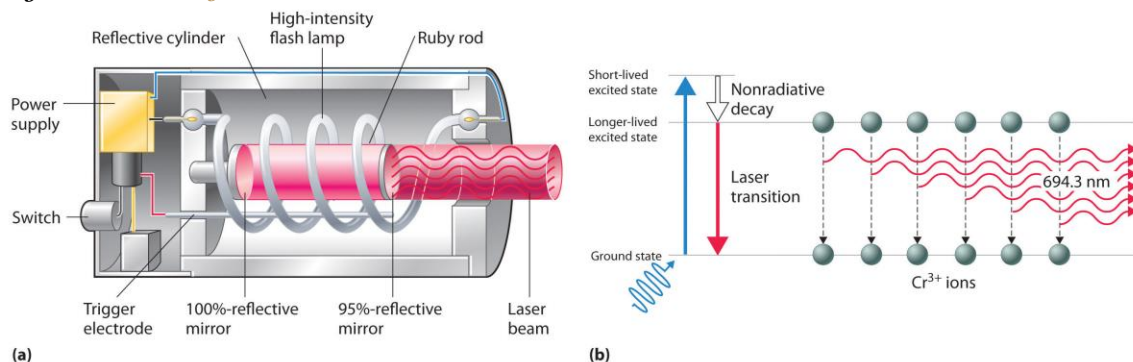
Most light emitted by atoms is *polychromatic*—containing more than one wavelength. In contrast, *lasers* (from light amplification by stimulated emission of radiation) emit *monochromatic* light—a single wavelength only. Lasers have many applications in fiber-optic telecommunications, the reading and recording of compact discs (CDs) and digital video discs (DVDs), steel cutting, and supermarket checkout scanners. Laser beams are generated by the same general phenomenon that gives rise to emission spectra, with one difference: only a single excited state is produced, which in principle results in only a single frequency of emitted light. In practice, however, inexpensive commercial lasers actually emit light with a very narrow range of wavelengths.

How a CD player uses a laser to read a CD. Inside a CD is a flat, light-reflecting layer called “land.” On the land are many “pits” recorded in a spiral-shaped track. (From the laser’s point of view, pits are actually the “bumps” shown here because the master disc with pits is duplicated negatively, turning the pits into bumps.) Pits have the same light-reflecting surface as land, but there are differences in the frequencies of the reflected light in the pit and the land, making light reflected by pits relatively dark compared with light reflected by land.

The operation of a ruby laser, the first type of laser used commercially, is shown schematically in Figure 6.16 “A Ruby Laser”. Ruby is an impure form of aluminum oxide (Al_2O_3) in which Cr^{3+} replaces some of the Al^{3+} ions. The red color of the gem is caused by the absorption of light in the blue region of the visible spectrum by Cr^{3+} ions, which leaves only the longer wavelengths to be reflected back to the eye. One end of a ruby bar is coated with a fully reflecting mirror, and the mirror on the other end is only partially reflecting. When flashes of white light from a flash lamp excite the Cr^{3+} ions, they initially decay to a relatively long-lived excited state and can subsequently decay to the ground state by emitting a photon of red light. Some of these photons are reflected back and forth by the mirrored surfaces. As shown in part (b) in Figure 6.16 “A Ruby Laser”, each time a photon interacts with an excited Cr^{3+} ion, it can stimulate that ion to emit another photon that has the same wavelength and is synchronized (*in phase*) with the first wave. This

process produces a *cascade* of photons traveling back and forth, until the intense beam emerges through the partially reflecting mirror. Ruby is only one substance that is used to produce a laser; the choice of material determines the wavelength of light emitted, from infrared to ultraviolet, and the light output can be either continuous or pulsed.

Figure 6.16 A Ruby Laser



(a) This cutaway view of a ruby laser shows the ruby rod, the flash lamp used to excite the Cr³⁺ ions in the ruby, and the totally and partially reflective mirrors. (b) This schematic drawing illustrates how light from the flash lamp excites the Cr³⁺ ions to a short-lived excited state, which is followed by decay to a longer-lived excited state that is responsible for the stimulated in-phase emission of light by the laser.

When used in a DVD player or a CD player, light emitted by a laser passes through a transparent layer of plastic on the CD and is reflected by an underlying aluminum layer, which contains pits or flat regions that were created when the CD was recorded. Differences in the frequencies of the transmitted and reflected light are detected by light-sensitive equipment that converts these differences into binary code, a series of 1s and 0s, which is translated electronically into recognizable sounds and images.

KEY EQUATION

Rydberg equation

$$\text{Equation 6.8: } 1/\lambda = R(1/n_1^2 - 1/n_2^2)$$

Summary

Atoms of individual elements emit light at only specific wavelengths, producing **line spectrum** rather than the continuous spectrum of all wavelengths produced by a hot object. Niels Bohr explained the line spectrum of the hydrogen atom by assuming that the electron moved in circular orbits and that orbits

with only certain radii were allowed. Lines in the spectrum were due to transitions in which an electron moved from a higher-energy orbit with a larger radius to a lower-energy orbit with smaller radius. The orbit closest to the nucleus represented the **ground state** of the atom and was most stable; orbits farther away were higher-energy **excited states**. Transitions from an excited state to a lower-energy state resulted in the emission of light with only a limited number of wavelengths. Bohr's model could not, however, explain the spectra of atoms heavier than hydrogen.

Most light is polychromatic and contains light of many wavelengths. Light that has only a single wavelength is monochromatic and is produced by devices called lasers, which use transitions between two atomic energy levels to produce light in a very narrow range of wavelengths. Atoms can also absorb light of certain energies, resulting in a transition from the ground state or a lower-energy excited state to a higher-energy excited state. This produces an **absorption spectrum**, which has dark lines in the same position as the bright lines in the **emission spectrum** of an element.

KEY TAKEAWAY

- There is an intimate connection between the atomic structure of an atom and its spectral characteristics.

CONCEPTUAL PROBLEMS

1. Is the spectrum of the light emitted by isolated atoms of an element discrete or continuous? How do these spectra differ from those obtained by heating a bulk sample of a solid element? Explain your answers.
2. Explain why each element has a characteristic emission and absorption spectra. If spectral emissions had been found to be continuous rather than discrete, what would have been the implications for Bohr's model of the atom?
3. Explain the differences between a ground state and an excited state. Describe what happens in the spectrum of a species when an electron moves from a ground state to an excited state. What happens in the spectrum when the electron falls from an excited state to a ground state?
4. What phenomenon causes a neon sign to have a characteristic color? If the emission spectrum of an element is constant, why do some neon signs have more than one color?
5. How is light from a laser different from the light emitted by a light source such as a light bulb? Describe how a laser produces light.

NUMERICAL PROBLEMS

- Using a Bohr model and the transition from $n = 2$ to $n = 3$ in an atom with a single electron, describe the mathematical relationship between an emission spectrum and an absorption spectrum. What is the energy of this transition? What does the sign of the energy value represent in this case? What range of light is associated with this transition?
- If a hydrogen atom is excited from an $n = 1$ state to an $n = 3$ state, how much energy does this correspond to? Is this an absorption or an emission? What is the wavelength of the photon involved in this process? To what region of the electromagnetic spectrum does this correspond?
- The hydrogen atom emits a photon with a 486 nm wavelength, corresponding to an electron decaying from the $n = 4$ level to which level? What is the color of the emission?
- An electron in a hydrogen atom can decay from the $n = 3$ level to $n = 2$ level. What is the color of the emitted light? What is the energy of this transition?
- Calculate the wavelength and energy of the photon that gives rise to the third line in order of increasing energy in the Lyman series in the emission spectrum of hydrogen. In what region of the spectrum does this wavelength occur? Describe qualitatively what the absorption spectrum looks like.
- The wavelength of one of the lines in the Lyman series of hydrogen is 121 nm. In what region of the spectrum does this occur? To which electronic transition does this correspond?
- Removing an electron from solid potassium requires 222 kJ/mol. Would you expect to observe a photoelectric effect for potassium using a photon of blue light ($\lambda = 485$ nm)? What is the longest wavelength of energy capable of ejecting an electron from potassium? What is the corresponding color of light of this wavelength?
- The binding energy of an electron is the energy needed to remove an electron from its lowest energy state. According to Bohr's postulates, calculate the binding energy of an electron in a hydrogen atom in kilojoules per mole. What wavelength in nanometers is required to remove such an electron?
- As a radio astronomer, you have observed spectral lines for hydrogen corresponding to a state with $n = 320$, and you would like to produce these lines in the laboratory. Is this feasible? Why or why not?

ANSWERS

- 656 nm; red light
-
- $n = 2$, blue-green light

- 4.
5. 97.2 nm, 2.04×10^{-18} J/photon, ultraviolet light, absorption spectrum is a single dark line at a wavelength of 97.2 nm
- 6.
7. Violet: 390 nm, 307 kJ/mol photons; Blue-purple: 440 nm, 272 kJ/mol photons; Blue-green: 500 nm, 239 kJ/mol photons; Orange: 580 nm, 206 kJ/mol photons; Red: 650 nm, 184 kJ/mol photons
- 8.
9. 1313 kJ/mol, $\lambda \leq 91.1$ nm
10. [1] The negative sign in Equation 6.9 is a convention indicating that the electron-nucleus pair has a lower energy when they are near each other than when they are infinitely far apart, corresponding to $n = \infty$. The latter condition is arbitrarily assigned an energy of zero.

6.4 The Relationship between Energy and Mass

LEARNING OBJECTIVE

1. To understand the wave–particle duality of matter.

Einstein's photons of light were individual packets of energy having many of the characteristics of particles. Recall that the collision of an electron (a particle) with a sufficiently energetic photon can eject a *photoelectron* from the surface of a metal. Any excess energy is transferred to the electron and is converted to the kinetic energy of the ejected electron. Einstein's hypothesis that energy is concentrated in localized bundles, however, was in sharp contrast to the classical notion that energy is spread out uniformly in a wave. We now describe Einstein's theory of the relationship between energy and mass, a theory that others built on to develop our current model of the atom.

The Wave Character of Matter

Einstein initially assumed that photons had zero mass, which made them a peculiar sort of particle indeed. In 1905, however, he published his special theory of relativity, which related energy and mass according to the following equation:

Equation 6.13

$$E = h\nu = hc/\lambda = mc^2$$

According to this theory, a photon of wavelength λ and frequency ν has a nonzero mass, which is given as follows:

Equation 6.14

$$m = E/c^2 = h\nu/c^2 = h/\lambda c$$

That is, light, which had always been regarded as a wave, also has properties typical of particles, a condition known as wave–particle duality. Depending on conditions, light could be viewed as either a wave or a particle.

In 1922, the American physicist Arthur Compton (1892–1962) reported the results of experiments involving the collision of x-rays and electrons that supported the particle nature of light. At about the same time, a young French physics student, Louis de Broglie (1892–1972), began to wonder whether the converse was true: Could particles exhibit the properties of waves? In his PhD dissertation submitted to the Sorbonne in 1924, de Broglie proposed that a particle such as an electron could be described by a wave whose wavelength is given by

Equation 6.15

$$\lambda = h/mv$$
 where h is Planck's constant, m is the mass of the particle, and v is the velocity of the particle.

This revolutionary idea was quickly confirmed by American physicists Clinton Davisson (1881–1958) and Lester Germer (1896–1971), who showed that beams of electrons, regarded as particles, were diffracted by a sodium chloride crystal in the same manner as x-rays, which were regarded as waves. It was proven experimentally that electrons do exhibit the properties of waves. For his work, de Broglie received the Nobel Prize in Physics in 1929.

If particles exhibit the properties of waves, why had no one observed them before? The answer lies in the numerator of de Broglie's equation, which is an extremely small number. As you will calculate in Example 4, Planck's constant (6.63×10^{-34} J·s) is so small that the wavelength of a particle with a large mass is too short (less than the diameter of an atomic nucleus) to be noticeable.

EXAMPLE 4

Calculate the wavelength of a baseball, which has a mass of 149 g and a speed of 100 mi/h.

Given: mass and speed of object

Asked for: wavelength

Strategy:

A Convert the speed of the baseball to the appropriate SI units: meters per second.

B Substitute values into Equation 6.15 and solve for the wavelength.

Solution:

The wavelength of a particle is given by $\lambda = h/mv$. We know that $m = 0.149 \text{ kg}$, so all we need to find is the speed of the baseball:

$$= 44.69 \text{ m/s}$$

B Recall that the joule is a derived unit, whose units are $(\text{kg} \cdot \text{m}^2)/\text{s}^2$. Thus the wavelength of the baseball is $= 9.95 \times 10^{-35} \text{ m}$

(You should verify that the units cancel to give the wavelength in meters.) Given that the diameter of the nucleus of an atom is approximately 10^{-14} m , the wavelength of the baseball is almost unimaginably small.

Exercise

Calculate the wavelength of a neutron that is moving at $3.00 \times 10^3 \text{ m/s}$.

Answer: $1.32 \text{ \AA}$, or 132 pm

As you calculated in Example 4, objects such as a baseball or a neutron have such short wavelengths that they are best regarded primarily as particles. In contrast, objects with very small masses (such as photons) have large wavelengths and can be viewed primarily as waves. Objects with intermediate masses, such as electrons, exhibit the properties of both particles and waves. Although we still usually think of electrons as particles, the wave nature of electrons is employed in an *electron microscope*, which has revealed most of what we know about the microscopic structure of living organisms and materials. Because the wavelength of an electron beam is much shorter than the wavelength of a beam of visible light, this instrument can resolve smaller details than a light microscope can (Figure 6.17 "A Comparison of Images Obtained Using a Light Microscope and an Electron Microscope").

Standing Waves

De Broglie also investigated why only certain orbits were allowed in Bohr's model of the hydrogen atom. He hypothesized that the electron behaves like a standing wave, a wave that does not travel in space. An example of a standing wave is the motion of a string of a violin or guitar. When the string is plucked, it vibrates at certain fixed frequencies because it is fastened at both ends (Figure 6.18 "Standing Waves on a Vibrating String"). If the length of the string is L , then the lowest-energy vibration (the fundamental) has wavelength

Equation 6.16

$$\lambda/2 = L \quad \lambda = 2L$$

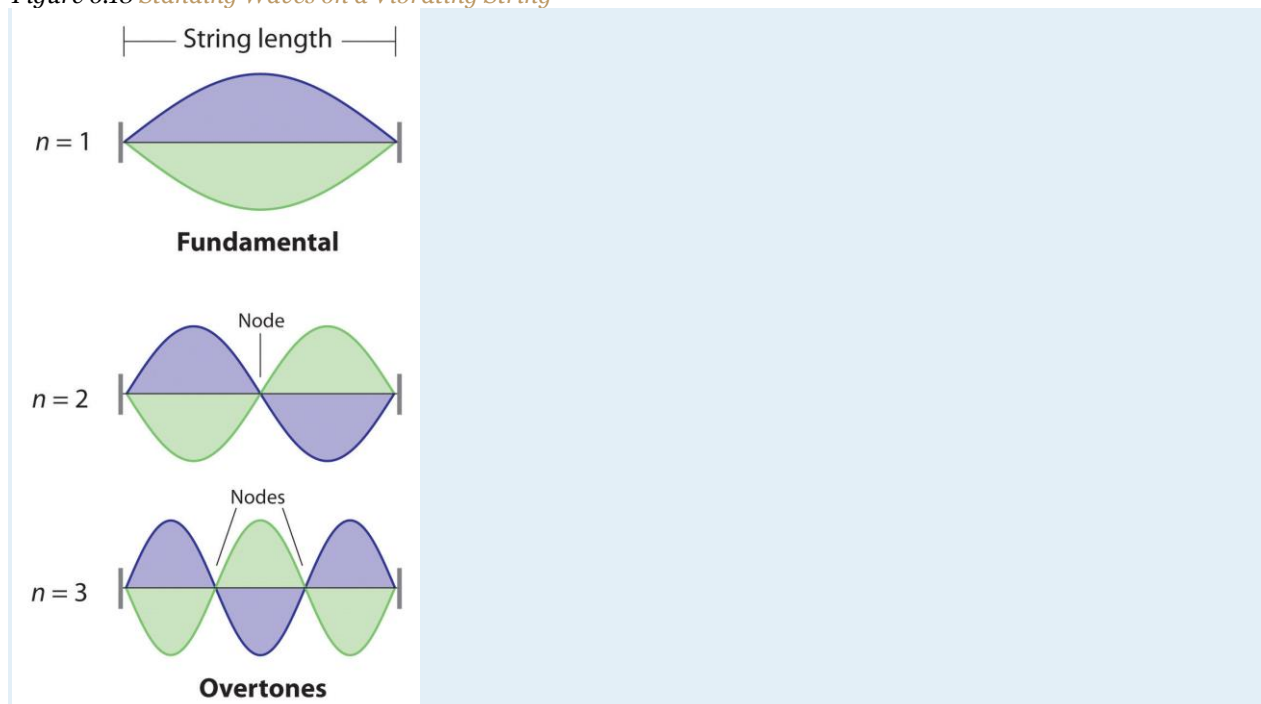
Higher-energy vibrations (overtones) are produced when the string is plucked more strongly; they have wavelengths given by

Equation 6.17

$$\lambda = 2L/n$$

where n has any integral value. Thus the vibrational energy of the string is quantized, and only certain wavelengths and frequencies are possible. Notice in Figure 6.18 "Standing Waves on a Vibrating String" that all overtones have one or more nodes, points where the string does not move. The amplitude of the wave at a node is zero.

Figure 6.18 *Standing Waves on a Vibrating String*



Quantized vibrations and overtones containing nodes are not restricted to one-dimensional systems, such as strings. A two-dimensional surface, such as a drumhead, also has quantized vibrations. Similarly, when the ends of a string are joined to form a circle, the only allowed vibrations are those with wavelength

Equation 6.18

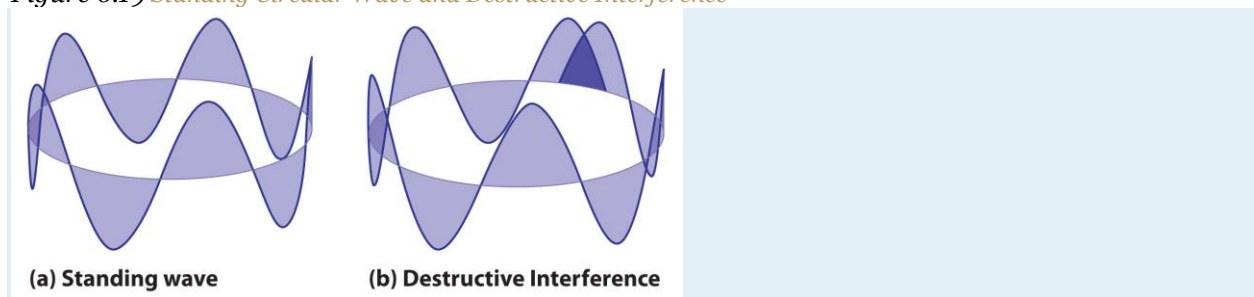
$$2\pi r = n\lambda$$

where r is the radius of the circle. De Broglie argued that Bohr's allowed orbits could be understood if the electron behaved like a *standing circular wave* (Figure 6.19 "Standing Circular Wave and Destructive Interference"). The standing wave could exist only if the circumference of the circle was an integral multiple of the wavelength such that the propagated waves were all in phase, thereby increasing the net amplitudes and causing *constructive*

interference. Otherwise, the propagated waves would be out of phase, resulting in a net decrease in amplitude and causing *destructive interference*. De Broglie's idea explained Bohr's allowed orbits and energy levels nicely: in the lowest energy level, corresponding to $n = 1$ in Equation 6.18, one complete wavelength would close the circle. Higher energy levels would have successively higher values of n with a corresponding number of nodes.

Standing waves are often observed on rivers, reservoirs, ponds, and lakes when seismic waves from an earthquake travel through the area. The waves are called *seismic seiches*, a term first used in 1955 when lake levels in England and Norway oscillated from side to side as a result of the Assam earthquake of 1950 in Tibet. They were first described in the Proceedings of the Royal Society in 1755 when they were seen in English harbors and ponds after a large earthquake in Lisbon, Portugal. Seismic seiches were also observed in many places in North America after the Alaska earthquake of March 28, 1964. Those occurring in western reservoirs lasted for two hours or longer, and amplitudes reached as high as nearly 6 ft along the Gulf Coast. The height of seiches is approximately proportional to the thickness of surface sediments; a deeper channel will produce a higher seiche.

Figure 6.19 *Standing Circular Wave and Destructive Interference*



(a) In a standing circular wave with $n = 5$, the circumference of the circle corresponds to exactly five wavelengths, which results in constructive interference of the wave with itself when overlapping occurs. (b) If the circumference of the circle is not equal to an integral multiple of wavelengths, then the wave does not overlap exactly with itself, and the resulting destructive interference will result in cancellation of the wave. Consequently, a standing wave cannot exist under these conditions.

As you will see, several of de Broglie's ideas are retained in the modern theory of the electronic structure of the atom: the wave behavior of the electron, the concept of standing waves, and the presence of nodes that increase in number as the energy level increases. Unfortunately, his explanation also contains one major feature that we know to be incorrect: in the currently accepted model, the electron in a given orbit is *not* always at the same distance from the nucleus.

The Heisenberg Uncertainty Principle

Because a wave is a disturbance that travels in space, it has no fixed position. One might therefore expect that it would also be hard to specify the exact position of a *particle* that exhibits wavelike behavior. This situation was described mathematically by the German physicist Werner Heisenberg (1901–1976; Nobel Prize in Physics, 1932), who related the position of a particle to its momentum. Referring to the electron, Heisenberg stated that “at every moment the electron has only an inaccurate position and an inaccurate velocity, and between these two inaccuracies there is this uncertainty relation.” Mathematically, the Heisenberg uncertainty principle states that the uncertainty in the position of a particle (Δx) multiplied by the uncertainty in its momentum [$\Delta(mv)$] is greater than or equal to Planck’s constant divided by 4π :

Equation 6.19

$(\Delta x)(\Delta(mv)) \geq h/4\pi$ Because Planck’s constant is a very small number, the Heisenberg uncertainty principle is important only for particles such as electrons that have very low masses. These are the same particles predicted by de Broglie’s equation to have measurable wavelengths.

If the precise position x of a particle is known absolutely ($\Delta x = 0$), then the uncertainty in its momentum must be infinite:

Equation 6.20

$$\Delta(mv) = h/4\pi(\Delta x) = h/4\pi(0) = \infty$$

Because the mass of the electron at rest (m) is both constant and accurately known, the uncertainty in $\Delta(mv)$ must be due to the Δv term, which would have to be infinitely large for $\Delta(mv)$ to equal infinity. That is, according to Equation 6.20, the more accurately we know the exact position of the electron (as $\Delta x \rightarrow 0$), the less accurately we know the speed and the kinetic energy of the electron ($1/2 mv^2$) because $\Delta(mv) \rightarrow \infty$. Conversely, the more accurately we know the precise momentum (and the energy) of the electron [as $\Delta(mv) \rightarrow 0$], then $\Delta x \rightarrow \infty$ and we have no idea where the electron is.

Bohr’s model of the hydrogen atom violated the Heisenberg uncertainty principle by trying to specify simultaneously both the position (an orbit of a particular radius) and the energy (a quantity related to the momentum) of the electron. Moreover, given its mass and wavelike nature, the electron in the hydrogen atom could not possibly orbit the nucleus in a well-defined circular path as predicted by Bohr. You will

see, however, that the *most probable radius* of the electron in the hydrogen atom is exactly the one predicted by Bohr's model.

EXAMPLE 5

Calculate the minimum uncertainty in the position of the pitched baseball from Example 4 that has a mass of exactly 149 g and a speed of 100 ± 1 mi/h.

Given: mass and speed of object

Asked for: minimum uncertainty in its position

Strategy:

A Rearrange the inequality that describes the Heisenberg uncertainty principle (Equation 6.19) to solve for the minimum uncertainty in the position of an object (Δx).

B Find Δv by converting the velocity of the baseball to the appropriate SI units: meters per second.

C Substitute the appropriate values into the expression for the inequality and solve for Δx .

Solution:

A The Heisenberg uncertainty principle tells us that $(\Delta x)[\Delta(mv)] = h/4\pi$. Rearranging the inequality gives

$$\Delta x \geq (h/4\pi)(1/\Delta(mv))$$

B We know that $h = 6.626 \times 10^{-34}$ J·s and $m = 0.149$ kg. Because there is no uncertainty in the mass of the baseball, $\Delta(mv) = m\Delta v$ and $\Delta v = \pm 1$ mi/h. We have

$$\Delta v = 0.4469 \text{ m/s}$$

C Therefore,

$$\Delta x \geq (6.626 \times 10^{-34} \text{ J} \cdot \text{s}) / (4(0.149 \text{ kg})(0.4469 \text{ m/s}))$$

Inserting the definition of a joule ($1 \text{ J} = 1 \text{ kg} \cdot \text{m}^2/\text{s}^2$) gives

$$\Delta x \geq 7.92 \times 10^{-32} \text{ m}$$

This is equal to 3.12×10^{-32} inches. We can safely say that if a batter misjudges the speed of a fastball by 1 mi/h (about 1%), he will not be able to blame Heisenberg's uncertainty principle for striking out.

Exercise

Calculate the minimum uncertainty in the position of an electron traveling at one-third the speed of light, if the uncertainty in its speed is $\pm 0.1\%$. Assume its mass to be equal to its mass at rest.

Answer: 6×10^{-10} m, or 0.6 nm (about the diameter of a benzene molecule)

KEY EQUATIONS

Einstein's relationship between mass and energy

Equation 6.13: $E = h\eta = hc/\lambda = mc^2$

De Broglie's relationship between mass, speed, and wavelength

Equation 6.15: $\lambda = h/mv$

Heisenberg's uncertainty principle

Equation 6.19: $(\Delta x)(\Delta p) \geq h/4\pi$

Summary

The modern model for the electronic structure of the atom is based on recognizing that an electron possesses particle and wave properties, the so-called **wave–particle duality**. Louis de Broglie showed that the wavelength of a particle is equal to Planck's constant divided by the mass times the velocity of the particle. The electron in Bohr's circular orbits could thus be described as a **standing wave**, one that does not move through space. Standing waves are familiar from music: the lowest-energy standing wave is the **fundamental** vibration, and higher-energy vibrations are **overtones** and have successively more **nodes**, points where the amplitude of the wave is always zero. Werner Heisenberg's **uncertainty principle** states that it is impossible to precisely describe both the location and the speed of particles that exhibit wavelike behavior.

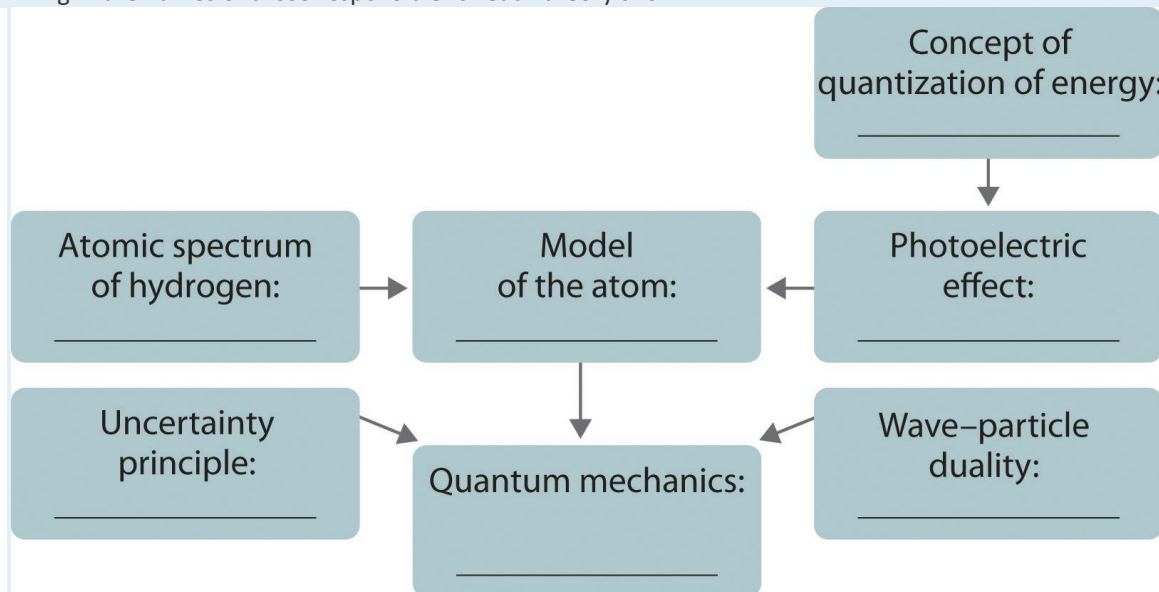
KEY TAKEAWAY

- An electron possesses both particle and wave properties.

CONCEPTUAL PROBLEMS

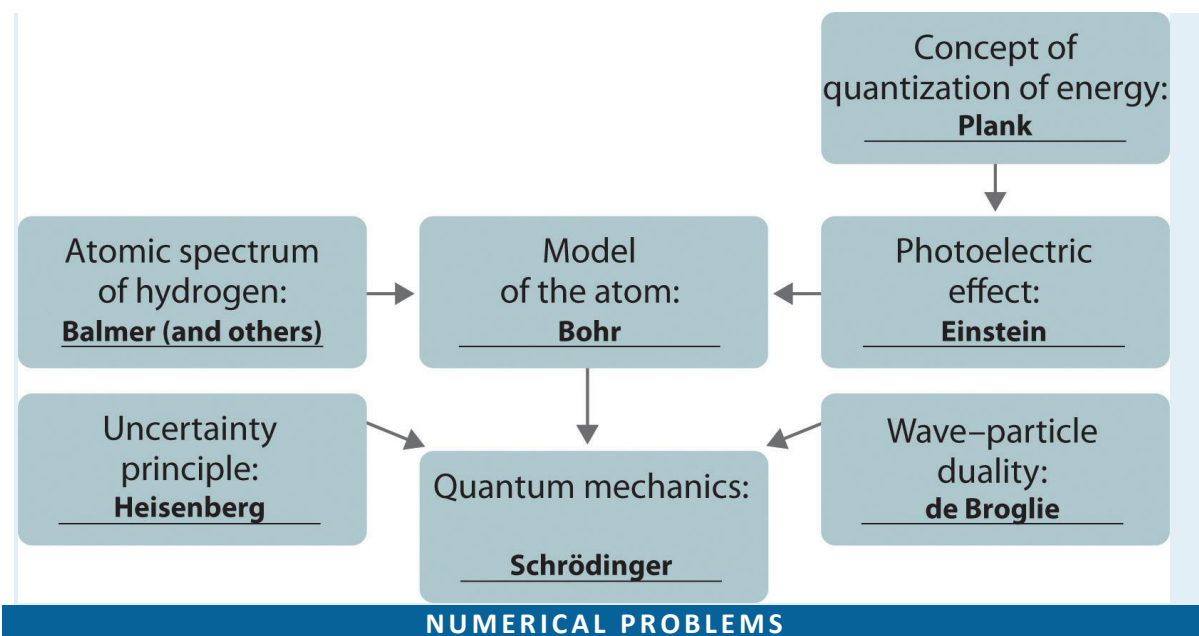
1. Explain what is meant by each term and illustrate with a sketch:
 - a. standing wave
 - b. fundamental
 - c. overtone
 - d. node
2. How does Einstein's theory of relativity illustrate the wave–particle duality of light? What properties of light can be explained by a wave model? What properties can be explained by a particle model?
3. In the modern theory of the electronic structure of the atom, which of de Broglie's ideas have been retained? Which proved to be incorrect?

4. According to Bohr, what is the relationship between an atomic orbit and the energy of an electron in that orbit? Is Bohr's model of the atom consistent with Heisenberg's uncertainty principle? Explain your answer.
5. The development of ideas frequently builds on the work of predecessors. Complete the following chart by filling in the names of those responsible for each theory shown.



ANSWER

5.



- How much heat is generated by shining a carbon dioxide laser with a wavelength of $1.065\ \mu\text{m}$ on a $68.95\ \text{kg}$ sample of water if $1.000\ \text{mol}$ of photons is absorbed and converted to heat? Is this enough heat to raise the temperature of the water 4°C ?
- Show the mathematical relationship between energy and mass and between wavelength and mass. What is the effect of doubling the
 - mass of an object on its energy?
 - mass of an object on its wavelength?
 - frequency on its mass?
- What is the de Broglie wavelength of a $39\ \text{g}$ bullet traveling at $1020\ \text{m/s} \pm 10\ \text{m/s}$? What is the minimum uncertainty in the bullet's position?
- What is the de Broglie wavelength of a $6800\ \text{tn}$ aircraft carrier traveling at $18 \pm 0.1\ \text{knots}$ ($1\ \text{knot} = 1.15\ \text{mi/h}$)? What is the minimum uncertainty in its position?
- Calculate the mass of a particle if it is traveling at $2.2 \times 10^6\ \text{m/s}$ and has a frequency of $6.67 \times 10^7\ \text{Hz}$. If the uncertainty in the velocity is known to be 0.1% , what is the minimum uncertainty in the position of the particle?
- Determine the wavelength of a $2800\ \text{lb}$ automobile traveling at $80\ \text{mi/h} \pm 3\%$. How does this compare with the diameter of the nucleus of an atom? You are standing $3\ \text{in.}$ from the edge of the highway. What is the minimum uncertainty in the position of the automobile in inches?

ANSWERS

1. $E = 112.3 \text{ kJ}$, $\Delta T = 0.3893^\circ\text{C}$, over ten times more light is needed for a 4.0°C increase in temperature
- 2.
3. $1.7 \times 10^{-35} \text{ m}$, uncertainty in position is $\geq 1.4 \times 10^{-34} \text{ m}$
- 4.
5. $9.1 \times 10^{-39} \text{ kg}$, uncertainty in position $\geq 2.6 \text{ m}$

6.5 Atomic Orbitals and Their Energies

LEARNING OBJECTIVE

1. To apply the results of quantum mechanics to chemistry.

The paradox described by Heisenberg's uncertainty principle and the wavelike nature of subatomic particles such as the electron made it impossible to use the equations of classical physics to describe the motion of electrons in atoms. Scientists needed a new approach that took the wave behavior of the electron into account. In 1926, an Austrian physicist, Erwin Schrödinger (1887–1961; Nobel Prize in Physics, 1933), developed *wave mechanics*, a mathematical technique that describes the relationship between the motion of a particle that exhibits wavelike properties (such as an electron) and its allowed energies. In doing so, Schrödinger developed the theory of quantum mechanics, which is used today to describe the energies and spatial distributions of electrons in atoms and molecules.

Erwin Schrödinger (1887–1961)

Schrödinger's unconventional approach to atomic theory was typical of his unconventional approach to life. He was notorious for his intense dislike of memorizing data and learning from books. When Hitler came to power in Germany, Schrödinger escaped to Italy. He then worked at Princeton University in the United States but eventually moved to the Institute for Advanced Studies in Dublin, Ireland, where he remained until his retirement in 1955.

Although quantum mechanics uses sophisticated mathematics, you do not need to understand the mathematical details to follow our discussion of its general conclusions. We focus on the properties of the *wave functions* that are the solutions of Schrödinger's equations.

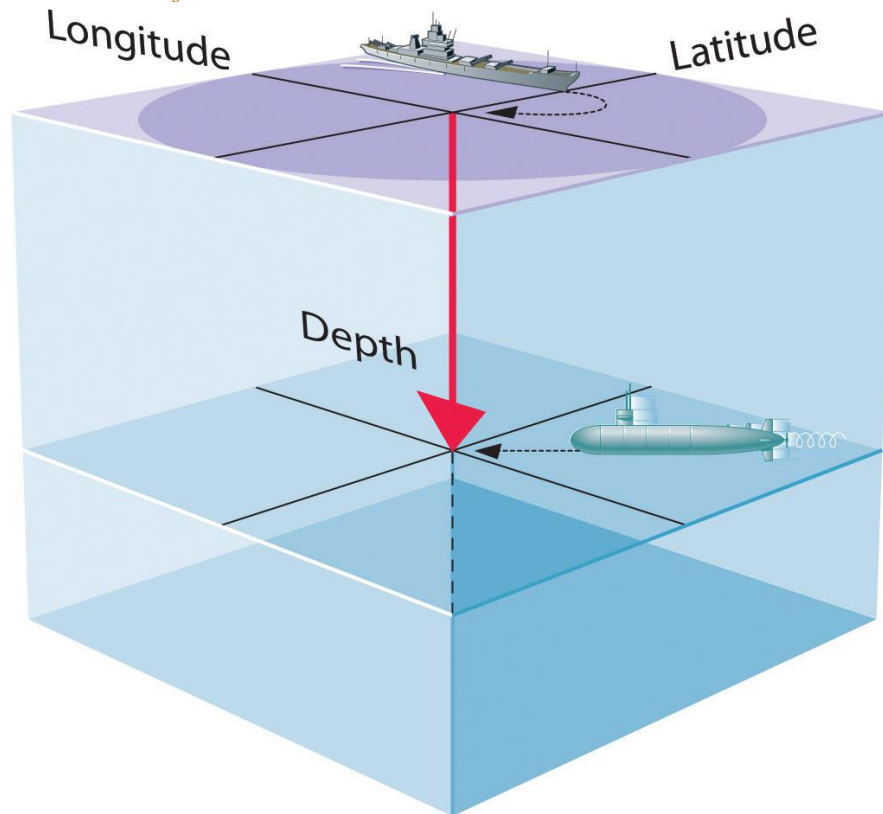
Wave Functions

A wave function (Ψ)^[1] is a mathematical function that relates the location of an electron at a given point in space (identified by x , y , and z coordinates) to the amplitude of its wave, which corresponds to its

energy. Thus each wave function is associated with a particular energy E . The properties of wave functions derived from quantum mechanics are summarized here:

- **A wave function uses three variables to describe the position of an electron.** A fourth variable is usually required to fully describe the location of objects in motion. Three specify the position in space (as with the Cartesian coordinates x , y , and z), and one specifies the time at which the object is at the specified location. For example, if you wanted to intercept an enemy submarine, you would need to know its latitude, longitude, and depth, as well as the time at which it was going to be at this position (Figure 6.20 "The Four Variables (Latitude, Longitude, Depth, and Time) Required to Precisely Locate an Object"). For electrons, we can ignore the time dependence because we will be using standing waves, which by definition do not change with time, to describe the position of an electron.

Figure 6.20 The Four Variables (Latitude, Longitude, Depth, and Time) Required to Precisely Locate an Object



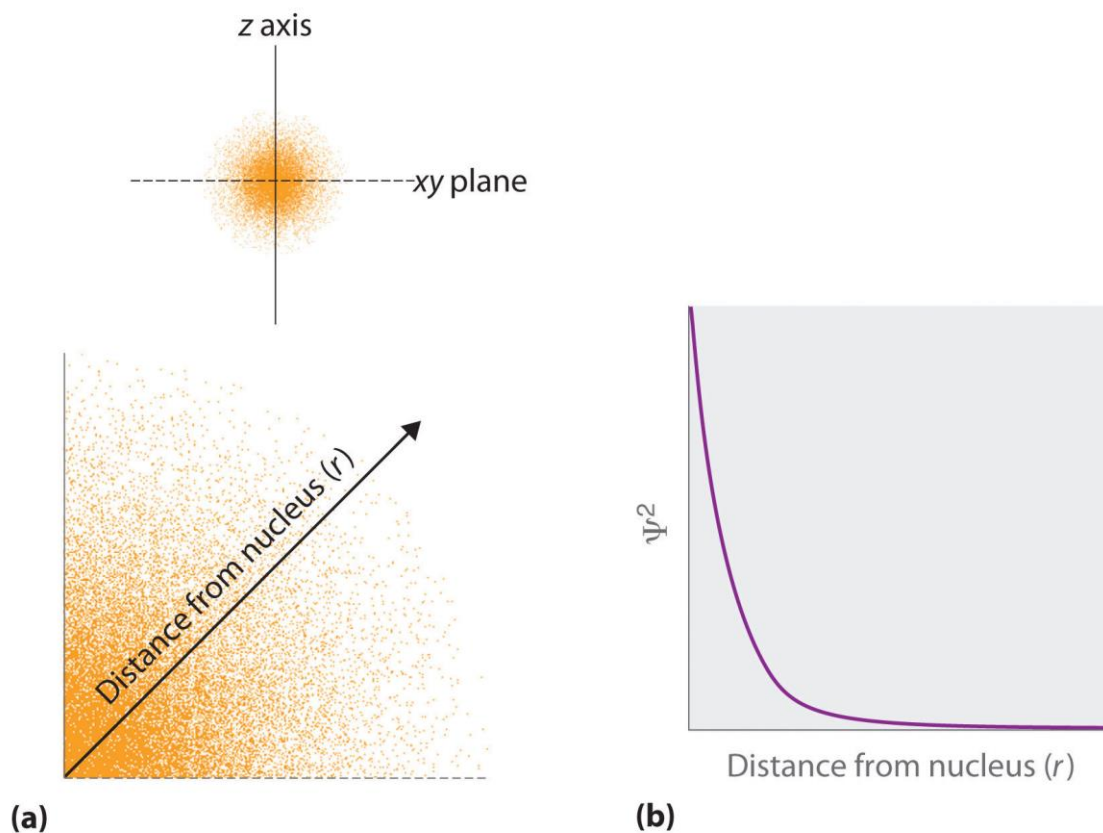
If you are the captain of a ship trying to intercept an enemy submarine, you need to deliver your depth charge to the right location at the right time.

- **The magnitude of the wave function at a particular point in space is proportional to the amplitude of the wave at that point.** Many wave functions are complex functions, which is a mathematical term indicating that they contain $-1 - \sqrt{-1}$, represented as i . Hence the amplitude of the wave has no real physical significance. In

contrast, the sign of the wave function (either positive or negative) corresponds to the phase of the wave, which will be important in our discussion of chemical bonding in Chapter 9 "Molecular Geometry and Covalent Bonding Models". The sign of the wave function should *not* be confused with a positive or negative electrical charge.

- **The square of the wave function at a given point is proportional to the probability of finding an electron at that point, which leads to a distribution of probabilities in space.** The square of the wave function (Ψ^2) is always a real quantity [recall that $(-1)^2 = 1$] that is proportional to the probability of finding an electron at a given point.^[2] We use probabilities because, according to Heisenberg's uncertainty principle, we cannot precisely specify the position of an electron. The probability of finding an electron at any point in space depends on several factors, including the distance from the nucleus and, in many cases, the atomic equivalent of latitude and longitude. As one way of graphically representing the probability distribution, the probability of finding an electron is indicated by the density of colored dots, as shown for the ground state of the hydrogen atom in Figure 6.21 "Probability of Finding the Electron in the Ground State of the Hydrogen Atom at Different Points in Space".

Figure 6.21 Probability of Finding the Electron in the Ground State of the Hydrogen Atom at Different Points in Space



(a) The density of the dots shows electron probability. (b) In this plot of Ψ^2 versus r for the ground state of the hydrogen atom, the electron probability density is greatest at $r = 0$ (the nucleus) and falls off with increasing r . Because the line never actually reaches the horizontal axis, the probability of finding the electron at very large values of r is very small but not zero.

- **Describing the electron distribution as a standing wave leads to sets of quantum numbers that are characteristic of each wave function.** From the patterns of one- and two-dimensional standing waves shown in Figure 6.18 "Standing Waves on a Vibrating String" and Figure 6.19 "Standing Circular Wave and Destructive Interference", you might expect (correctly) that the patterns of three-dimensional standing waves would be complex. Fortunately, however, in the 18th century, a French mathematician, Adrien Legendre (1752–1783), developed a set of equations to describe the motion of tidal waves on the surface of a flooded planet. Schrödinger incorporated Legendre's equations into his wave functions. The requirement that the waves must be in phase with one another to avoid cancellation and produce a standing wave results in a limited number of solutions (wave functions), each of which is specified by a set of numbers called quantum numbers.
- **Each wave function is associated with a particular energy.** As in Bohr's model, the energy of an electron in an atom is quantized; it can have only certain allowed values. The major difference between Bohr's model and Schrödinger's approach is that Bohr had to impose the idea of quantization arbitrarily, whereas in Schrödinger's approach, quantization is a natural consequence of describing an electron as a standing wave.

Quantum Numbers

Schrödinger's approach uses three quantum numbers (n , l , and ml) to specify any wave function. The quantum numbers provide information about the spatial distribution of an electron. Although n can be any positive integer, only certain values of l and ml are allowed for a given value of n .

The Principal Quantum Number

The principal quantum number (n) tells the average relative distance of an electron from the nucleus:

Equation 6.21

$$n = 1, 2, 3, 4, \dots$$

As n increases for a given atom, so does the average distance of an electron from the nucleus. A negatively charged electron that is, on average, closer to the positively charged nucleus is attracted to the nucleus more strongly than an electron that is farther out in space. This means that electrons with higher values of n are easier to remove from an atom. All wave functions that have the same value of n are said to

constitute a principal shell because those electrons have similar average distances from the nucleus. As you will see, the principal quantum number n corresponds to the n used by Bohr to describe electron orbits and by Rydberg to describe atomic energy levels.

The Azimuthal Quantum Number

The second quantum number is often called the azimuthal quantum number (l). The value of l describes the *shape* of the region of space occupied by the electron. The allowed values of l depend on the value of n and can range from 0 to $n - 1$:

Equation 6.22

$$l = 0, 1, 2, \dots, n - 1$$

For example, if $n = 1$, l can be only 0; if $n = 2$, l can be 0 or 1; and so forth. For a given atom, all wave functions that have the same values of both n and l form a subshell. The regions of space occupied by electrons in the same subshell usually have the same shape, but they are oriented differently in space.

The Magnetic Quantum Number

The third quantum number is the magnetic quantum number (m_l). The value of m_l describes the *orientation* of the region in space occupied by an electron with respect to an applied magnetic field. The allowed values of m_l depend on the value of l : m_l can range from $-l$ to l in integral steps:

Equation 6.23

$$m_l = -l, -l + 1, \dots, 0, \dots, l - 1, l$$

For example, if $l = 0$, m_l can be only 0; if $l = 1$, m_l can be -1 , 0, or $+1$; and if $l = 2$, m_l can be -2 , -1 , 0, $+1$, or $+2$.

Each wave function with an allowed combination of n , l , and m_l values describes an atomic orbital, a particular spatial distribution for an electron. For a given set of quantum numbers, each principal shell has a fixed number of subshells, and each subshell has a fixed number of orbitals.

EXAMPLE 6

How many subshells and orbitals are contained within the principal shell with $n = 4$?

Given: value of n

Asked for: number of subshells and orbitals in the principal shell

Strategy:

A Given $n = 4$, calculate the allowed values of l . From these allowed values, count the number of subshells.

B For each allowed value of l , calculate the allowed values of ml . The sum of the number of orbitals in each subshell is the number of orbitals in the principal shell.

Solution:

A We know that l can have all integral values from 0 to $n - 1$. If $n = 4$, then l can equal 0, 1, 2, or 3. Because the shell has four values of l , it has four subshells, each of which will contain a different number of orbitals, depending on the allowed values of ml .

B For $l = 0$, ml can be only 0, and thus the $l = 0$ subshell has only one orbital. For $l = 1$, ml can be 0 or ± 1 ; thus the $l = 1$ subshell has three orbitals. For $l = 2$, ml can be 0, ± 1 , or ± 2 , so there are five orbitals in the $l = 2$ subshell. The last allowed value of l is $l = 3$, for which ml can be 0, ± 1 , ± 2 , or ± 3 , resulting in seven orbitals in the $l = 3$ subshell. The total number of orbitals in the $n = 4$ principal shell is the sum of the number of orbitals in each subshell and is equal to n^2 :

$$1(l = 0) + 3(l = 1) + 5(l = 2) + 7(l = 3) = 16 \text{ orbitals} \\ = (4 \text{ principal shells})^2$$

Exercise

How many subshells and orbitals are in the principal shell with $n = 3$?

Answer: three subshells; nine orbitals

Rather than specifying all the values of n and l every time we refer to a subshell or an orbital, chemists use an abbreviated system with lowercase letters to denote the value of l for a particular subshell or orbital:

$l =$	0	1	2	3
Designation	<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>

The principal quantum number is named first, followed by the letter *s*, *p*, *d*, or *f* as appropriate. These orbital designations are derived from corresponding spectroscopic characteristics: sharp, principle, diffuse, and fundamental. A *1s* orbital has $n = 1$ and $l = 0$; a *2p* subshell has $n = 2$ and $l = 1$ (and has three *2p* orbitals, corresponding to $ml = -1, 0$, and $+1$); a *3d* subshell has $n = 3$ and $l = 2$ (and has five *3d* orbitals, corresponding to $ml = -2, -1, 0, +1$, and $+2$); and so forth.

We can summarize the relationships between the quantum numbers and the number of subshells and orbitals as follows (Table 6.3 "Values of "):

- Each principal shell has n subshells. For $n = 1$, only a single subshell is possible (*1s*); for $n = 2$, there are two subshells (*2s* and *2p*); for $n = 3$, there are three subshells (*3s*, *3p*, and *3d*); and so forth. Every shell has an *ns* subshell, any shell

with $n \geq 2$ also has an np subshell, and any shell with $n \geq 3$ also has an nd subshell. Because a $2d$ subshell would require both $n = 2$ and $l = 2$, which is not an allowed value of l for $n = 2$, a $2d$ subshell does not exist.

- Each subshell has $2l + 1$ orbitals. This means that all ns subshells contain a single orbital, all np subshells contain three p orbitals, all nd subshells contain five d orbitals, and all nf subshells contain seven f orbitals.

Note the Pattern

Each principal shell has n subshells, and each subshell has $2l + 1$ orbitals.

Table 6.3 Values of n , l , and m_l through $n = 4$

n	l	Subshell Designation	m_l	Number of Orbitals in Subshell	Number of Orbitals in Shell
1	0	$1s$	0	1	1
2	0	$2s$	0	1	4
	1	$2p$	-1, 0, 1	3	
3	0	$3s$	0	1	9
	1	$3p$	-1, 0, 1	3	
	2	$3d$	-2, -1, 0, 1, 2	5	
4	0	$4s$	0	1	16
	1	$4p$	-1, 0, 1	3	
	2	$4d$	-2, -1, 0, 1, 2	5	
	3	$4f$	-3, -2, -1, 0, 1, 2, 3	7	

Orbital Shapes

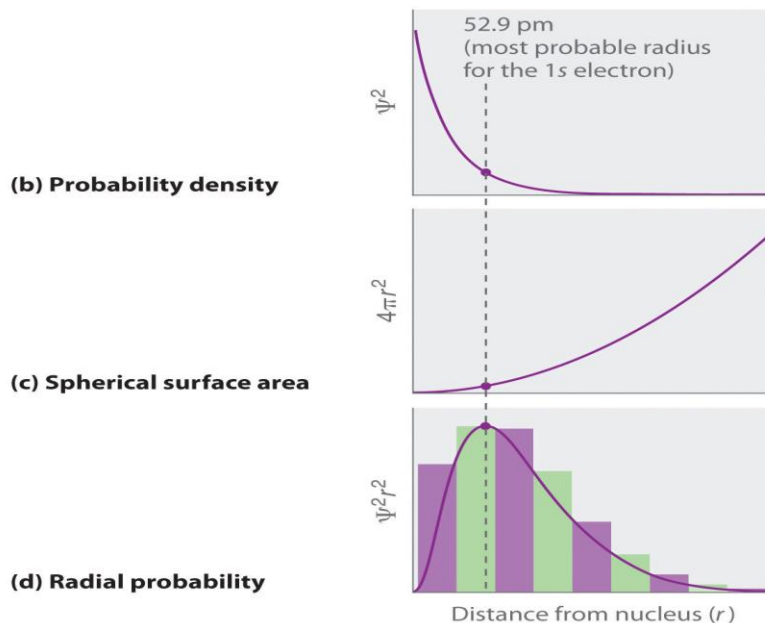
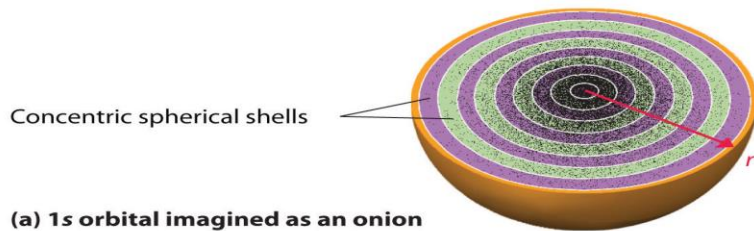
An orbital is the quantum mechanical refinement of Bohr's orbit. In contrast to his concept of a simple circular orbit with a fixed radius, orbitals are mathematically derived regions of space with different *probabilities* of having an electron.

One way of representing electron probability distributions was illustrated in Figure 6.21 "Probability of Finding the Electron in the Ground State of the Hydrogen Atom at Different Points in Space" for the $1s$ orbital of hydrogen. Because Ψ^2 gives the probability of finding an electron in a given volume of space (such as a cubic picometer), a plot of Ψ^2 versus distance from the nucleus (r) is a plot of the *probability density*. The $1s$ orbital is spherically symmetrical, so the probability of finding a $1s$ electron at any given point depends *only* on its distance from the nucleus. The probability density is greatest at $r = 0$ (at the

nucleus) and decreases steadily with increasing distance. At very large values of r , the electron probability density is very small but *not* zero.

In contrast, we can calculate the *radial probability* (the probability of finding a 1selectron at a distance r from the nucleus) by adding together the probabilities of an electron being at all points on a series of x spherical shells of radius $r_1, r_2, r_3, \dots, r_{x-1}, r_x$. In effect, we are dividing the atom into very thin concentric shells, much like the layers of an onion (part (a) in Figure 6.22 "Most Probable Radius for the Electron in the Ground State of the Hydrogen Atom"), and calculating the probability of finding an electron on each spherical shell. Recall that the electron probability density is greatest at $r = 0$ (part (b) in Figure 6.22 "Most Probable Radius for the Electron in the Ground State of the Hydrogen Atom"), so the density of dots is greatest for the smallest spherical shells in part (a) in Figure 6.22 "Most Probable Radius for the Electron in the Ground State of the Hydrogen Atom". In contrast, the surface area of each spherical shell is equal to $4\pi r^2$, which increases very rapidly with increasing r (part (c) in Figure 6.22 "Most Probable Radius for the Electron in the Ground State of the Hydrogen Atom"). Because the surface area of the spherical shells increases more rapidly with increasing r than the electron probability density decreases, the plot of radial probability has a maximum at a particular distance (part (d) in Figure 6.22 "Most Probable Radius for the Electron in the Ground State of the Hydrogen Atom"). Most important, when r is very small, the surface area of a spherical shell is so small that the *total* probability of finding an electron close to the nucleus is very low; at the nucleus, the electron probability vanishes (part (d) in Figure 6.22 "Most Probable Radius for the Electron in the Ground State of the Hydrogen Atom").

Figure 6.22 Most Probable Radius for the Electron in the Ground State of the Hydrogen Atom



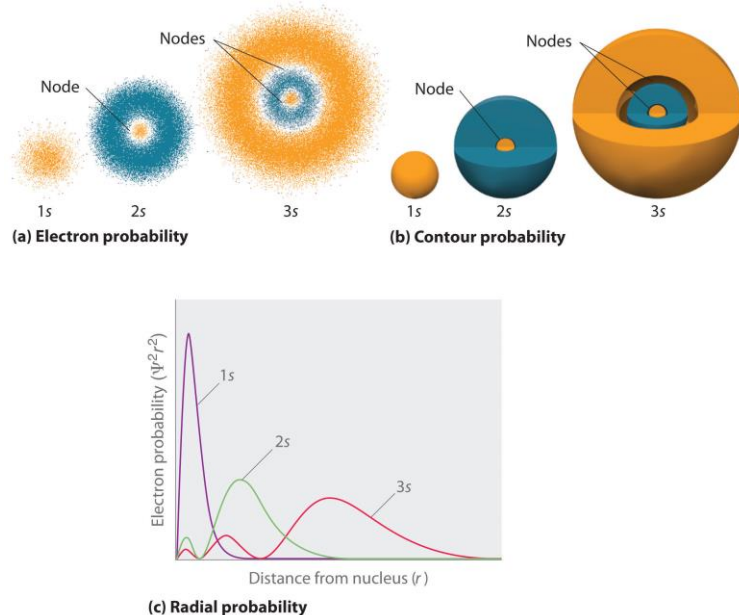
(a) Imagine dividing the atom's total volume into very thin concentric shells as shown in the onion drawing. (b) A plot of electron probability density Ψ^2 versus r shows that the electron probability density is greatest at $r = 0$ and falls off smoothly with increasing r . The density of the dots is therefore greatest in the innermost shells of the onion. (c) The surface area of each shell, given by $4\pi r^2$, increases rapidly with increasing r . (d) If we count the number of dots in each spherical shell, we obtain the total probability of finding the electron at a given value of r . Because the surface area of each shell increases more rapidly with increasing r than the electron probability density decreases, a plot of electron probability versus r (the radial probability) shows a peak. This peak corresponds to the most probable radius for the electron, 52.9 pm, which is exactly the radius predicted by Bohr's model of the hydrogen atom.

For the hydrogen atom, the peak in the radial probability plot occurs at $r = 0.529 \text{ \AA}$ (52.9 pm), which is exactly the radius calculated by Bohr for the $n = 1$ orbit. Thus the *most probable radius* obtained from quantum mechanics is identical to the radius calculated by classical mechanics. In Bohr's model, however, the electron was assumed to be at this distance 100% of the time, whereas in the Schrödinger model, it is at this distance only some of the time. The

difference between the two models is attributable to the wavelike behavior of the electron and the Heisenberg uncertainty principle.

Figure 6.23 "Probability Densities for the 1" compares the electron probability densities for the hydrogen 1s, 2s, and 3s orbitals. Note that all three are spherically symmetrical. For the 2s and 3s orbitals, however (and for all other s orbitals as well), the electron probability density does not fall off smoothly with increasing r . Instead, a series of minima and maxima are observed in the radial probability plots (part (c) in Figure 6.23 "Probability Densities for the 1"). The minima correspond to spherical nodes (regions of zero electron probability), which alternate with spherical regions of nonzero electron probability.

Figure 6.23 *Probability Densities for the 1s, 2s, and 3s Orbitals of the Hydrogen Atom*



a) The electron probability density in any plane that contains the nucleus is shown. Note the presence of circular regions, or nodes, where the probability density is zero. (b) Contour surfaces enclose 90% of the electron probability, which illustrates the different sizes of the 1s, 2s, and 3s orbitals. The cutaway drawings give partial views of the internal spherical nodes. The orange color corresponds to regions of space where the phase of the wave function is positive, and the blue color corresponds to regions of space where the phase of the wave function is negative. (c) In these plots of electron probability as a function of distance from the nucleus (r) in all directions (radial probability), the most probable radius increases as n increases, but the 2s and 3s orbitals have regions of significant electron probability at small values of r .

s Orbitals

Three things happen to s orbitals as n increases (Figure 6.23 "Probability Densities for the 1"):

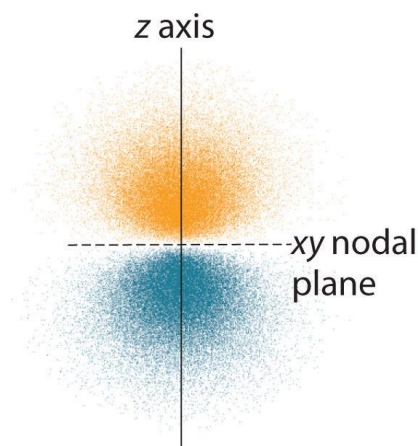
1. They become larger, extending farther from the nucleus.
2. They contain more nodes. This is similar to a standing wave that has regions of significant amplitude separated by nodes, points with zero amplitude.
3. For a given atom, the s orbitals also become higher in energy as n increases because of their increased distance from the nucleus.

Orbitals are generally drawn as three-dimensional surfaces that enclose 90% of the electron density, as was shown for the hydrogen $1s$, $2s$, and $3s$ orbitals in part (b) in Figure 6.23 "Probability Densities for the 1". Although such drawings show the relative sizes of the orbitals, they do not normally show the spherical nodes in the $2s$ and $3s$ orbitals because the spherical nodes lie inside the 90% surface. Fortunately, the positions of the spherical nodes are not important for chemical bonding.

p Orbitals

Only s orbitals are spherically symmetrical. As the value of l increases, the number of orbitals in a given subshell increases, and the shapes of the orbitals become more complex. Because the $2p$ subshell has $l = 1$, with three values of m_l (-1 , 0 , and $+1$), there are three $2p$ orbitals.

Figure 6.24 Electron Probability Distribution for a Hydrogen $2p$ Orbital

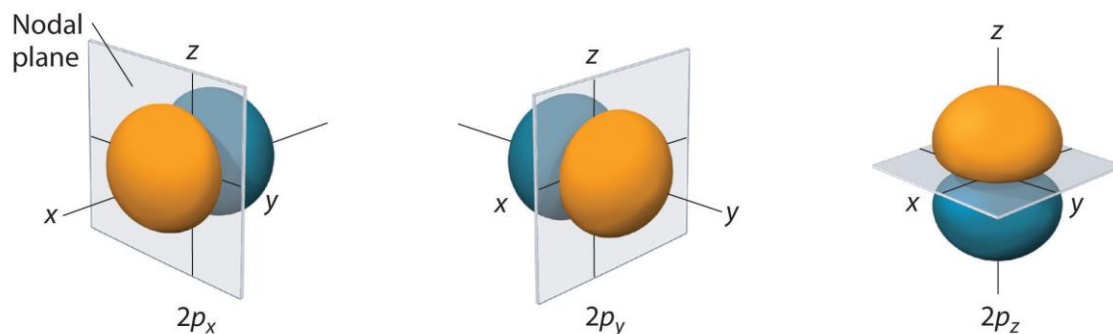


The nodal plane of zero electron density separates the two lobes of the $2p$ orbital. As in Figure 6.23 "Probability Densities for the 1", the colors correspond to regions of space where the phase of the wave function is positive (orange) and negative (blue).

The electron probability distribution for one of the hydrogen $2p$ orbitals is shown in Figure 6.24 "Electron Probability Distribution for a Hydrogen 2". Because this orbital has two lobes of electron density arranged along the z axis, with an electron density of zero in the xy plane (i.e., the xy plane is a nodal plane), it is a $2p_z$ orbital. As shown in Figure 6.25 "The Three Equivalent 2", the other two $2p$ orbitals have identical shapes, but they lie along the x axis ($2p_x$)

and y axis ($2p_y$), respectively. Note that each p orbital has just one nodal plane. In each case, the phase of the wave function for each of the $2p$ orbitals is positive for the lobe that points along the positive axis and negative for the lobe that points along the negative axis. It is important to emphasize that these signs correspond to the *phase* of the wave that describes the electron motion, *not* to positive or negative charges.

Figure 6.25 *The Three Equivalent $2p$ Orbitals of the Hydrogen Atom*



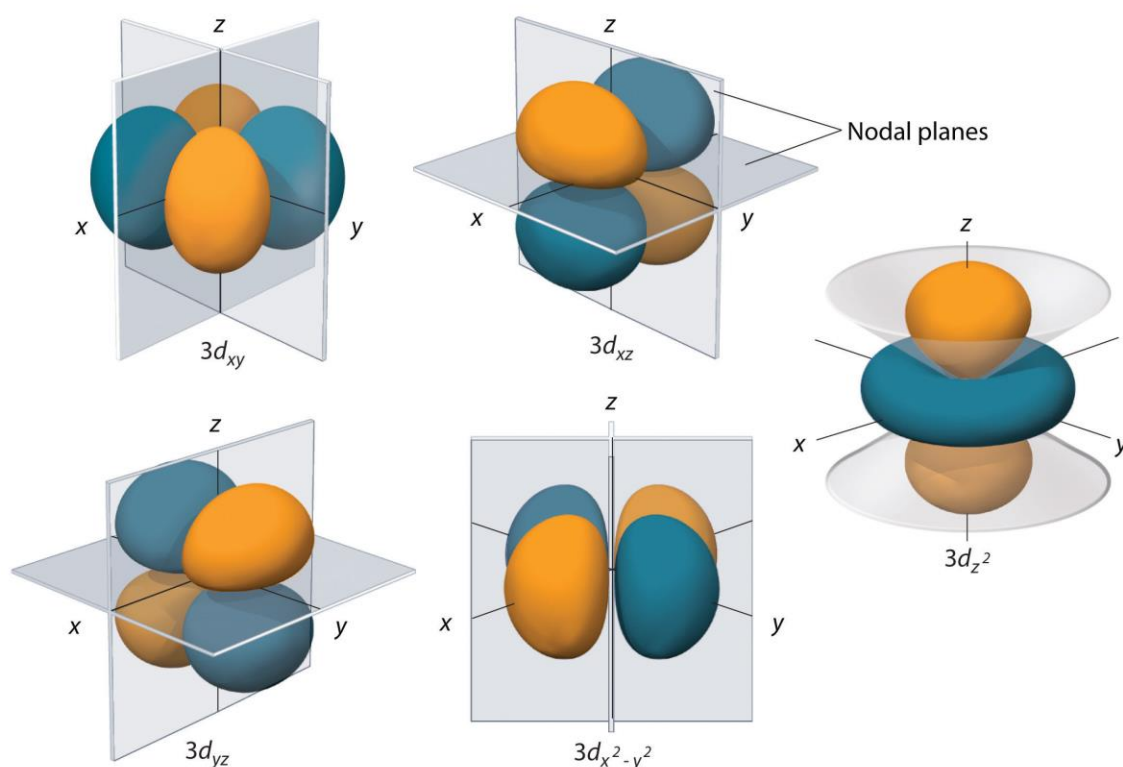
The surfaces shown enclose 90% of the total electron probability for the $2p_x$, $2p_y$, and $2p_z$ orbitals. Each orbital is oriented along the axis indicated by the subscript and a nodal plane that is perpendicular to that axis bisects each $2p$ orbital. The phase of the wave function is positive (orange) in the region of space where x , y , or z is positive and negative (blue) where x , y , or z is negative.

Just as with the s orbitals, the size and complexity of the p orbitals for any atom increase as the principal quantum number n increases. The shapes of the 90% probability surfaces of the $3p$, $4p$, and higher-energy p orbitals are, however, essentially the same as those shown in Figure 6.25 "The Three Equivalent $2p$ ".

d Orbitals

Subshells with $l = 2$ have five d orbitals; the first principal shell to have a d subshell corresponds to $n = 3$. The five d orbitals have m_l values of -2 , -1 , 0 , $+1$, and $+2$.

Figure 6.26 *The Five Equivalent $3d$ Orbitals of the Hydrogen Atom*



The surfaces shown enclose 90% of the total electron probability for the five hydrogen $3d$ orbitals. Four of the five $3d$ orbitals consist of four lobes arranged in a plane that is intersected by two perpendicular nodal planes. These four orbitals have the same shape but different orientations. The fifth $3d$ orbital, $3d_{z^2}$, has a distinct shape even though it is mathematically equivalent to the others. The phase of the wave function for the different lobes is indicated by color: orange for positive and blue for negative.

The hydrogen $3d$ orbitals, shown in Figure 6.26 "The Five Equivalent 3", have more complex shapes than the $2p$ orbitals. All five $3d$ orbitals contain two nodal surfaces, as compared to one for each p orbital and zero for each s orbital. In three of the d orbitals, the lobes of electron density are oriented between the x and y , x and z , and y and z planes; these orbitals are referred to as the $3d_{xy}$, $3d_{xz}$, and $3d_{yz}$ orbitals, respectively. A fourth d orbital has lobes lying along the x and y axes; this is the $3d_{x^2-y^2}$ orbital. The fifth $3d$ orbital, called the $3d_{z^2}$ orbital, has a unique shape: it looks like a $2p_z$ orbital combined with an additional doughnut of electron probability lying in the xy plane. Despite its peculiar shape, the $3d_{z^2}$ orbital is mathematically equivalent to the other four and has the same energy. In contrast to p orbitals, the phase of the wave function for d orbitals is the same for opposite pairs of lobes. As shown in Figure

6.26 "The Five Equivalent 3", the phase of the wave function is positive for the two lobes of the dz^2 orbital that lie along the z axis, whereas the phase of the wave function is negative for the doughnut of electron density in the xy plane. Like the s and p orbitals, as n increases, the size of the d orbitals increases, but the overall shapes remain similar to those depicted in Figure 6.26 "The Five Equivalent 3".

f Orbitals

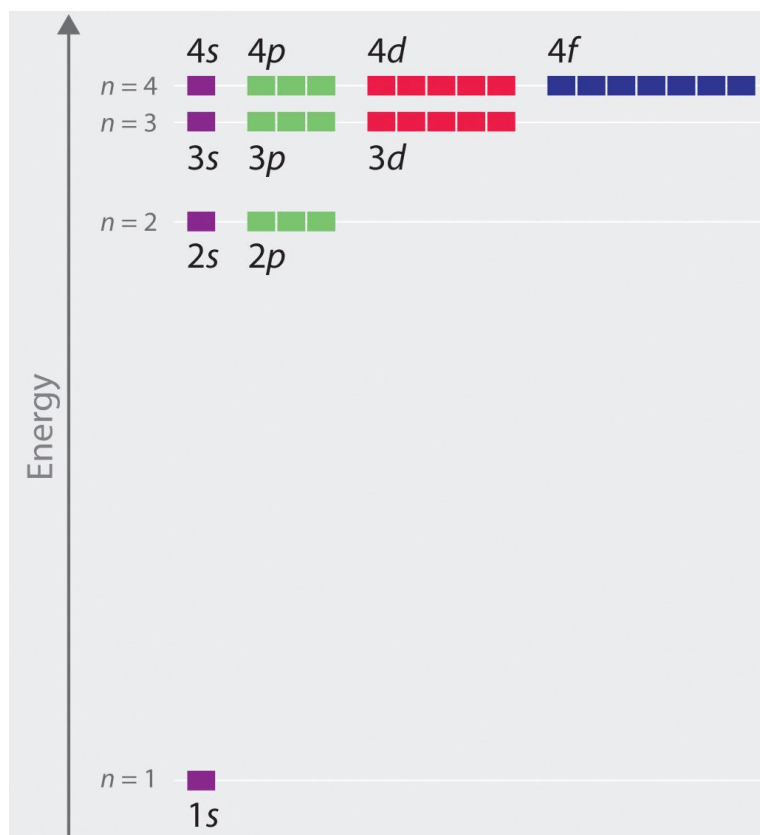
Principal shells with $n = 4$ can have subshells with $l = 3$ and ml values of $-3, -2, -1, 0, +1, +2$, and $+3$. These subshells consist of seven f orbitals. Each f orbital has three nodal surfaces, so their shapes are complex. Because f orbitals are not particularly important for our purposes, we do not discuss them further, and orbitals with higher values of l are not discussed at all.

Orbital Energies

Although we have discussed the shapes of orbitals, we have said little about their comparative energies. We begin our discussion of orbital energies by considering atoms or ions with only a single electron (such as H or He^+).

The relative energies of the atomic orbitals with $n \leq 4$ for a hydrogen atom are plotted in Figure 6.27 "Orbital Energy Level Diagram for the Hydrogen Atom"; note that the orbital energies depend on *only* the principal quantum number n . Consequently, the energies of the $2s$ and $2p$ orbitals of hydrogen are the same; the energies of the $3s$, $3p$, and $3d$ orbitals are the same; and so forth. The orbital energies obtained for hydrogen using quantum mechanics are exactly the same as the allowed energies calculated by Bohr. In contrast to Bohr's model, however, which allowed only one orbit for each energy level, quantum mechanics predicts that there are 4 orbitals with different electron density distributions in the $n = 2$ principal shell (one $2s$ and three $2p$ orbitals), 9 in the $n = 3$ principal shell, and 16 in the $n = 4$ principal shell.^[3] As we have just seen, however, quantum mechanics also predicts that in the hydrogen atom, all orbitals with the same value of n (e.g., the three $2p$ orbitals) are degenerate, meaning that they have the same energy. Figure 6.27 "Orbital Energy Level Diagram for the Hydrogen Atom" shows that the energy levels become closer and closer together as the value of n increases, as expected because of the $1/n^2$ dependence of orbital energies.

Figure 6.27 *Orbital Energy Level Diagram for the Hydrogen Atom*



Each box corresponds to one orbital. Note that the difference in energy between orbitals decreases rapidly with increasing values of n .

The energies of the orbitals in any species with only one electron can be calculated by a minor variation of Bohr's equation (Equation 6.9), which can be extended to other single-electron species by incorporating the nuclear charge Z (the number of protons in the nucleus):

Equation 6.24

$$E = -Z^2 n^2 R h c$$

In general, both energy and radius decrease as the nuclear charge increases. Thus the most stable orbitals (those with the lowest energy) are those closest to the nucleus. For example, in the ground state of the hydrogen atom, the single electron is in the $1s$ orbital, whereas in the first excited state, the atom has absorbed energy and the electron has been promoted to one of the $n = 2$ orbitals. In ions with only a single electron, the energy of a given orbital depends on only n , and all subshells within a principal shell, such as the p_x , p_y , and p_z orbitals, are degenerate.

Effective Nuclear Charges

For an atom or an ion with only a single electron, we can calculate the potential energy by considering only the electrostatic attraction between the positively charged nucleus and the negatively charged

electron. When more than one electron is present, however, the total energy of the atom or the ion depends not only on attractive electron-nucleus interactions but also on repulsive electron-electron interactions. When there are two electrons, the repulsive interactions depend on the positions of *both* electrons at a given instant, but because we cannot specify the exact positions of the electrons, it is impossible to exactly calculate the repulsive interactions. Consequently, we must use approximate methods to deal with the effect of electron-electron repulsions on orbital energies.

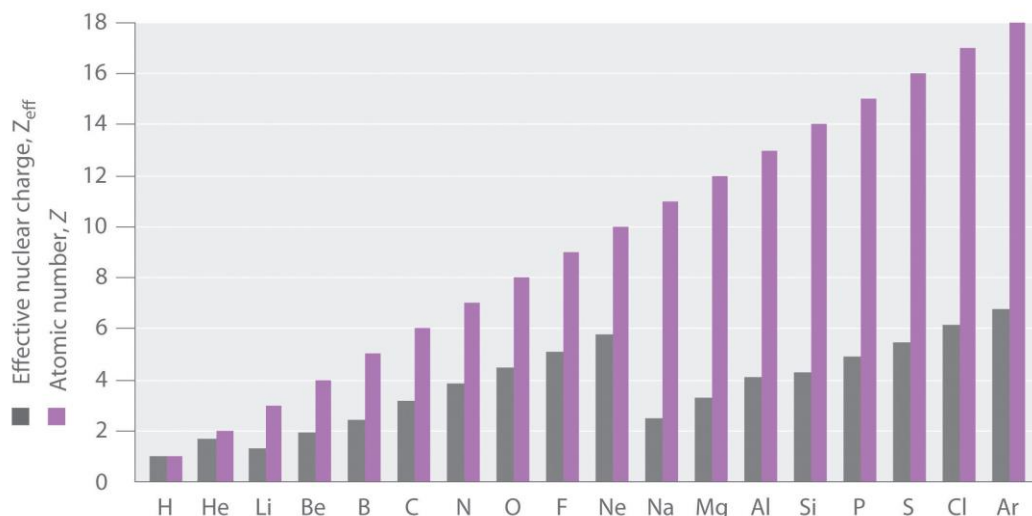
If an electron is far from the nucleus (i.e., if the distance r between the nucleus and the electron is large), then at any given moment, most of the other electrons will be *between* that electron and the nucleus.

Hence the electrons will cancel a portion of the positive charge of the nucleus and thereby decrease the attractive interaction between it and the electron farther away. As a result, the electron farther away experiences an effective nuclear charge (Z_{eff}) that is *less* than the actual nuclear charge Z . This effect is called electron shielding. As the distance between an electron and the nucleus approaches

infinity, Z_{eff} approaches a value of 1 because all the other $(Z - 1)$ electrons in the neutral atom are, on the average, between it and the nucleus. If, on the other hand, an electron is very close to the nucleus, then at any given moment most of the other electrons are farther from the nucleus and do not shield the nuclear charge. At $r \approx 0$, the positive charge experienced by an electron is approximately the full nuclear charge, or $Z_{\text{eff}} \approx Z$. At intermediate values of r , the effective nuclear charge is somewhere between 1 and Z : $1 \leq Z_{\text{eff}} \leq Z$. Thus the actual Z_{eff} experienced by an electron in a given orbital depends not only on the spatial distribution of the electron in that orbital but also on the distribution of all the other electrons present.

This leads to large differences in Z_{eff} for different elements, as shown in Figure 6.28 "Relationship between the Effective Nuclear Charge " for the elements of the first three rows of the periodic table. Notice that only for hydrogen does $Z_{\text{eff}} = Z$, and only for helium are Z_{eff} and Z comparable in magnitude.

Figure 6.28 Relationship between the Effective Nuclear Charge Z_{eff} and the Atomic Number Z for the Outer Electrons of the Elements of the First Three Rows of the Periodic Table



Except for hydrogen, Z_{eff} is always less than Z , and Z_{eff} increases from left to right as you go across a row.

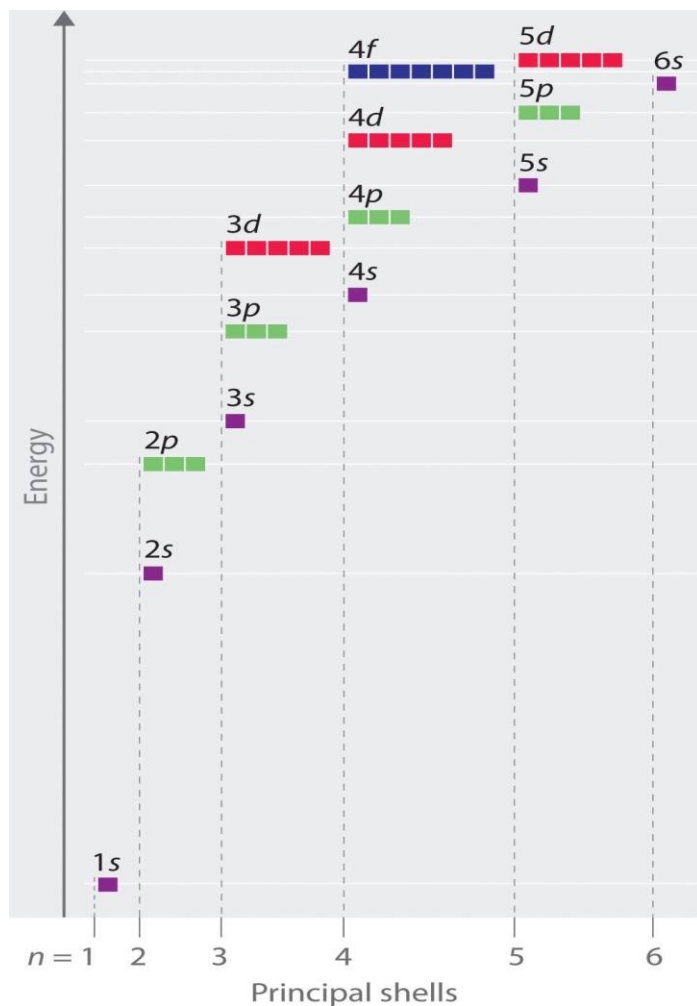
The energies of the different orbitals for a typical multielectron atom are shown in Figure 6.29 "Orbital Energy Level Diagram for a Typical Multielectron Atom". Within a given principal shell of a multielectron atom, the orbital energies increase with increasing l . An ns orbital always lies below the corresponding np orbital, which in turn lies below the nd orbital. These energy differences are caused by the effects of shielding and *penetration*, the extent to which a given orbital lies inside other filled orbitals. As shown in Figure 6.30 "Orbital Penetration", for example, an electron in the $2s$ orbital penetrates inside a filled $1s$ orbital more than an electron in a $2p$ orbital does. Hence in an atom with a filled $1s$ orbital, the Z_{eff} experienced by a $2s$ electron is greater than the Z_{eff} experienced by a $2p$ electron.

Consequently, the $2s$ electron is more tightly bound to the nucleus and has a lower energy, consistent with the order of energies shown in Figure 6.29 "Orbital Energy Level Diagram for a Typical Multielectron Atom".

Note the Pattern

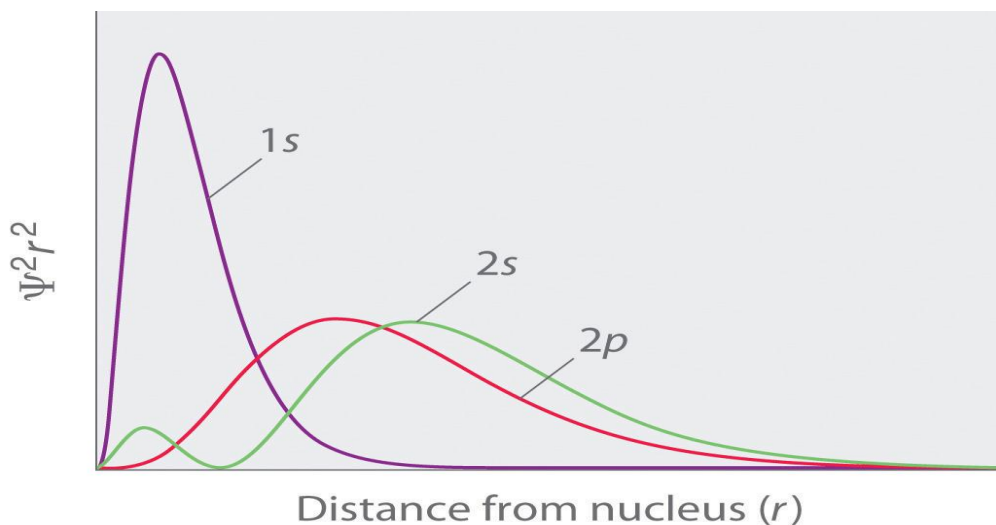
Due to electron shielding, Z_{eff} increases more rapidly going across a row of the periodic table than going down a column.

Figure 6.29 Orbital Energy Level Diagram for a Typical Multielectron Atom



Because of the effects of shielding and the different radial distributions of orbitals with the same value of n but different values of l , the different subshells are not degenerate in a multielectron atom. (Compare this with Figure 6.27 "Orbital Energy Level Diagram for the Hydrogen Atom".) For a given value of n , the ns orbital is always lower in energy than the np orbitals, which are lower in energy than the nd orbitals, and so forth. As a result, some subshells with higher principal quantum numbers are actually lower in energy than subshells with a lower value of n ; for example, the $4s$ orbital is lower in energy than the $3d$ orbitals for most atoms.

Figure 6.30 Orbital Penetration



A comparison of the radial probability distribution of the 2s and 2p orbitals for various states of the hydrogen atom shows that the 2s orbital penetrates inside the 1s orbital more than the 2p orbital does. Consequently, when an electron is in the small inner lobe of the 2s orbital, it experiences a relatively large value of Z_{eff} , which causes the energy of the 2s orbital to be lower than the energy of the 2p orbital.

Notice in Figure 6.29 "Orbital Energy Level Diagram for a Typical Multielectron Atom" that the difference in energies between subshells can be so large that the energies of orbitals from different principal shells can become approximately equal. For example, the energy of the 3d orbitals in most atoms is actually *between* the energies of the 4s and the 4p orbitals.

KEY EQUATION

energy of hydrogen-like orbitals

Equation 6.24: $E = -Z^2n^2Rhc$

Summary

Because of wave–particle duality, scientists must deal with the probability of an electron being at a particular point in space. To do so required the development of **quantum mechanics**, which uses **wave functions (Ψ)** to describe the mathematical relationship between the motion of electrons in atoms and molecules and their energies. Wave functions have five important properties: (1) the wave function uses three variables (Cartesian axes x , y , and z) to describe the position of an electron; (2) the magnitude of the wave function is proportional to the intensity of the wave; (3) the probability of finding an electron at a given point is proportional to the square of the wave function at that point, leading to a distribution of

probabilities in space that is often portrayed as an **electron density** plot; (4) describing electron distributions as standing waves leads naturally to the existence of sets of **quantum numbers** characteristic of each wave function; and (5) each spatial distribution of the electron described by a wave function with a given set of quantum numbers has a particular energy.

Quantum numbers provide important information about the energy and spatial distribution of an electron. The **principal quantum number** n can be any positive integer; as n increases for an atom, the average distance of the electron from the nucleus also increases. All wave functions with the same value of n constitute a **principal shell** in which the electrons have similar average distances from the nucleus. The **azimuthal quantum number** l can have integral values between 0 and $n - 1$; it describes the shape of the electron distribution. Wave functions that have the same values of both n and l constitute a **subshell**, corresponding to electron distributions that usually differ in orientation rather than in shape or average distance from the nucleus. The **magnetic quantum number** ml can have $2l + 1$ integral values, ranging from $-l$ to $+l$, and describes the orientation of the electron distribution. Each wave function with a given set of values of n , l , and ml describes a particular spatial distribution of an electron in an atom, an **atomic orbital**.

The four chemically important types of atomic orbital correspond to values of $l = 0, 1, 2$, and 3 . Orbitals with $l = 0$ are s orbitals and are spherically symmetrical, with the greatest probability of finding the electron occurring at the nucleus. All orbitals with values of $n > 1$ and $l = 0$ contain one or more nodes. Orbitals with $l = 1$ are p orbitals and contain a nodal plane that includes the nucleus, giving rise to a dumbbell shape. Orbitals with $l = 2$ are d orbitals and have more complex shapes with at least two nodal surfaces. Orbitals with $l = 3$ are f orbitals, which are still more complex.

Because its average distance from the nucleus determines the energy of an electron, each atomic orbital with a given set of quantum numbers has a particular energy associated with it, the **orbital energy**. In atoms or ions with only a single electron, all orbitals with the same value of n have the same energy (they are **degenerate**), and the energies of the principal shells increase smoothly as n increases. An atom or ion with the electron(s) in the lowest-energy orbital(s) is said to be in its ground state, whereas an atom or ion in which one or more electrons occupy higher-energy orbitals is said to be in an excited state. The calculation of orbital energies in atoms or ions with more than one electron (multielectron atoms or ions) is complicated by repulsive interactions between the electrons. The concept of **electron shielding**, in

which intervening electrons act to reduce the positive nuclear charge experienced by an electron, allows the use of hydrogen-like orbitals and an **effective nuclear charge** (Z_{eff}) to describe electron distributions in more complex atoms or ions. The degree to which orbitals with different values of l and the same value of n overlap or penetrate filled inner shells results in slightly different energies for different subshells in the same principal shell in most atoms.

KEY TAKEAWAY

- There is a relationship between the motions of electrons in atoms and molecules and their energies that is described by quantum mechanics.

CONCEPTUAL PROBLEMS

1. Why does an electron in an orbital with $n = 1$ in a hydrogen atom have a lower energy than a free electron ($n = \infty$)?
2. What four variables are required to fully describe the position of any object in space? In quantum mechanics, one of these variables is not explicitly considered. Which one and why?
3. Chemists generally refer to the square of the wave function rather than to the wave function itself. Why?
4. Orbital energies of species with only one electron are defined by only one quantum number. Which one? In such a species, is the energy of an orbital with $n = 2$ greater than, less than, or equal to the energy of an orbital with $n = 4$? Justify your answer.
5. In each pair of subshells for a hydrogen atom, which has the higher energy? Give the principal and the azimuthal quantum number for each pair.
 - a. $1s, 2p$
 - b. $2p, 2s$
 - c. $2s, 3s$
 - d. $3d, 4s$
6. What is the relationship between the energy of an orbital and its average radius? If an electron made a transition from an orbital with an average radius of 846.4 pm to an orbital with an average radius of 476.1 pm, would an emission spectrum or an absorption spectrum be produced? Why?
7. In making a transition from an orbital with a principal quantum number of 4 to an orbital with a principal quantum number of 7, does the electron of a hydrogen atom emit or absorb a photon of energy? What

would be the energy of the photon? To what region of the electromagnetic spectrum does this energy correspond?

8. What quantum number defines each of the following?
 - a. the overall shape of an orbital
 - b. the orientation of an electron with respect to a magnetic field
 - c. the orientation of an orbital in space
 - d. the average energy and distance of an electron from the nucleus
9. In an attempt to explain the properties of the elements, Niels Bohr initially proposed electronic structures for several elements with orbits holding a certain number of electrons, some of which are in the following table:

Element	Number of Electrons	Electrons in orbits with $n =$			
		4	3	2	1
H	1				1
He	2				2
Ne	10			8	2
Ar	18		8	8	2
Li	3			1	2
Na	11		1	8	2
K	19	1	8	8	2
Be	4			2	2

- a. Draw the electron configuration of each atom based only on the information given in the table. What are the differences between Bohr's initially proposed structures and those accepted today?
 - b. Using Bohr's model, what are the implications for the reactivity of each element?
 - c. Give the actual electron configuration of each element in the table.
10. What happens to the energy of a given orbital as the nuclear charge Z of a species increases? In a multielectron atom and for a given nuclear charge, the Z_{eff} experienced by an electron depends on its value of l . Why?
 11. The electron density of a particular atom is divided into two general regions. Name these two regions and describe what each represents.

12. As the principal quantum number increases, the energy difference between successive energy levels decreases. Why? What would happen to the electron configurations of the transition metals if this decrease did not occur?
13. Describe the relationship between electron shielding and Z_{eff} on the outermost electrons of an atom. Predict how chemical reactivity is affected by a decreased effective nuclear charge.
14. If a given atom or ion has a single electron in each of the following subshells, which electron is easier to remove?
 - a. $2s$, $3s$
 - b. $3p$, $4d$
 - c. $2p$, $1s$
 - d. $3d$, $4s$

NUMERICAL PROBLEMS

1. How many subshells are possible for $n = 3$? What are they?
2. How many subshells are possible for $n = 5$? What are they?
3. What value of l corresponds to a d subshell? How many orbitals are in this subshell?
4. What value of l corresponds to an f subshell? How many orbitals are in this subshell?
5. State the number of orbitals and electrons that can occupy each subshell.
 - a. $2s$
 - b. $3p$
 - c. $4d$
 - d. $6f$
6. State the number of orbitals and electrons that can occupy each subshell.
 - a. $1s$
 - b. $4p$
 - c. $5d$
 - d. $4f$
7. How many orbitals and subshells are found within the principal shell $n = 6$? How do these orbital energies compare with those for $n = 4$?
8. How many nodes would you expect a $4p$ orbital to have? A $5s$ orbital?

9. A p orbital is found to have one node in addition to the nodal plane that bisects the lobes. What would you predict to be the value of n ? If an s orbital has two nodes, what is the value of n ?

ANSWERS

1. Three subshells, with $l = 0$ (s), $l = 1$ (p), and $l = 2$ (d).
- 2.
3. A d subshell has $l = 2$ and contains 5 orbitals.
- 4.
5.
 - a. 2 electrons; 1 orbital
 - b. 6 electrons; 3 orbitals
 - c. 10 electrons; 5 orbitals
 - d. 14 electrons; 7 orbitals
- 6.
7. A principal shell with $n = 6$ contains six subshells, with $l = 0, 1, 2, 3, 4$, and 5, respectively. These subshells contain 1, 3, 5, 7, 9, and 11 orbitals, respectively, for a total of 36 orbitals. The energies of the orbitals with $n = 6$ are higher than those of the corresponding orbitals with the same value of l for $n = 4$.
8. [1] Ψ is the uppercase Greek psi.
9. [2] More accurately, the probability is given by the product of the wave function Ψ and its complex conjugate Ψ^* , in which all terms that contain i are replaced by $-i$.
10. [3] The different values of l and m_l for the individual orbitals within a given principal shell are not important for understanding the emission or absorption spectra of the hydrogen atom under most conditions, but they do explain the splittings of the main lines that are observed when hydrogen atoms are placed in a magnetic field.

6.6 Building Up the Periodic Table

LEARNING OBJECTIVE

1. To write the electron configuration of any element and relate its electron configuration to its position in the periodic table.

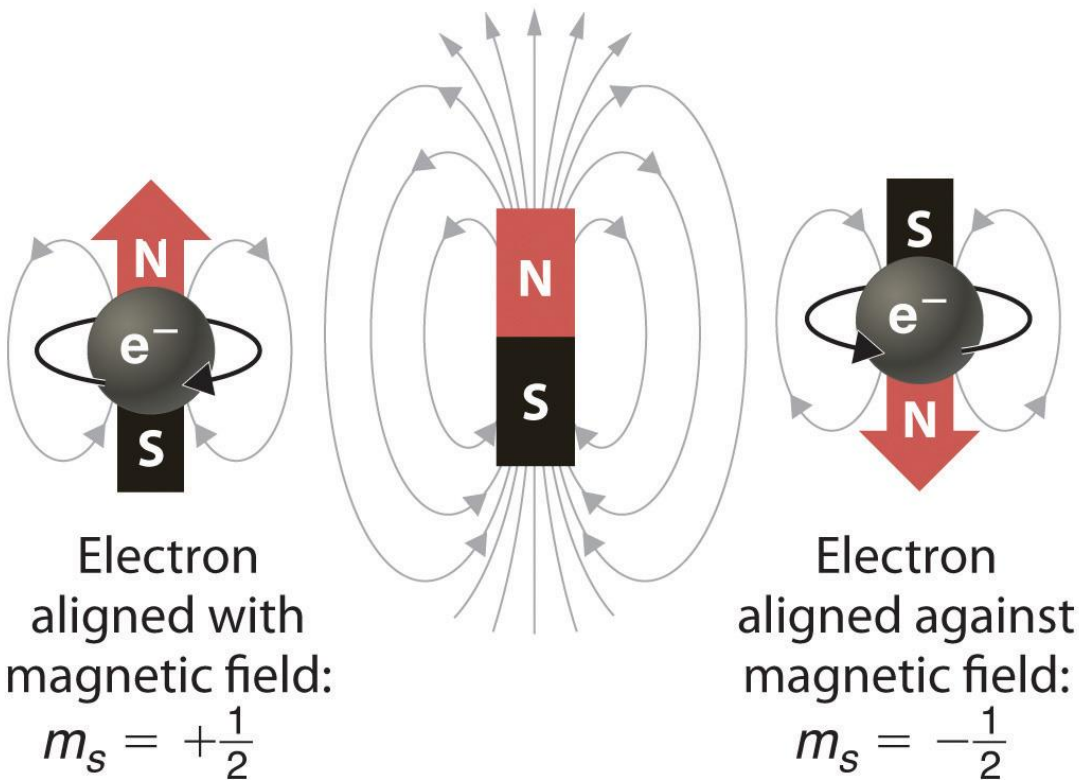
Now you can use the information you learned in Section 6.5 "Atomic Orbitals and Their Energies" to determine the electronic structure of every element in the periodic table. The process of describing each atom's electronic structure

consists, essentially, of beginning with hydrogen and adding one proton and one electron at a time to create the next heavier element in the table.^[1] Before demonstrating how to do this, however, we must introduce the concept of electron spin and the Pauli principle.

Electron Spin: The Fourth Quantum Number

When scientists analyzed the emission and absorption spectra of the elements more closely, they saw that for elements having more than one electron, nearly all the lines in the spectra were actually *pairs* of very closely spaced lines. Because each line represents an energy level available to electrons in the atom, there are twice as many energy levels available as would be predicted solely based on the quantum numbers n , l , and ml . Scientists also discovered that applying a magnetic field caused the lines in the pairs to split farther apart. In 1925, two graduate students in physics in the Netherlands, George Uhlenbeck (1900–1988) and Samuel Goudsmit (1902–1978), proposed that the splittings were caused by an electron spinning about its axis, much as Earth spins about its axis. When an electrically charged object spins, it produces a magnetic moment parallel to the axis of rotation, making it behave like a magnet. Although the electron cannot be viewed solely as a particle, spinning or otherwise, it is indisputable that it does have a magnetic moment. This magnetic moment is called electron spin.

Figure 6.31 Electron Spin



In a magnetic field, an electron has two possible orientations with different energies, one with spin up, aligned with the magnetic field, and one with spin down, aligned against it. All other orientations are forbidden.

In an external magnetic field, the electron has two possible orientations (Figure 6.31 "Electron Spin"). These are described by a fourth quantum number (m_s), which for any electron can have only two possible values, designated $+\frac{1}{2}$ (up) and $-\frac{1}{2}$ (down) to indicate that the two orientations are opposites; the subscript s is for spin. An electron behaves like a magnet that has one of two possible orientations, aligned either with the magnetic field or against it.

The Pauli Principle

The implications of electron spin for chemistry were recognized almost immediately by an Austrian physicist, Wolfgang Pauli (1900–1958; Nobel Prize in Physics, 1945), who determined that each orbital can contain no more than two electrons. He developed the Pauli exclusion principle: *No two electrons in an atom can have the same values of all four quantum numbers (n, l, m_l, m_s).*

By giving the values of n, l , and m_l , we also specify a particular orbital (e.g., $1s$ with $n = 1, l = 0, m_l = 0$). Because m_s has only two possible values ($+\frac{1}{2}$ or $-\frac{1}{2}$), two electrons, *and only two electrons*, can occupy

any given orbital, one with spin up and one with spin down. With this information, we can proceed to construct the entire periodic table, which, as you learned in Chapter 1 "Introduction to Chemistry", was originally based on the physical and chemical properties of the known elements.

EXAMPLE 7

List all the allowed combinations of the four quantum numbers (n, l, m_l, m_s) for electrons in a $2p$ orbital and predict the maximum number of electrons the $2p$ subshell can accommodate.

Given: orbital

Asked for: allowed quantum numbers and maximum number of electrons in orbital

Strategy:

A List the quantum numbers (n, l, m_l) that correspond to an $n = 2p$ orbital. List all allowed combinations of (n, l, m_l).

B Build on these combinations to list all the allowed combinations of (n, l, m_l, m_s).

C Add together the number of combinations to predict the maximum number of electrons the $2p$ subshell can accommodate.

Solution:

A For a $2p$ orbital, we know that $n = 2$, $l = n - 1 = 1$, and $m_l = -l, (-l + 1), \dots, (l - 1), l$. There are only three possible combinations of (n, l, m_l): (2, 1, 1), (2, 1, 0), and (2, 1, -1).

B Because m_s is independent of the other quantum numbers and can have values of only $+\frac{1}{2}$ and $-\frac{1}{2}$, there are six possible combinations of (n, l, m_l, m_s): (2, 1, 1, $+\frac{1}{2}$), (2, 1, 1, $-\frac{1}{2}$), (2, 1, 0, $+\frac{1}{2}$), (2, 1, 0, $-\frac{1}{2}$), (2, 1, -1, $+\frac{1}{2}$), and (2, 1, -1, $-\frac{1}{2}$).

C Hence the $2p$ subshell, which consists of three $2p$ orbitals ($2p_x$, $2p_y$, and $2p_z$), can contain a total of six electrons, two in each orbital.

Exercise

List all the allowed combinations of the four quantum numbers (n, l, m_l, m_s) for a $6s$ orbital, and predict the total number of electrons it can contain.

Answer: (6, 0, 0, $+\frac{1}{2}$), (6, 0, 0, $-\frac{1}{2}$); two electrons

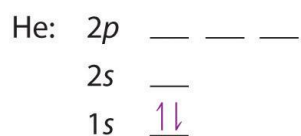
Electron Configurations of the Elements

The electron configuration of an element is the arrangement of its electrons in its atomic orbitals. By knowing the electron configuration of an element, we can predict and explain a great deal of its chemistry.

The Aufbau Principle

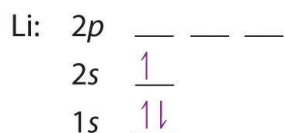
We construct the periodic table by following the aufbau principle (from German, meaning “building up”). First we determine the number of electrons in the atom; then we add electrons one at a time to the lowest-energy orbital available *without violating the Pauli principle*. We use the orbital energy diagram of Figure 6.29 "Orbital Energy Level Diagram for a Typical Multielectron Atom", recognizing that each orbital can hold two electrons, one with spin up $\uparrow$, corresponding to $m_s = +1/2$, which is arbitrarily written first, and one with spin down $\downarrow$, corresponding to $m_s = -1/2$. A filled orbital is indicated by $\uparrow\downarrow$, in which the electron spins are said to be *paired*. Here is a schematic orbital diagram for a hydrogen atom in its ground state:

From the orbital diagram, we can write the electron configuration in an abbreviated form in which the occupied orbitals are identified by their principal quantum number n and their value of l (s , p , d , or f), with the number of electrons in the subshell indicated by a superscript. For hydrogen, therefore, the single electron is placed in the $1s$ orbital, which is the orbital lowest in energy (Figure 6.29 "Orbital Energy Level Diagram for a Typical Multielectron Atom"), and the electron configuration is written as $1s^1$ and read as “one-s-one.” A neutral helium atom, with an atomic number of 2 ($Z = 2$), has two electrons. We place one electron in the orbital that is lowest in energy, the $1s$ orbital. From the Pauli exclusion principle, we know that an orbital can contain two electrons with opposite spin, so we place the second electron in the same orbital as the first but pointing down, so that the electrons are paired. The orbital diagram for the helium atom is therefore



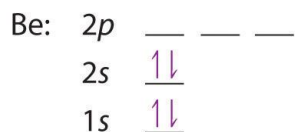
written as $1s^2$, where the superscript 2 implies the pairing of spins. Otherwise, our configuration would violate the Pauli principle.

The next element is lithium, with $Z = 3$ and three electrons in the neutral atom. We know that the $1s$ orbital can hold two of the electrons with their spins paired. Figure 6.29 "Orbital Energy Level Diagram for a Typical Multielectron Atom" tells us that the next lowest energy orbital is $2s$, so the orbital diagram for lithium is

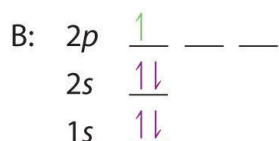


This electron configuration is written as $1s^2 2s^1$.

The next element is beryllium, with $Z = 4$ and four electrons. We fill both the $1s$ and $2s$ orbitals to achieve a $1s^2 2s^2$ electron configuration:



When we reach boron, with $Z = 5$ and five electrons, we must place the fifth electron in one of the $2p$ orbitals. Because all three $2p$ orbitals are degenerate, it doesn't matter which one we select. The electron configuration of boron is $1s^2 2s^2 2p^1$:

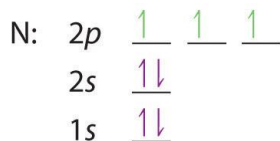


At carbon, with $Z = 6$ and six electrons, we are faced with a choice. Should the sixth electron be placed in the same $2p$ orbital that already has an electron, or should it go in one of the empty $2p$ orbitals? If it goes in an empty $2p$ orbital, will the sixth electron have its spin aligned with or be opposite to the spin of the fifth? In short, which of the following three orbital diagrams is correct for carbon, remembering that the $2p$ orbitals are degenerate?

Because of electron-electron repulsions, it is more favorable energetically for an electron to be in an unoccupied orbital than in one that is already occupied; hence we can eliminate choice a. Similarly, experiments have shown that choice b is slightly higher in energy (less stable) than choice c because electrons in degenerate orbitals prefer to line up with their spins parallel; thus, we can eliminate choice b. Choice c illustrates Hund's rule (named after the German physicist Friedrich H. Hund, 1896–1997), which today says that the lowest-energy electron configuration for an atom is the one that has the maximum number of electrons with parallel spins in degenerate orbitals. By Hund's rule, the electron configuration of carbon, which is $1s^2 2s^2 2p^2$, is understood to correspond to the orbital diagram shown in c.

Experimentally, it is found that the ground state of a neutral carbon atom does indeed contain two unpaired electrons.

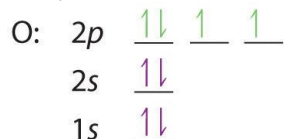
When we get to nitrogen ($Z = 7$, with seven electrons), Hund's rule tells us that the lowest-energy arrangements



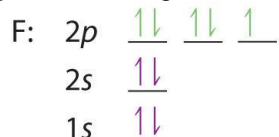
with three unpaired electrons. The electron configuration of nitrogen is thus $1s^2 2s^2 2p^3$.

At oxygen, with $Z = 8$ and eight electrons, we have no choice. One electron must be paired with another in one of the $2p$ orbitals, which gives us two unpaired electrons and a $1s^2 2s^2 2p^4$ electron configuration.

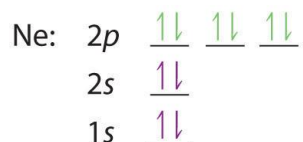
Because all the $2p$ orbitals are degenerate, it doesn't matter which one has the pair of electrons.



Similarly, fluorine has the electron configuration $1s^2 2s^2 2p^5$:



When we reach neon, with $Z = 10$, we have filled the $2p$ subshell, giving a $1s^2 2s^2 2p^6$ electron configuration:



Notice that for neon, as for helium, all the orbitals through the $2p$ level are completely filled. This fact is very important in dictating both the chemical reactivity and the bonding of helium and neon, as you will see.

Valence Electrons

As we continue through the periodic table in this way, writing the electron configurations of larger and larger atoms, it becomes tedious to keep copying the configurations of the filled inner subshells. In practice, chemists simplify the notation by using a bracketed noble gas symbol to represent the configuration of the noble gas from the preceding row because all the orbitals in a noble gas are filled. For example, [Ne] represents the $1s^2 2s^2 2p^6$ electron configuration of neon ($Z = 10$), so the electron configuration of sodium, with $Z = 11$, which is $1s^2 2s^2 2p^6 3s^1$, is written as [Ne] $3s^1$:

Neon	$Z = 10$	$1s^2 2s^2 2p^6$
Sodium	$Z = 11$	$1s^2 2s^2 2p^6 3s^1 = [\text{Ne}]3s^1$

Because electrons in filled inner orbitals are closer to the nucleus and more tightly bound to it, they are rarely involved in chemical reactions. This means that the chemistry of an atom depends mostly on the electrons in its outermost shell, which are called the valence electrons. The simplified notation allows us to see the valence-electron configuration more easily. Using this notation to compare the electron configurations of sodium and lithium, we have:

Sodium	$1s^2 2s^2 2p^6 3s^1 = [\text{Ne}] 3s^1$
Lithium	$1s^2 2s^1 = [\text{He}] 2s^1$

It is readily apparent that both sodium and lithium have one s electron in their valence shell. We would therefore predict that sodium and lithium have very similar chemistry, which is indeed the case.

As we continue to build the eight elements of period 3, the 3s and 3p orbitals are filled, one electron at a time. This row concludes with the noble gas argon, which has the electron configuration $[\text{Ne}] 3s^2 3p^6$, corresponding to a filled valence shell.

EXAMPLE 8

Draw an orbital diagram and use it to derive the electron configuration of phosphorus, $Z = 15$. What is its valence electron configuration?

Given: atomic number

Asked for: orbital diagram and valence electron configuration for phosphorus

Strategy:

A Locate the nearest noble gas preceding phosphorus in the periodic table. Then subtract its number of electrons from those in phosphorus to obtain the number of valence electrons in phosphorus.

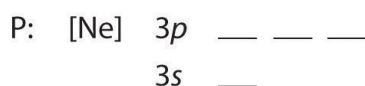
B Referring to Figure 6.29 "Orbital Energy Level Diagram for a Typical Multielectron Atom", draw an orbital diagram to represent those valence orbitals. Following Hund's rule, place the valence electrons in the available orbitals, beginning with the orbital that is lowest in energy. Write the electron configuration from your orbital diagram.

C Ignore the inner orbitals (those that correspond to the electron configuration of the nearest noble gas) and write the valence electron configuration for phosphorus.

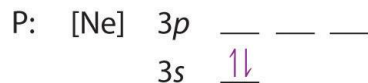
Solution:

A Because phosphorus is in the third row of the periodic table, we know that it has a [Ne] closed shell with 10 electrons. We begin by subtracting 10 electrons from the 15 in phosphorus.

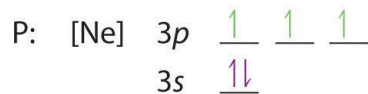
B The additional five electrons are placed in the next available orbitals, which Figure 6.29 "Orbital Energy Level Diagram for a Typical Multielectron Atom" tells us are the 3s and 3p orbitals:



Because the 3s orbital is lower in energy than the 3p orbitals, we fill it first:



Hund's rule tells us that the remaining three electrons will occupy the degenerate 3p orbitals separately but with their spins aligned:



The electron configuration is $[\text{Ne}]3s^23p^3$.

C We obtain the valence electron configuration by ignoring the inner orbitals, which for phosphorus means that we ignore the [Ne] closed shell. This gives a valence-electron configuration of $3s^23p^3$.

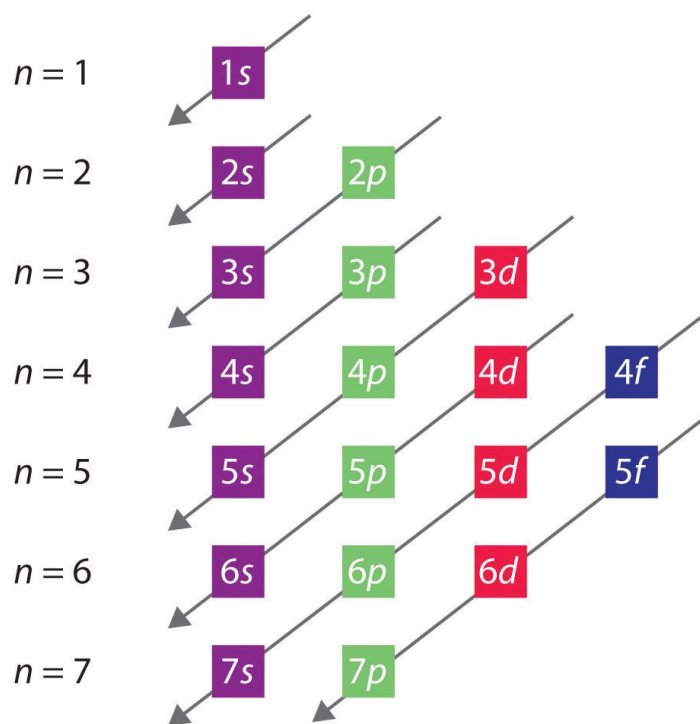
Exercise

Draw an orbital diagram and use it to derive the electron configuration of chlorine, $Z = 17$. What is its valence electron configuration?

Answer: $[\text{Ne}]3s^23p^5; 3s^23p^5$

The general order in which orbitals are filled is depicted in Figure 6.32 "Predicting the Order in Which Orbitals Are Filled in Multielectron Atoms". Subshells corresponding to each value of n are written from left to right on successive horizontal lines, where each row represents a row in the periodic table. The order in which the orbitals are filled is indicated by the diagonal lines running from the upper right to the lower left. Accordingly, the 4s orbital is filled prior to the 3d orbital because of shielding and penetration effects. Consequently, the electron configuration of potassium, which begins the fourth period, is $[\text{Ar}]4s^1$, and the configuration of calcium is $[\text{Ar}]4s^2$. Five 3d orbitals are filled by the next 10 elements, the transition metals, followed by three 4p orbitals. Notice that the last member of this row is the noble gas krypton ($Z = 36$), $[\text{Ar}]4s^23d^{10}4p^6 = [\text{Kr}]$, which has filled 4s, 3d, and 4p orbitals. The fifth row of the periodic table is essentially the same as the fourth, except that the 5s, 4d, and 5p orbitals are filled sequentially.

Figure 6.32 *Predicting the Order in Which Orbitals Are Filled in Multielectron Atoms*



If you write the subshells for each value of the principal quantum number on successive lines, the observed order in which they are filled is indicated by a series of diagonal lines running from the upper right to the lower left.

The sixth row of the periodic table will be different from the preceding two because the $4f$ orbitals, which can hold 14 electrons, are filled between the $6s$ and the $5d$ orbitals. The elements that contain $4f$ orbitals in their valence shell are the lanthanides. When the $6p$ orbitals are finally filled, we have reached the next (and last known) noble gas, radon ($Z = 86$), $[\text{Xe}]6s^2 4f^{14} 5d^{10} 6p^6 = [\text{Rn}]$. In the last row, the $5f$ orbitals are filled between the $7s$ and the $6d$ orbitals, which gives the 14 actinide elements. Because the large number of protons makes their nuclei unstable, all the actinides are radioactive.

EXAMPLE 9

Write the electron configuration of mercury ($Z = 80$), showing all the inner orbitals.

Given: atomic number

Asked for: complete electron configuration

Strategy:

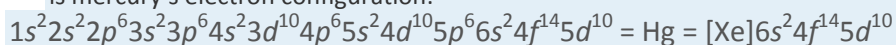
Using the orbital diagram in Figure 6.32 "Predicting the Order in Which Orbitals Are Filled in Multielectron Atoms" and the periodic table as a guide, fill the orbitals until all 80 electrons have been placed.

Solution:

By placing the electrons in orbitals following the order shown in Figure 6.32 "Predicting the Order in Which Orbitals Are Filled in Multielectron Atoms" and using the periodic table as a guide, we obtain

$1s^2$	row 1	2 electrons
$2s^2 2p^6$	row 2	8 electrons
$3s^2 3p^6$	row 3	8 electrons
$4s^2 3d^{10} 4p^6$	row 4	18 electrons
$5s^2 4d^{10} 5p^6$	row 5	18 electrons
	row 1–5	54 electrons

After filling the first five rows, we still have $80 - 54 = 26$ more electrons to accommodate. According to Figure 6.33 "The Periodic Table, Showing How the Elements Are Grouped According to the Kind of Subshell", we need to fill the $6s$ (2 electrons), $4f$ (14 electrons), and $5d$ (10 electrons) orbitals. The result is mercury's electron configuration:



with a filled $5d$ subshell, a $6s^2 4f^{14} 5d^{10}$ valence shell configuration, and a total of 80 electrons. (You should always check to be sure that the total number of electrons equals the atomic number.)

Exercise

Although element 114 is not stable enough to occur in nature, two isotopes of element 114 were created for the first time in a nuclear reactor in 1999 by a team of Russian and American scientists. Write the complete electron configuration for element 114.

Answer: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2 5f^{14} 6d^{10} 7p^2$

The electron configurations of the elements are presented in Figure 6.34 "Electron Configurations of the Elements", which lists the orbitals in the order in which they are filled. In several cases, the ground state electron configurations are different from those predicted by Figure 6.32 "Predicting the Order in Which Orbitals Are Filled in Multielectron Atoms". Some of these anomalies occur as the $3d$ orbitals are filled. For example, the observed ground state electron configuration of chromium is $[\text{Ar}] 4s^1 3d^5$ rather than the predicted $[\text{Ar}] 4s^2 3d^4$. Similarly, the observed electron configuration of copper is $[\text{Ar}] 4s^1 3d^{10}$ instead of $[\text{Ar}] 4s^2 3d^9$. The actual electron configuration may be rationalized in terms of an added stability associated with a half-filled (ns^1 , np^3 , nd^5 , nf^4) or filled (ns^2 , np^6 , nd^{10} , nf^{14}) subshell. Given the small differences

between higher energy levels, this added stability is enough to shift an electron from one orbital to another. In heavier elements, other more complex effects can also be important, leading to some of the additional anomalies indicated in Figure 6.34 "Electron Configurations of the Elements". For example, cerium has an electron configuration of $[\text{Xe}]6s^24f^15d^1$, which is impossible to rationalize in simple terms. In most cases, however, these apparent anomalies do not have important chemical consequences.

Note the Pattern

Additional stability is associated with half-filled or filled subshells.

Blocks in the Periodic Table

As you have learned, the electron configurations of the elements explain the otherwise peculiar shape of the periodic table. Although the table was originally organized on the basis of physical and chemical similarities between the elements within groups, these similarities are ultimately attributable to orbital energy levels and the Pauli principle, which cause the individual subshells to be filled in a particular order. As a result, the periodic table can be divided into “blocks” corresponding to the type of subshell that is being filled, as illustrated in Figure 6.34 "Electron Configurations of the Elements". For example, the two columns on the left, known as the *s block*, consist of elements in which the *ns* orbitals are being filled. The six columns on the right, elements in which the *np* orbitals are being filled, constitute the *p block*. In between are the 10 columns of the *d block*, elements in which the $(n - 1)d$ orbitals are filled. At the bottom lie the 14 columns of the *f block*, elements in which the $(n - 2)f$ orbitals are filled. Because two electrons can be accommodated per orbital, the number of columns in each block is the same as the maximum electron capacity of the subshell: 2 for *ns*, 6 for *np*, 10 for $(n - 1)d$, and 14 for $(n - 2)f$. Within each column, each element has the same valence electron configuration—for example, *ns*¹ (group 1) or *ns*²*np*¹ (group 13). As you will see, this is reflected in important similarities in the chemical reactivity and the bonding for the elements in each column.

Note the Pattern

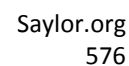
Because each orbital can have a maximum of 2 electrons, there are 2 columns in the *s block*, 6 columns in the *p block*, 10 columns in the *d block*, and 14 columns in the *f block*.

Figure 6.33 The Periodic Table, Showing How the Elements Are Grouped According to the Kind of Subshell (s, p, d, f) Being Filled with Electrons in the Valence Shell of Each Element

[illegible]

Hydrogen and helium are placed somewhat arbitrarily. Although hydrogen is not an alkali metal, its $1s^1$ electron configuration suggests a similarity to lithium ($[\text{He}]2s^1$) and the other elements in the first column. Although helium, with a filled ns subshell, should be similar chemically to other elements with an ns^2 electron configuration, the closed principal shell dominates its chemistry, justifying its placement above neon on the right. In Chapter 7 "The Periodic Table and Periodic Trends", we will examine how electron configurations affect the properties and reactivity of the elements.

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Atomic number	Symbol	Electron configuration	Atomic number	Symbol	Electron configuration	Atomic number	Symbol	Electron configuration
1	H	1s ¹	37	Rb	[Kr]5s ¹	73	Ta	[Xe]6s ² 4f ¹⁴ 5d ³
2	He	1s ²	38	Sr	[Kr]5s ²	74	W	[Xe]6s ² 4f ¹⁴ 5d ⁴
3	Li	[He]2s ¹	39	Y	[Kr]5s ² 4d ¹	75	Re	[Xe]6s ² 4f ¹⁴ 5d ⁵
4	Be	[He]2s ²	40	Zr	[Kr]5s ² 4d ²	76	Os	[Xe]6s ² 4f ¹⁴ 5d ⁶
5	B	[He]2s ² 2p ¹	41	Nb	[Kr]5s ¹ 4d ⁴	77	Ir	[Xe]6s ² 4f ¹⁴ 5d ⁷
6	C	[He]2s ² 2p ²	42	Mo	[Kr]5s ¹ 4d ⁵	78	Pt	[Xe]6s ¹ 4f ¹⁴ 5d ⁹
7	N	[He]2s ² 2p ³	43	Tc	[Kr]5s ² 4d ⁵	79	Au	[Xe]6s ¹ 4f ¹⁴ 5d ¹⁰
8	O	[He]2s ² 2p ⁴	44	Ru	[Kr]5s ¹ 4d ⁷	80	Hg	[Xe]6s ² 4f ¹⁴ 5d ¹⁰
9	F	[He]2s ² 2p ⁵	45	Rh	[Kr]5s ¹ 4d ⁸	81	Tl	[Xe]6s ² 4f ¹⁴ 5d ¹⁰ 6p ¹
10	Ne	[He]2s ² 2p ⁶	46	Pd	[Kr]4d ¹⁰	82	Pb	[Xe]6s ² 4f ¹⁴ 5d ¹⁰ 6p ²
11	Na	[Ne]3s ¹	47	Ag	[Kr]5s ¹ 4d ¹⁰	83	Bi	[Xe]6s ² 4f ¹⁴ 5d ¹⁰ 6p ³
12	Mg	[Ne]3s ²	48	Cd	[Kr]5s ² 4d ¹⁰	84	Po	[Xe]6s ² 4f ¹⁴ 5d ¹⁰ 6p ⁴
13	Al	[Ne]3s ² 3p ¹	49	In	[Kr]5s ¹ 4d ¹⁰ 5p ¹	85	At	[Xe]6s ² 4f ¹⁴ 5d ¹⁰ 6p ⁵
14	Si	[Ne]3s ² 3p ²	50	Sn	[Kr]5s ¹ 4d ¹⁰ 5p ²	86	Rn	[Xe]6s ² 4f ¹⁴ 5d ¹⁰ 6p ⁶
15	P	[Ne]3s ² 3p ³	51	Sb	[Kr]5s ¹ 4d ¹⁰ 5p ³	87	Fr	[Rn]7s ¹
16	S	[Ne]3s ² 3p ⁴	52	Te	[Kr]5s ¹ 4d ¹⁰ 5p ⁴	88	Ra	[Rn]7s ²
17	Cl	[Ne]3s ² 3p ⁵	53	I	[Kr]5s ¹ 4d ¹⁰ 5p ⁵	89	Ac	[Rn]7s ² 6d ¹
18	Ar	[Ne]3s ² 3p ⁶	54	Xe	[Kr]5s ¹ 4d ¹⁰ 5p ⁶	90	Th	[Rn]7s ² 6d ²
19	K	[Ar]4s ¹	55	Cs	[Xe]6s ¹	91	Pa	[Rn]7s ² 5f ⁶ 6d ¹
20	Ca	[Ar]4s ²	56	Ba	[Xe]6s ²	92	U	[Rn]7s ² 5f ⁶ 6d ¹
21	Sc	[Ar]4s ² 3d ¹	57	La	[Xe]6s ² 5d ¹	93	Np	[Rn]7s ² 5f ⁶ 6d ¹
22	Ti	[Ar]4s ² 3d ²	58	Ce	[Xe]6s ² 4f ¹ 5d ¹	94	Pu	[Rn]7s ² 5f ⁶
23	V	[Ar]4s ² 3d ³	59	Pr	[Xe]6s ² 4f ³	95	Am	[Rn]7s ² 5f ⁷
24	Cr	[Ar]4s ² 3d ⁵	60	Nd	[Xe]6s ² 4f ⁴	96	Cm	[Rn]7s ² 5f ⁷ 6d ¹
25	Mn	[Ar]4s ² 3d ⁵	61	Pm	[Xe]6s ² 4f ⁵	97	Bk	[Rn]7s ² 5f ⁷
26	Fe	[Ar]4s ² 3d ⁶	62	Sm	[Xe]6s ² 4f ⁶	98	Cf	[Rn]7s ² 5f ¹⁰
27	Co	[Ar]4s ² 3d ⁷	63	Eu	[Xe]6s ² 4f ⁷	99	Es	[Rn]7s ² 5f ¹¹
28	Ni	[Ar]4s ² 3d ⁸	64	Gd	[Xe]6s ² 4f ⁷ 5d ¹	100	Fm	[Rn]7s ² 5f ¹²
29	Cu	[Ar]4s ² 3d ¹⁰	65	Tb	[Xe]6s ² 4f ⁹	101	Md	[Rn]7s ² 5f ¹³
30	Zn	[Ar]4s ² 3d ¹⁰	66	Dy	[Xe]6s ² 4f ¹⁰	102	No	[Rn]7s ² 5f ¹⁴
31	Ga	[Ar]4s ² 3d ¹⁰ 4p ¹	67	Ho	[Xe]6s ² 4f ¹¹	103	Lr	[Rn]7s ² 5f ¹⁴ 6d ¹
32	Ge	[Ar]4s ² 3d ¹⁰ 4p ²	68	Er	[Xe]6s ² 4f ¹²	104	Rf	[Rn]7s ² 5f ¹⁴ 6d ²
33	As	[Ar]4s ² 3d ¹⁰ 4p ³	69	Tm	[Xe]6s ² 4f ¹³	105	Db	[Rn]7s ² 5f ¹⁴ 6d ³
34	Se	[Ar]4s ² 3d ¹⁰ 4p ⁴	70	Yb	[Xe]6s ² 4f ¹⁴	106	Sg	[Rn]7s ² 5f ¹⁴ 6d ⁴
35	Br	[Ar]4s ² 3d ¹⁰ 4p ⁵	71	Lu	[Xe]6s ² 4f ¹⁴ 5d ¹	107	Bh	[Rn]7s ² 5f ¹⁴ 6d ⁵
36	Kr	[Ar]4s ² 3d ¹⁰ 4p ⁶	72	Hf	[Xe]6s ² 4f ¹⁴ 5d ²	108	Hs	[Rn]7s ² 5f ¹⁴ 6d ⁶
						109	Mt	[Rn]7s ² 5f ¹⁴ 6d ⁷
						110	Ds	[Rn]7s ¹ 5f ¹⁴ 6d ⁹
						111	Rg	[Rn]7s ¹ 5f ¹⁴ 6d ¹⁰

The electron configurations of elements indicated in red are exceptions due to the added stability associated with half-filled and filled subshells. The electron configurations of the elements indicated in blue are also anomalous, but the reasons for the observed configurations are more complex. For elements after No, the electron configurations are tentative.

EXAMPLE 10

Use the periodic table to predict the valence electron configuration of all the elements of group 2 (beryllium, magnesium, calcium, strontium, barium, and radium).

Given: series of elements

Asked for: valence electron configurations

Strategy:

A Identify the block in the periodic table to which the group 2 elements belong. Locate the nearest noble gas preceding each element and identify the principal quantum number of the valence shell of each element.

B Write the valence electron configuration of each element by first indicating the filled inner shells using the symbol for the nearest preceding noble gas and then listing the principal quantum number of its valence shell, its valence orbitals, and the number of valence electrons in each orbital as superscripts.

Solution:

A The group 2 elements are in the s block of the periodic table, and as group 2 elements, they all have two valence electrons. Beginning with beryllium, we see that its nearest preceding noble gas is helium and that the principal quantum number of its valence shell is $n = 2$.

B Thus beryllium has an $[\text{He}]s^2$ electron configuration. The next element down, magnesium, is expected to have exactly the same arrangement of electrons in the $n = 3$ principal shell: $[\text{Ne}]s^2$. By extrapolation, we expect all the group 2 elements to have an ns^2 electron configuration.

Exercise

Use the periodic table to predict the characteristic valence electron configuration of the halogens in group 17.

Answer: All have an ns^2np^5 electron configuration, one electron short of a noble gas electron configuration. (Note that the heavier halogens also have filled $(n - 1)d^{10}$ subshells, as well as an $(n - 2)f^4$ subshell for Rn; these do not, however, affect their chemistry in any significant way.)

Summary

In addition to the three quantum numbers (n, l, m_l) dictated by quantum mechanics, a fourth quantum number is required to explain certain properties of atoms. This is the **electron spin** quantum number (m_s), which can have values of $+1/2$ or $-1/2$ for any electron, corresponding to the two possible orientations of an electron in a magnetic field. The concept of electron spin has important consequences for chemistry because the **Pauli exclusion principle** implies that no orbital can contain more than two electrons (with opposite spin). Based on the Pauli principle and a knowledge of orbital energies obtained using hydrogen-like orbitals, it is possible to construct the periodic table by filling up the available orbitals

beginning with the lowest-energy orbitals (the **aufbau principle**), which gives rise to a particular arrangement of electrons for each element (its **electron configuration**). **Hund's rule** says that the lowest-energy arrangement of electrons is the one that places them in degenerate orbitals with their spins parallel. For chemical purposes, the most important electrons are those in the outermost principal shell, the **valence electrons**. The arrangement of atoms in the periodic table results in blocks corresponding to filling of the *ns*, *np*, *nd*, and *nf* orbitals to produce the distinctive chemical properties of the elements in the **s block**, **p block**, **d block**, and **f block**, respectively.

KEY TAKEAWAY

- The arrangement of atoms in the periodic table arises from the lowest energy arrangement of electrons in the valence shell.

CONCEPTUAL PROBLEMS

1. A set of four quantum numbers specifies each wave function. What information is given by each quantum number? What does the specified wave function describe?
2. List two pieces of evidence to support the statement that electrons have a spin.
3. The periodic table is divided into blocks. Identify each block and explain the principle behind the divisions. Which quantum number distinguishes the horizontal rows?
4. Identify the element with each ground state electron configuration.
 - a. $[\text{He}]2s^22p^3$
 - b. $[\text{Ar}]4s^23d^1$
 - c. $[\text{Kr}]5s^24d^{10}5p^3$
 - d. $[\text{Xe}]6s^24f^6$
5. Identify the element with each ground state electron configuration.
 - a. $[\text{He}]2s^22p^1$
 - b. $[\text{Ar}]4s^23d^8$
 - c. $[\text{Kr}]5s^24d^{10}5p^4$
 - d. $[\text{Xe}]6s^2$
6. Propose an explanation as to why the noble gases are inert.

NUMERICAL PROBLEMS

1. How many magnetic quantum numbers are possible for a $4p$ subshell? A $3d$ subshell? How many orbitals are in these subshells?
2. How many magnetic quantum numbers are possible for a $6s$ subshell? A $4f$ subshell? How many orbitals does each subshell contain?
3. If $l = 2$ and $ml = 2$, give all the allowed combinations of the four quantum numbers (n, l, ml, ms) for electrons in the corresponding $3d$ subshell.
4. Give all the allowed combinations of the four quantum numbers (n, l, ml, ms) for electrons in a $4d$ subshell. How many electrons can the $4d$ orbital accommodate? How would this differ from a situation in which there were only three quantum numbers (n, l, m)?
5. Given the following sets of quantum numbers (n, l, ml, ms), identify each principal shell and subshell.
 - a. $1, 0, 0, \frac{1}{2}$
 - b. $2, 1, 0, \frac{1}{2}$
 - c. $3, 2, 0, \frac{1}{2}$
 - d. $4, 3, 3, \frac{1}{2}$
6. Is each set of quantum numbers allowed? Explain your answers.
 - a. $n = 2; l = 1; ml = 2; ms = +\frac{1}{2}$
 - b. $n = 3, l = 0; ml = -1; ms = -\frac{1}{2}$
 - c. $n = 2; l = 2; ml = 1; ms = +\frac{1}{2}$
 - d. $n = 3; l = 2; ml = 2; ms = +\frac{1}{2}$
7. List the set of quantum numbers for each electron in the valence shell of each element.
 - a. beryllium
 - b. xenon
 - c. lithium
 - d. fluorine
8. List the set of quantum numbers for each electron in the valence shell of each element.
 - a. carbon
 - b. magnesium
 - c. bromine
 - d. sulfur

9. Sketch the shape of the periodic table if there were three possible values of m_s for each electron ($+\frac{1}{2}$, $-\frac{1}{2}$, and 0); assume that the Pauli principle is still valid.
10. Predict the shape of the periodic table if eight electrons could occupy the p subshell.
11. If the electron could only have spin $+\frac{1}{2}$, what would the periodic table look like?
12. If three electrons could occupy each s orbital, what would be the electron configuration of each species?
- sodium
 - titanium
 - fluorine
 - calcium
13. If Hund's rule were not followed and maximum pairing occurred, how many unpaired electrons would each species have? How do these numbers compare with the number found using Hund's rule?
- phosphorus
 - iodine
 - manganese
14. Write the electron configuration for each element in the ground state.
- aluminum
 - calcium
 - sulfur
 - tin
 - nickel
 - tungsten
 - neodymium
 - americium
15. Write the electron configuration for each element in the ground state.
- boron
 - rubidium
 - bromine
 - germanium
 - vanadium

- f. palladium
 - g. bismuth
 - h. europium
16. Give the complete electron configuration for each element.
- a. magnesium
 - b. potassium
 - c. titanium
 - d. selenium
 - e. iodine
 - f. uranium
 - g. germanium
17. Give the complete electron configuration for each element.
- a. tin
 - b. copper
 - c. fluorine
 - d. hydrogen
 - e. thorium
 - f. yttrium
 - g. bismuth
18. Write the valence electron configuration for each element:
- a. samarium
 - b. praseodymium
 - c. boron
 - d. cobalt
19. Using the Pauli exclusion principle and Hund's rule, draw valence orbital diagrams for each element.
- a. barium
 - b. neodymium
 - c. iodine
20. Using the Pauli exclusion principle and Hund's rule, draw valence orbital diagrams for each element.

- a. chlorine
 - b. silicon
 - c. scandium
21. How many unpaired electrons does each species contain?
- a. lead
 - b. cesium
 - c. copper
 - d. silicon
 - e. selenium
22. How many unpaired electrons does each species contain?
- a. helium
 - b. oxygen
 - c. bismuth
 - d. silver
 - e. boron
23. For each element, give the complete electron configuration, draw the valence electron configuration, and give the number of unpaired electrons present.
- a. lithium
 - b. magnesium
 - c. silicon
 - d. cesium
 - e. lead
24. Use an orbital diagram to illustrate the aufbau principle, the Pauli exclusion principle, and Hund's rule for each element.
- a. carbon
 - b. sulfur

ANSWERS

1. For a $4p$ subshell, $n = 4$ and $l = 1$. The allowed values of the magnetic quantum number, ml , are therefore $+1$, 0 , -1 , corresponding to three $4p$ orbitals. For a $3d$ subshell, $n = 3$ and $l = 2$. The allowed values of the magnetic quantum number, ml , are therefore $+2$, $+1$, 0 , -1 , -2 , corresponding to five $3d$ orbitals.
3. 1. $n = 3, l = 2, ml = 2, ms = +\frac{1}{2}; n = 3, l = 2, ml = 2, ms = -\frac{1}{2}$

[1] All stable nuclei other than hydrogen also contain one or more neutrons. Because neutrons have no electrical charge, however, they can be ignored in the following discussion.

6.7 End-of-Chapter Material

APPLICATION PROBLEMS

1. The lamps in street lights use emission of light from excited states of atoms to produce a characteristic glow. Light is generated by electron bombardment of a metal vapor. Of calcium and strontium, which metal vapor would you use to produce yellow light? Which metal would you use to produce red light? Calculate the energy associated with each transition and propose an explanation for the colors of the emitted light.
2. Lasers have useful medical applications because their light is directional (permitting tight focus of the laser beam for precise cutting), monochromatic, and intense. Carbon dioxide lasers, emitting at a wavelength of 1.06×10^4 nm, are typically used in surgery.
 - a. What are the frequency and energy (in kilojoules per mole) of a photon from a carbon dioxide laser?
 - b. Why is monochromatic light desirable in a surgical procedure?
 - c. Biological tissue consists primarily of water, which absorbs electromagnetic radiation in the infrared region of the spectrum. Suggest a plausible reason for using carbon dioxide lasers in surgery.
3. An excimer (meaning “excited dimer”) laser emits light in the ultraviolet region of the spectrum. An example of such a laser is krypton fluoride (KrF), which emits light at a wavelength of 248 nm. What is the energy in joules of a mole of photons emitted from this laser? How much more energetic is a single photon of this wavelength than a photon from a carbon dioxide laser used in surgery (10,600 nm)?
4. Wavelengths less than 10 nm are needed to “see” objects on an atomic or molecular scale. Such imaging can be accomplished with an electron microscope, which uses electric and magnetic fields to focus and accelerate a beam of electrons to a high velocity. Electron microscopy is now a powerful tool in chemical research. What electron velocity is needed to produce electrons with a wavelength of 4×10^{-3} nm, which is

sufficient to produce an image of an atom? If electromagnetic radiation were used, what region of the electromagnetic spectrum would this correspond to?

5. Microwave ovens operate by emitting microwave radiation, which is primarily absorbed by water molecules in food. The absorbed radiation is converted to heat through rapid oscillations of polar water molecules, which cooks the food and warms beverages. If 7.2×10^{28} photons are needed to heat 150.0 g of water from 20.0°C to 100.0°C in a microwave oven, what is the frequency of the microwaves? Metal objects should not be placed in a microwave oven because they cause sparks. Why does this cause sparks?
6. The magnitude of the energy gap between an excited state and a ground state determines the color of visible light that is absorbed. The observed color of an object is not the color of the light it absorbs but rather the complement of that color. The accompanying rosette, first developed by Isaac Newton, shows the colors increasing in energy from red to violet. Any two colors that are opposite each other are said to be *complementary* (e.g., red and green are complementary).

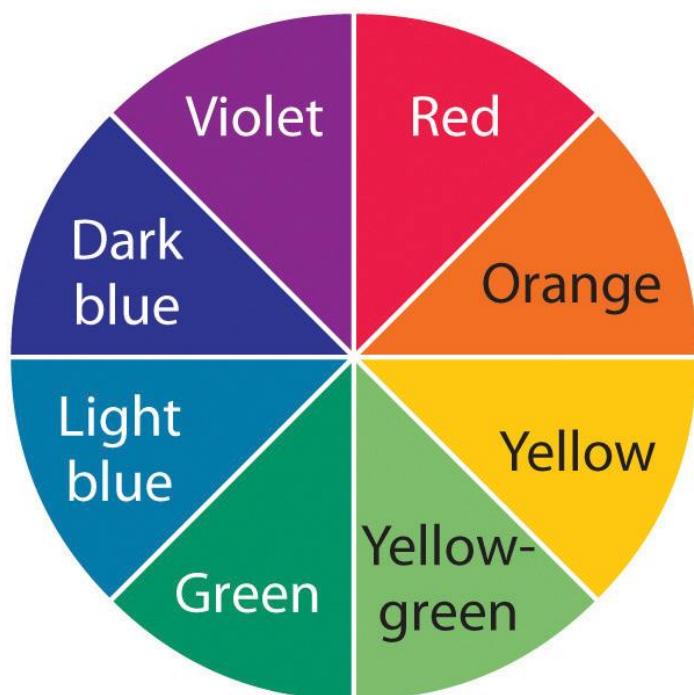
6.7 End-of-Chapter Material

APPLICATION PROBLEMS

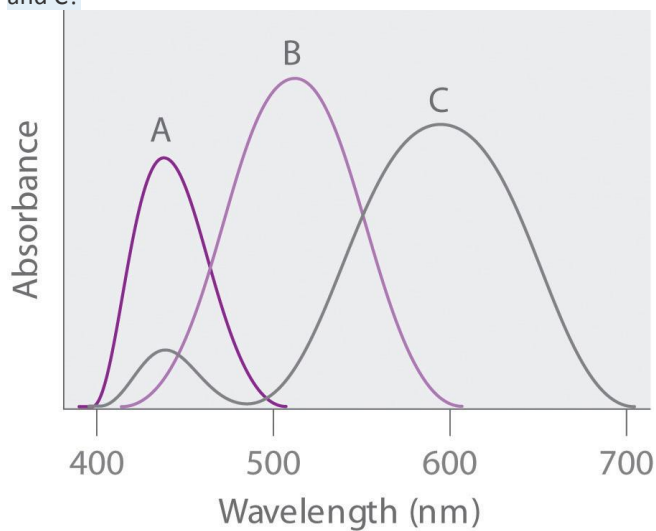
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a. Given the absorption spectra and following table, what are the colors of the objects that produce spectra A, B, and C?



1.

a.

Wavelength (nm)	Color of Light
390–453	violet
453–492	blue
492–577	green
577–597	yellow
597–622	orange

Wavelength (nm)	Color of Light
622–780	red

- b. The decomposition of a pigment depends on many factors, but the rate of decomposition often depends on the energy of the radiation absorbed by the pigment. Which of these compounds—A, B, or C—will likely fade fastest?
 - c. A painter has a sample of yellow paint. What would you expect the absorption spectrum of the paint to look like? What would the absorption spectrum look like if the paint had been contaminated with traces of a violet pigment?
- Photodegradation of atmospheric ozone occurs via the reaction $\text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O}$; the maximum absorption occurs at approximately 255 nm. In what region of the electromagnetic spectrum does this occur? Based on this information, what would be the effect of depleting the ozone layer of Earth's atmosphere?
 - A microscope's resolution (its ability to distinguish between two points separated by a given distance) depends on the wavelength of light used to illuminate an object. The resolution R is given by the equation $R = \lambda/2N$, where N is a constant related to the aperture. If a microscope has an aperture constant of 0.25, what is the smallest distance between two objects that can be resolved using the following light sources?
 - a. red light ($E = 171 \text{ kJ/mol}$)
 - b. ultraviolet light ($E = 1.20 \times 10^3 \text{ kJ/mol}$)
 - c. x-rays ($E = 1.20 \times 10^5 \text{ kJ/mol}$)
 - Silver bromide is the photosensitive material in 35 mm photographic film. When monochromatic light falls on film, the photons are recorded if they contain sufficient energy to react with silver bromide in the film. Given that the minimum energy needed to do this is approximately 57.9 kJ/mol, explain why red light is used to light a darkroom. What happens when the door to the darkroom is opened, allowing yellow light to enter?
 - A lighting system has recently been developed that uses a quartz bulb the size of a golf ball filled with an inert gas and a small amount of sulfur. When irradiated by microwaves, the bulb puts out as much light as hundreds of high-intensity mercury vapor lamps. Because 1000 kJ/mol is needed to ionize sulfur, can this process occur simply by irradiating sulfur atoms with microwaves? Explain your answer.
 - The following table lists the ionization energies of some common atmospheric species:

Species	Ionization Energy (kJ/mol)
NO	897

Species	Ionization Energy (kJ/mol)
CO ₂	1330
O ₂	1170

- a. Can radiant energy corresponding to the lowest energy line in the Lyman series be used to ionize these molecules?
- b. According to the table, can radiation of this energy be transmitted through an oxygen atmosphere?
7. An artist used a pigment that has a significant absorption peak at 450 nm, with a trace absorption at 530 nm. Based on the color chart and table in Problem 6, what was the color of the paint? Draw the absorption pattern. What would the absorption spectrum have looked like if the artist had wanted green? Using absorption spectra, explain why an equal combination of red and yellow paints produces orange.
8. You live in a universe where an electron has four different spins ($ms = +\frac{1}{2}, +\frac{1}{4}, -\frac{1}{2}, -\frac{1}{4}$) and the periodic table has only 36 elements. Which elements would be noble gases? What would the periodic table look like? (Assume that the Pauli exclusion principle is still valid.)
9. If you were living on a planet where there were three quantum numbers (n, l, m) instead of four, what would be the allowed combinations for an electron in a $3p$ orbital? How many electrons would this orbital contain assuming the Pauli exclusion principle were still in effect? How does this compare with the actual number of allowed combinations found on Earth?
10. X-rays are frequently used to project images of the human body. Recently, however, a superior technique called magnetic resonance imaging (MRI) has been developed that uses *proton* spin to image tissues in spectacular detail. In MRI, spinning hydrogen nuclei in an organic material are irradiated with photons that contain enough energy to flip the protons to the opposite orientation. If 33.121 kJ/mol of energy is needed to flip a proton, what is the resonance frequency required to produce an MRI spectrum? Suggest why this frequency of electromagnetic radiation would be preferred over x-rays.
11. Vanadium has been found to be a key component in a biological catalyst that reduces nitrogen to ammonia. What is the valence electron configuration of vanadium? What are the quantum numbers for each valence electron? How many unpaired electrons does vanadium have?
12. Tellurium, a metal used in semiconductor devices, is also used as a coloring agent in porcelains and enamels. Illustrate the aufbau principle, the Pauli exclusion principle, and Hund's rule using tellurium metal.

13. A new element is believed to have been discovered by a team of Russian and American scientists, although its existence is yet to be independently confirmed. Six atoms of element 117, temporarily named ununseptium, were created by smashing together isotopes of calcium with the element berkelium. Give the following:
- the complete electron configuration of this element
 - the valence electron configuration
 - the number of unpaired electrons in the valence shell

Chapter 7

The Periodic Table and Periodic Trends

In , we presented the contemporary quantum mechanical model of the atom. In using this model to describe the electronic structures of the elements in order of increasing atomic number, we saw that periodic similarities in electron configuration correlate with periodic similarities in properties, which is the basis for the structure of the periodic table. For example, the noble gases have what is often called filled or closed-shell valence electron configurations. These closed shells are actually filled *s* and *p* subshells with a total of eight electrons, which are called *octets*; helium is an exception, with a closed *1s* shell that has only two electrons. Because of their filled valence shells, the noble gases are generally unreactive. In contrast, the alkali metals have a single valence electron outside a closed shell and readily lose this electron to elements that require electrons to achieve an octet, such as the halogens. Thus because of their periodic similarities in electron configuration, atoms in the same column of the periodic table tend to form compounds with the same oxidation states and stoichiometries. ended with the observation that, because all the elements in a column have the same valence electron configuration, the periodic table can be used to find the electron configuration of most of the elements at a glance.

Crookes's Spiral Periodic Table, 1888. Created by Sir William Crookes (1832–1919), the spiral represents the relationships between the elements and the order of evolution of the elements from what he believed to be primal matter.

In this chapter, we explore the relationship between the electron configurations of the elements, as reflected in their arrangement in the periodic table, and their physical and chemical properties. In particular, we focus on the

similarities between elements in the same column and on the trends in properties that are observed across horizontal rows or down vertical columns. By the end of this chapter, your understanding of these trends and relationships will provide you with clues as to why argon is used in incandescent light bulbs, why coal and wood burst into flames when they come in contact with pure F_2 , why aluminum was discovered so late despite being the third most abundant element in Earth's crust, and why lithium is commonly used in batteries. We begin by expanding on the brief discussion of the history of the periodic table presented in and describing how it was created many years before electrons had even been discovered, much less discussed in terms of shells, subshells, orbitals, and electron spin.

7.1 The History of the Periodic Table

LEARNING OBJECTIVE

1. To become familiar with the history of the periodic table.

The modern periodic table has evolved through a long history of attempts by chemists to arrange the elements according to their properties as an aid in predicting chemical behavior. One of the first to suggest such an arrangement was the German chemist Johannes Dobereiner (1780–1849), who noticed that many of the known elements could be grouped in triads, sets of three elements that have similar properties—for example, chlorine, bromine, and iodine; or copper, silver, and gold. Dobereiner proposed that all elements could be grouped in such triads, but subsequent attempts to expand his concept were unsuccessful. We now know that portions of the periodic table—the *d* block in particular—contain triads of elements with substantial similarities. The middle three members of most of the other columns, such as sulfur, selenium, and tellurium in group 16 or aluminum, gallium, and indium in group 13, also have remarkably similar chemistry.

By the mid-19th century, the atomic masses of many of the elements had been determined. The English chemist John Newlands (1838–1898), hypothesizing that the chemistry of the elements might be related to their masses, arranged the known elements in order of increasing atomic mass and discovered that every seventh element had similar properties (Figure 7.1 "The Arrangement of the Elements into Octaves as Proposed by Newlands"). (The noble gases were still unknown.) Newlands therefore suggested that the elements could be classified into octaves, corresponding to the *horizontal* rows in the main group elements. Unfortunately, Newlands's "law of octaves" did not seem to work for elements heavier than calcium, and his idea was publicly ridiculed. At one scientific meeting, Newlands was asked why he didn't arrange the elements in alphabetical order instead of by atomic mass, since that would make just as much sense! Actually, Newlands was on the right track—with only a few exceptions, atomic mass does increase with atomic number, and similar properties occur every time a set of ns^2np^6 subshells is filled. Despite the fact that

Newlands's table had no logical place for the *d*-block elements, he was honored for his idea by the Royal Society of London in 1887.

John Newlands (1838–1898)

Newlands noticed that elemental properties repeated every seventh (or multiple of seven) element, as musical notes repeat every eighth note.

Figure 7.1 The Arrangement of the Elements into Octaves as Proposed by Newlands

No.	No.	No.	No.	No.	No.	No.	No.
H 1	F 8	Cl 15	Co & Ni 22	Br 29	Pd 36	I 42	Pt & Ir 50
Li 2	Na 9	K 16	Cu 23	Rb 30	Ag 37	Cs 44	Tl 51
G 3	Mg 10	Ca 17	Zn 25	Sr 31	Bd [sic-Cd] 38	Ba & V 45	Pb 54
Bo 4	Al 11	Cr 19	Y 24	Ce & La 33	U 40	Ta 46	Th 56
C 5	Si 12	Ti 18	In 26	Zr 32	Sn 39	W 47	Hg 52
N 6	P 13	Mn 20	As 27	Di & Mo 34	Sb 41	Nb 48	Bi 55
O 7	S 14	Fe 21	Se 28	Ro & Ru 35	Te 43	Au 49	Os 51

NOTE. Where two elements happen to have the same equivalent, both are designated by the same number.

The table shown here accompanied a letter from a 27-year-old Newlands to the editor of the journal Chemical News in which he wrote: “If the elements are arranged in the order of their equivalents, with a few slight transpositions, as in the accompanying table, it will be observed that elements belonging to the same group usually appear on the same horizontal line. It will also be seen that the numbers of analogous elements generally differ either by 7 or by some multiple of seven; in other words, members of the same group stand to each other in the same relation as the extremities of one or more octaves in music. Thus, in the nitrogen group, between nitrogen and phosphorus there are 7 elements; between phosphorus and arsenic, 14; between arsenic and antimony, 14; and lastly, between antimony and bismuth, 14 also. This peculiar relationship I propose to provisionally term the Law of Octaves. I am, &c. John A. R. Newlands, F.C.S. Laboratory, 19, Great St. Helen’s, E.C., August 8, 1865.”

The periodic table achieved its modern form through the work of the German chemist Julius Lothar Meyer (1830–1895) and the Russian chemist Dimitri Mendeleev (1834–1907), both of whom focused on the relationships between atomic mass and various physical and chemical properties. In 1869, they independently proposed essentially identical arrangements of the elements. Meyer aligned the elements in his table according to periodic variations in simple atomic properties, such as “atomic volume” (Figure 7.2 "Variation of Atomic Volume with Atomic Number, Adapted from Meyer’s Plot of 1870"), which he obtained by dividing the atomic mass (molar mass) in grams per mole by the

density of the element in grams per cubic centimeter. This property is equivalent to what is today defined as molar volume (measured in cubic centimeters per mole):

Equation 7.1

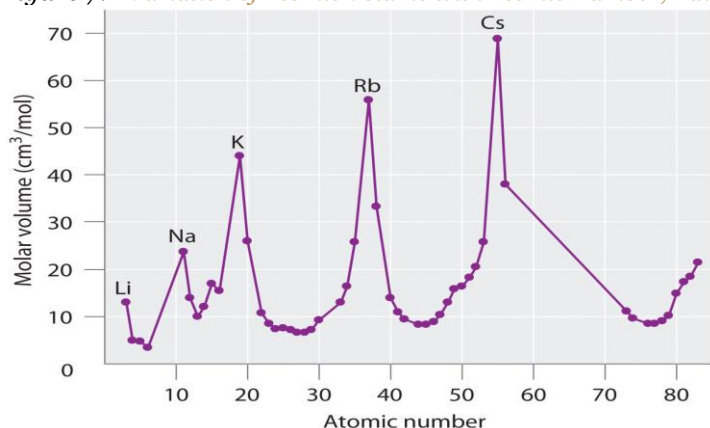
$$\text{molar mass (g/mol)} / \text{density (g/cm}^3\text{)} = \text{molar volume (cm}^3\text{/mol)}$$

As shown in Figure 7.2 "Variation of Atomic Volume with Atomic Number, Adapted from Meyer's Plot of 1870", the alkali metals have the highest molar volumes of the solid elements. In Meyer's plot of atomic volume versus atomic mass, the nonmetals occur on the rising portion of the graph, and metals occur at the peaks, in the valleys, and on the downslopes.

Dimitri Mendeleev (1834–1907)

When his family's glass factory was destroyed by fire, Mendeleev moved to St. Petersburg, Russia, to study science. He became ill and was not expected to recover, but he finished his PhD with the help of his professors and fellow students. In addition to the periodic table, another of Mendeleev's contributions to science was an outstanding textbook, *The Principles of Chemistry*, which was used for many years.

Figure 7.2 Variation of Atomic Volume with Atomic Number, Adapted from Meyer's Plot of 1870



Note the periodic increase and decrease in atomic volume. Because the noble gases had not yet been discovered at the time this graph was formulated, the peaks correspond to the alkali metals (group 1).

Mendeleev's Periodic Table

Mendeleev, who first published his periodic table in 1869 (Figure 7.3 "Mendeleev's Periodic Table, as Published in the German Journal "), is usually credited with the origin of the modern periodic table. The key difference between his arrangement of the elements and that of Meyer and others is that Mendeleev did not assume that all the elements had been discovered (actually, only about two-thirds of the naturally occurring elements were known at the time). Instead, he deliberately left blanks in his table at atomic

masses 44, 68, 72, and 100, in the expectation that elements with those atomic masses would be discovered. Those blanks correspond to the elements we now know as scandium, gallium, germanium, and technetium.

Figure 7.3 *Mendeleev's Periodic Table, as Published in the German Journal Annalen der Chemie und Pharmacie in 1872*

Reihen	Gruppe I. — R ² O	Gruppe II. — RO	Gruppe III. — R ² O ³	Gruppe IV. RH ⁴ RO ²	Gruppe V. RH ³ R ² O ⁵	Gruppe VI. RH ² RO ³	Gruppe VII. RH R ² O ⁷	Gruppe VIII. — RO ⁴
1	H=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	— =44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63.
5	(Cu=63)	Zn=65	— =68	— =72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	— =100	Ru=104, Rh=104, Pd=106, Ag=108.
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Ce= 40	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199.
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	
12	—	—	—	Th=231	—	U=240	—	— — — —

The column headings “Reihen” and “Gruppe” are German for “row” and “group.” Formulas indicate the type of compounds formed by each group, with “R” standing for “any element” and superscripts used where we now use subscripts. Atomic masses are shown after equal signs and increase across each row from left to right.

The most convincing evidence in support of Mendeleev’s arrangement of the elements was the discovery of two previously unknown elements whose properties closely corresponded with his predictions (Table 7.1 “Comparison of the Properties Predicted by Mendeleev in 1869 for ”). Two of the blanks Mendeleev had left in his original table were below aluminum and silicon, awaiting the discovery of two as-yet-unknown elements, *eka*-aluminum and *eka*-silicon (from the Sanskrit *eka*, meaning “one,” as in “one beyond aluminum”). The observed properties of gallium and germanium matched those of *eka*-aluminum and *eka*-silicon so well that once they were discovered, Mendeleev’s periodic table rapidly gained acceptance.

Table 7.1 Comparison of the Properties Predicted by Mendeleev in 1869 for *eka*-Aluminum and *eka*-Silicon with the Properties of Gallium (Discovered in 1875) and Germanium (Discovered in 1886)

Property	<i>eka</i> -Aluminum (predicted)	Gallium (observed)	<i>eka</i> -Silicon (predicted)	Germanium (observed)
atomic mass	68	69.723	72	72.64
element	metal	metal	dirty-gray metal	gray-white metal
	low mp*	mp = 29.8°C	high mp	mp = 938°C
	$d = 5.9 \text{ g/cm}^3$	$d = 5.91 \text{ g/cm}^3$	$d = 5.5 \text{ g/cm}^3$	$d = 5.323 \text{ g/cm}^3$
oxide	E_2O_3	Ga_2O_3	EO_2	GeO_2
	$d = 5.5 \text{ g/cm}^3$	$d = 6.0 \text{ g/cm}^3$	$d = 4.7 \text{ g/cm}^3$	$d = 4.25 \text{ g/cm}^3$
chloride	ECl_3	GaCl_3	ECl_4	GeCl_4
		mp = 78°C		
	volatile	bp* = 201°C	bp < 100°C	bp = 87°C
*mp = melting point; bp = boiling point.				

When the chemical properties of an element suggested that it might have been assigned the wrong place in earlier tables, Mendeleev carefully reexamined its atomic mass. He discovered, for example, that the atomic masses previously reported for beryllium, indium, and uranium were incorrect. The atomic mass of indium had originally been reported as 75.6, based on an assumed stoichiometry of InO for its oxide. If this atomic mass were correct, then indium would have to be placed in the middle of the nonmetals, between arsenic (atomic mass 75) and selenium (atomic mass 78). Because elemental indium is a silvery-white *metal*, however, Mendeleev postulated that the stoichiometry of its oxide was really In_2O_3 rather than InO . This would mean that indium's atomic mass was actually 113, placing the element between two other metals, cadmium and tin.

One group of elements that is absent from Mendeleev's table is the noble gases, all of which were discovered more than 20 years later, between 1894 and 1898, by Sir William Ramsay (1852–1916; Nobel Prize in Chemistry 1904). Initially, Ramsay did not know where to place these elements in the periodic table. Argon, the first to be discovered, had an atomic mass of 40. This was greater than chlorine's and comparable to that of potassium, so Ramsay, using the same kind of reasoning as Mendeleev, decided to place the noble gases between the halogens and the alkali metals.

The Role of the Atomic Number in the Periodic Table

Despite its usefulness, Mendeleev's periodic table was based entirely on empirical observation supported by very little understanding. It was not until 1913, when a young British physicist, H. G. J. Moseley (1887–1915), while analyzing the frequencies of x-rays emitted by the elements, discovered that the underlying foundation of the order of the elements was by the *atomic number*, not the atomic mass. Moseley hypothesized that the placement of each element in his series corresponded to its atomic number Z , which is the number of positive charges (protons) in its nucleus. Argon, for example, although having an atomic mass greater than that of potassium (39.9 amu versus 39.1 amu, respectively), was placed *before* potassium in the periodic table. While analyzing the frequencies of the emitted x-rays, Moseley noticed that the atomic number of argon is 18, whereas that of potassium is 19, which indicated that they were indeed placed correctly. Moseley also noticed three gaps in his table of x-ray frequencies, so he predicted the existence of three unknown elements: technetium ($Z = 43$), discovered in 1937; promethium ($Z = 61$), discovered in 1945; and rhenium ($Z = 75$), discovered in 1925.

H. G. J. Moseley (1887–1915)

Moseley left his research work at the University of Oxford to join the British army as a telecommunications officer during World War I. He was killed during the Battle of Gallipoli in Turkey.

EXAMPLE 1

Before its discovery in 1999, some theoreticians believed that an element with a Z of 114 existed in nature. Use Mendeleev's reasoning to name element 114 as *eka*-____; then identify the known element whose chemistry you predict would be most similar to that of element 114.

Given: atomic number

Asked for: name using prefix *eka*-

Strategy:

A Using the periodic table (see Chapter 32 "Appendix H: Periodic Table of Elements"), locate the $n = 7$ row. Identify the location of the unknown element with $Z = 114$; then identify the known element that is directly above this location.

B Name the unknown element by using the prefix *eka*- before the name of the known element.

Solution:

A The $n = 7$ row can be filled in by assuming the existence of elements with atomic numbers greater than 112, which is underneath mercury (Hg). Counting three boxes to the right gives element 114, which lies directly below lead (Pb). **B** If Mendeleev were alive today, he would call element 114 *eka*-lead.

Exercise

Use Mendeleev's reasoning to name element 112 as *eka*-____; then identify the known element whose chemistry you predict would be most similar to that of element 112.

Answer: *eka*-mercury

Summary

The periodic table arranges the elements according to their electron configurations, such that elements in the same column have the same valence electron configurations. Periodic variations in size and chemical properties are important factors in dictating the types of chemical reactions the elements undergo and the kinds of chemical compounds they form. The modern periodic table was based on empirical correlations of properties such as atomic mass; early models using limited data noted the existence of **triads** and **octaves** of elements with similar properties. The periodic table achieved its current form through the work of Dimitri Mendeleev and Julius Lothar Meyer, who both focused on the relationship between atomic mass and chemical properties. Meyer arranged the elements by their atomic volume, which today is equivalent to the **molar volume**, defined as molar mass divided by molar density. The correlation with the electronic structure of atoms was made when H. G. J. Moseley showed that the periodic arrangement of the elements was determined by atomic number, not atomic mass.

KEY TAKEAWAY

- The elements in the periodic table are arranged according to their properties, and the periodic table serves as an aid in predicting chemical behavior.

CONCEPTUAL PROBLEMS

1. Johannes Dobereiner is credited with developing the concept of chemical triads. Which of the group 15 elements would you expect to compose a triad? Would you expect B, Al, and Ga to act as a triad? Justify your answers.
2. Despite the fact that Dobereiner, Newlands, Meyer, and Mendeleev all contributed to the development of the modern periodic table, Mendeleev is credited with its origin. Why was Mendeleev's periodic table accepted so rapidly?

3. How did Moseley's contribution to the development of the periodic table explain the location of the noble gases?
4. The *eka*- naming scheme devised by Mendeleev was used to describe undiscovered elements.
 - a. Use this naming method to predict the atomic number of *eka*-mercury, *eka*-astatine, *eka*-thallium, and *eka*-hafnium.
 - b. Using the *eka*-prefix, identify the elements with these atomic numbers: 79, 40, 51, 117, and 121.

NUMERICAL PROBLEM

1. Based on the data given, complete the table.

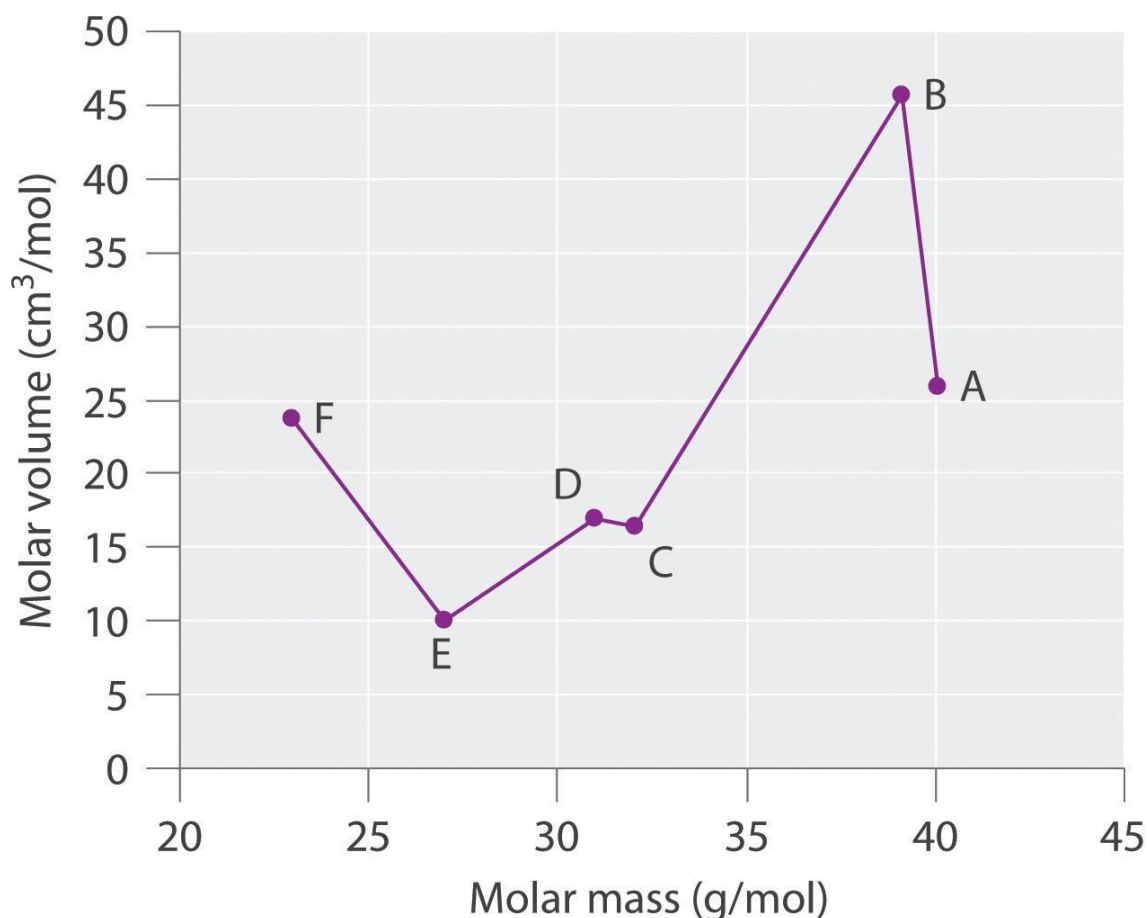
Species	Molar Mass (g/mol)	Density (g/cm ³)	Molar Volume (cm ³ /mol)
A	40.078		25.85
B	39.09	0.856	
C	32.065		16.35
D		1.823	16.98
E	26.98		9.992
F	22.98	0.968	

2. Plot molar volume versus molar mass for these substances. According to Meyer, which would be considered metals and which would be considered nonmetals?

ANSWER

- 1.

Species	Molar Mass (g/mol)	Density (g/cm ³)	Molar Volume (cm ³ /mol)
A	40.078	1.550	25.85
B	39.09	0.856	45.67
C	32.065	1.961	16.35
D	30.95	1.823	16.98
E	26.98	2.700	9.992
F	22.98	0.968	23.7



Meyer found that the alkali metals had the highest molar volumes, and that molar volumes decreased steadily with increasing atomic mass, then leveled off, and finally rose again. The elements located on the rising portion of a plot of molar volume versus molar mass were typically nonmetals. If we look at the plot of the data in the table, we can immediately identify those elements with the largest molar volumes (A, B, F) as metals located on the left side of the periodic table. The element with the smallest molar volume (E) is aluminum. The plot shows that the subsequent elements (C, D) have molar volumes that are larger than that of E, but smaller than those of A and B. Thus, C and D are most likely to be nonmetals (which is the case: C = sulfur, D = phosphorus).

7.2 Sizes of Atoms and Ions

LEARNING OBJECTIVES

1. To understand periodic trends in atomic radii.
2. To predict relative ionic sizes within an isoelectronic series.

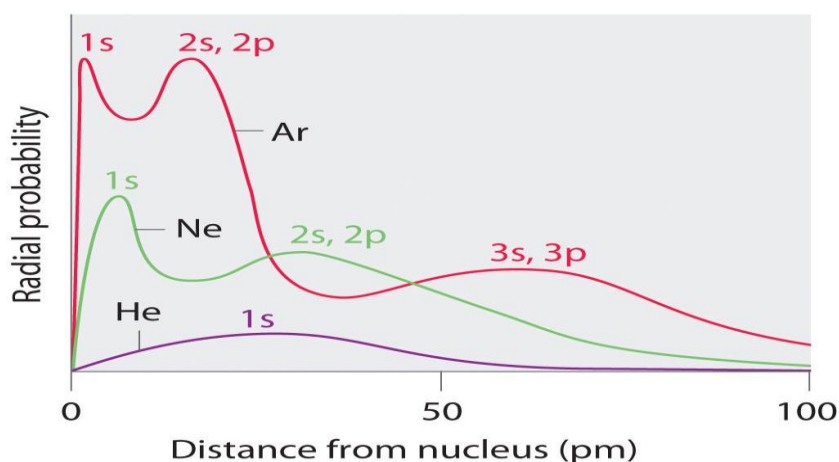
Although some people fall into the trap of visualizing atoms and ions as small, hard spheres similar to miniature table-tennis balls or marbles, the quantum mechanical model tells us that their shapes and boundaries are much less

definite than those images suggest. As a result, atoms and ions cannot be said to have exact sizes. In this section, we discuss how atomic and ion “sizes” are defined and obtained.

Atomic Radii

Recall from Chapter 6 "The Structure of Atoms" that the probability of finding an electron in the various available orbitals falls off slowly as the distance from the nucleus increases. This point is illustrated in Figure 7.4 "Plots of Radial Probability as a Function of Distance from the Nucleus for He, Ne, and Ar", which shows a plot of total electron density for all occupied orbitals for three noble gases as a function of their distance from the nucleus. Electron density diminishes gradually with increasing distance, which makes it impossible to draw a sharp line marking the boundary of an atom.

Figure 7.4 Plots of Radial Probability as a Function of Distance from the Nucleus for He, Ne, and Ar



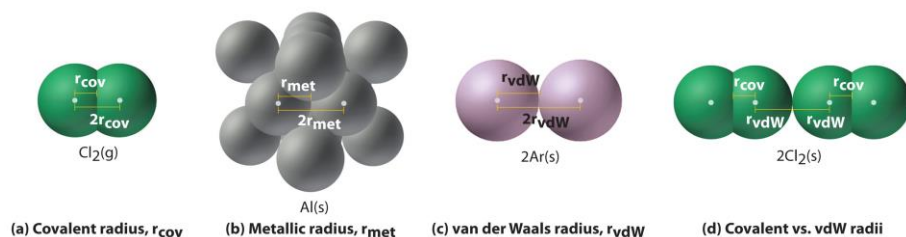
In He, the 1s electrons have a maximum radial probability at ≈ 30 pm from the nucleus. In Ne, the 1s electrons have a maximum at ≈ 8 pm, and the 2s and 2p electrons combine to form another maximum at ≈ 35 pm (the $n = 2$ shell). In Ar, the 1s electrons have a maximum at ≈ 2 pm, the 2s and 2p electrons combine to form a maximum at ≈ 18 pm, and the 3s and 3p electrons combine to form a maximum at ≈ 70 pm.

Figure 7.4 "Plots of Radial Probability as a Function of Distance from the Nucleus for He, Ne, and Ar" also shows that there are distinct peaks in the total electron density at particular distances and that these peaks occur at different distances from the nucleus for each element. Each peak in a given plot corresponds to the electron density in a given principal shell. Because helium has only one filled shell ($n = 1$), it shows only a single peak. In contrast, neon, with filled $n = 1$ and 2 principal shells, has two peaks. Argon, with filled $n = 1, 2$, and 3 principal shells, has three peaks. The peak for the filled $n = 1$ shell occurs at successively shorter distances for neon ($Z = 10$) and argon ($Z = 18$) because, with a greater number of protons, their nuclei are more positively charged than that of helium. Because the

1s² shell is closest to the nucleus, its electrons are very poorly shielded by electrons in filled shells with larger values of n . Consequently, the two electrons in the $n = 1$ shell experience nearly the full nuclear charge, resulting in a strong electrostatic interaction between the electrons and the nucleus. The energy of the $n = 1$ shell also decreases tremendously (the filled 1s orbital becomes more stable) as the nuclear charge increases. For similar reasons, the filled $n = 2$ shell in argon is located closer to the nucleus and has a lower energy than the $n = 2$ shell in neon.

Figure 7.4 "Plots of Radial Probability as a Function of Distance from the Nucleus for He, Ne, and Ar" illustrates the difficulty of measuring the dimensions of an individual atom. Because distances between the nuclei in pairs of covalently bonded atoms can be measured quite precisely, however, chemists use these distances as a basis for describing the approximate sizes of atoms. For example, the internuclear distance in the diatomic Cl₂ molecule is known to be 198 pm. We assign half of this distance to each chlorine atom, giving chlorine a covalent atomic radius (r_{cov}) of 99 pm or 0.99 Å (part (a) in Figure 7.5 "Definitions of the Atomic Radius").^[1]

Figure 7.5 *Definitions of the Atomic Radius*



(a) The covalent atomic radius, r_{cov} , is half the distance between the nuclei of two like atoms joined by a covalent bond in the same molecule, such as Cl₂. (b) The metallic atomic radius, r_{met} , is half the distance between the nuclei of two adjacent atoms in a pure solid metal, such as aluminum. (c) The van der Waals atomic radius, r_{vdW} , is half the distance between the nuclei of two like atoms, such as argon, that are closely packed but not bonded. (d) This is a depiction of covalent versus van der Waals radii of chlorine.

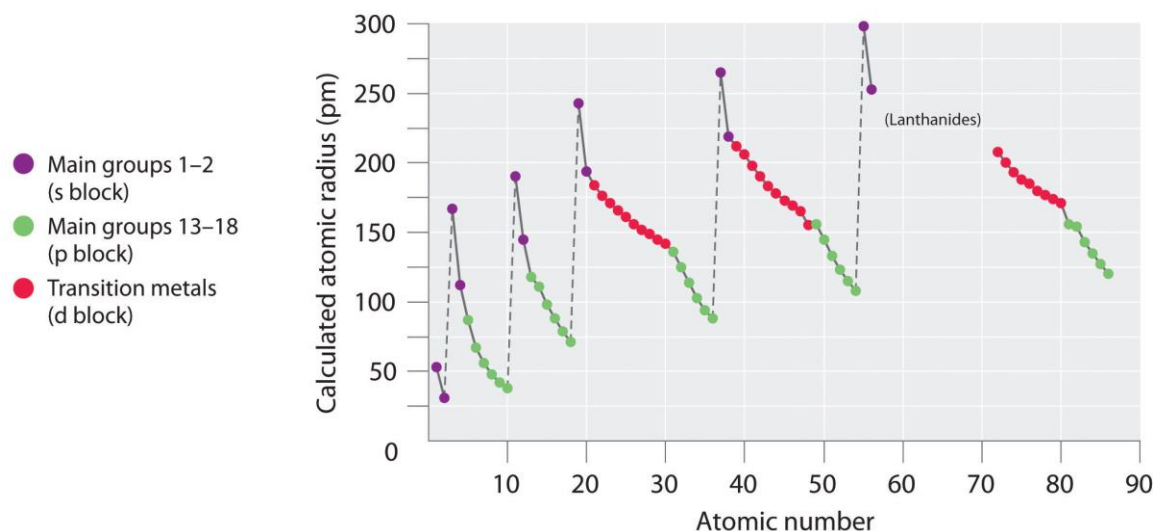
In a similar approach, we can use the lengths of carbon–carbon single bonds in organic compounds, which are remarkably uniform at 154 pm, to assign a value of 77 pm as the covalent atomic radius for carbon. If these values do indeed reflect the actual sizes of the atoms, then we should be able to predict the lengths of covalent bonds formed between different elements by adding them. For example, we would predict a carbon–chlorine distance of 77 pm + 99 pm = 176 pm for a C–Cl bond, which is very close to the average value observed in many organochlorine compounds.^[2]

Covalent atomic radii can be determined for most of the nonmetals, but how do chemists obtain atomic radii for elements that do not form covalent bonds? For these elements, a variety of other methods have been developed. With a metal, for example, the metallic atomic radius(r_{met}) is defined as half the distance between the nuclei of two adjacent metal atoms (part (b) in Figure 7.5 "Definitions of the Atomic Radius"). For elements such as the noble gases, most of which form no stable compounds, we can use what is called the van der Waals atomic radius(r_{vdW}), which is half the internuclear distance between two nonbonded atoms in the solid (part (c) in Figure 7.5 "Definitions of the Atomic Radius"). An atom such as chlorine has both a covalent radius (the distance between the two atoms in a Cl_2 molecule) and a van der Waals radius (the distance between two Cl atoms in different molecules in, for example, $\text{Cl}_2(\text{s})$ at low temperatures). These radii are generally not the same (part (d) in Figure 7.5 "Definitions of the Atomic Radius").

Periodic Trends in Atomic Radii

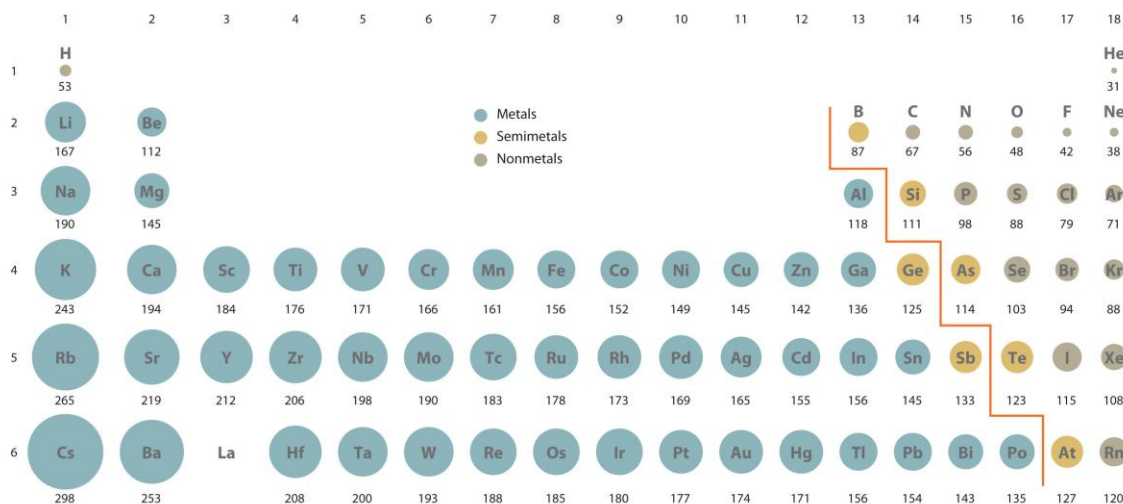
Because it is impossible to measure the sizes of both metallic and nonmetallic elements using any one method, chemists have developed a self-consistent way of calculating atomic radii using the quantum mechanical functions described in Chapter 6 "The Structure of Atoms". Although the radii values obtained by such calculations are not identical to any of the experimentally measured sets of values, they do provide a way to compare the intrinsic sizes of all the elements and clearly show that atomic size varies in a periodic fashion (Figure 7.6 "A Plot of Periodic Variation of Atomic Radius with Atomic Number for the First Six Rows of the Periodic Table"). In the periodic table, atomic radii decrease from left to right across a row and increase from top to bottom down a column. Because of these two trends, the largest atoms are found in the lower left corner of the periodic table, and the smallest are found in the upper right corner (Figure 7.7 "Calculated Atomic Radii (in Picometers) of the ").

Figure 7.6 A Plot of Periodic Variation of Atomic Radius with Atomic Number for the First Six Rows of the Periodic Table



There is a similarity to the plot of atomic volume versus atomic number (Figure 7.2 "Variation of Atomic Volume with Atomic Number, Adapted from Meyer's Plot of 1870")—a variation of Meyer's early plot.

Figure 7.7 Calculated Atomic Radii (in Picometers) of the s-, p-, and d-Block Elements



The sizes of the circles illustrate the relative sizes of the atoms. The calculated values are based on quantum mechanical wave functions.

Source: <http://www.webelements.com>.

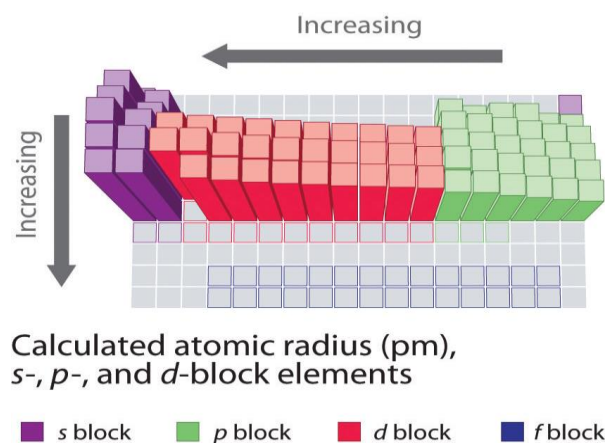
Note the Pattern

Atomic radii decrease from left to right across a row and increase from top to bottom down a column.

Trends in atomic size result from differences in the **effective nuclear charges (Z_{eff})** experienced by electrons in the outermost orbitals of the elements. As we described in Chapter 6 "The Structure of Atoms", for all elements except H, the effective nuclear charge is always *less* than the actual nuclear charge because of shielding effects. The

greater the effective nuclear charge, the more strongly the outermost electrons are attracted to the nucleus and the smaller the atomic radius.

The atoms in the second row of the periodic table (Li through Ne) illustrate the effect of electron shielding. (For more information on electron shielding, see Chapter 6 "The Structure of Atoms", Section 6.5 "Atomic Orbitals and Their Energies", and Figure 6.29 "Orbital Energy Level Diagram for a Typical Multielectron Atom".) All have a filled $1s^2$ inner shell, but as we go from left to right across the row, the nuclear charge increases from +3 to +10. Although electrons are being added to the $2s$ and $2p$ orbitals, *electrons in the same principal shell are not very effective at shielding one another from the nuclear charge*. Thus the single $2s$ electron in lithium experiences an effective nuclear charge of approximately +1 because the electrons in the filled $1s^2$ shell effectively neutralize two of the three positive charges in the nucleus. (More detailed calculations give a value of $Z_{\text{eff}} = +1.26$ for Li.) In contrast, the two $2s$ electrons in beryllium do not shield each other very well, although the filled $1s^2$ shell effectively neutralizes two of the four positive charges in the nucleus. This means that the effective nuclear charge experienced by the $2s$ electrons in beryllium is between +1 and +2 (the calculated value is +1.66). Consequently, beryllium is significantly smaller than lithium. Similarly, as we proceed across the row, the increasing nuclear charge is not effectively neutralized by the electrons being added to the $2s$ and $2p$ orbitals. The result is a steady increase in the effective nuclear charge and a steady decrease in atomic size.



The increase in atomic size going down a column is also due to electron shielding, but the situation is more complex because the principal quantum number n is not constant. As we saw in Chapter 6 "The Structure of Atoms", the size of the orbitals increases as n increases, *provided the nuclear charge remains the same*. In group 1, for example, the size of the atoms increases substantially going down the column. It may at first seem reasonable to attribute this effect to the successive addition of electrons to ns orbitals

with increasing values of n . However, it is important to remember that the radius of an orbital depends dramatically on the nuclear charge. As we go down the column of the group 1 elements, the principal quantum number n increases from 2 to 6, but the nuclear charge increases from +3 to +55! If the outermost electrons in cesium experienced the full nuclear charge of +55, a cesium atom would be very small indeed. In fact, the effective nuclear charge felt by the outermost electrons in cesium is much less than expected (6 rather than 55). This means that cesium, with a $6s^1$ valence electron configuration, is much larger than lithium, with a $2s^1$ valence electron configuration. The effective nuclear charge changes relatively little from lithium to cesium because *electrons in filled inner shells are highly effective at shielding electrons in outer shells from the nuclear charge*. Even though cesium has a nuclear charge of +55, it has 54 electrons in its filled $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6$ shells, abbreviated as $[\text{Xe}]5s^2 4d^{10} 5p^6$, which effectively neutralize most of the 55 positive charges in the nucleus. The same dynamic is responsible for the steady increase in size observed as we go down the other columns of the periodic table. Irregularities can usually be explained by variations in effective nuclear charge.

Note the Pattern

Electrons in the same principal shell are not very effective at shielding one another from the nuclear charge, whereas electrons in filled inner shells are highly effective at shielding electrons in outer shells from the nuclear charge.

EXAMPLE 2

On the basis of their positions in the periodic table, arrange these elements in order of increasing atomic radius: aluminum, carbon, and silicon.

Given: three elements

Asked for: arrange in order of increasing atomic radius

Strategy:

A Identify the location of the elements in the periodic table. Determine the relative sizes of elements located in the same column from their principal quantum number n . Then determine the order of elements in the same row from their effective nuclear charges. If the elements are not in the same column or row, use pairwise comparisons.

B List the elements in order of increasing atomic radius.

Solution:

A These elements are not all in the same column or row, so we must use pairwise comparisons. Carbon and silicon are both in group 14 with carbon lying above, so carbon is smaller than silicon ($C < Si$). Aluminum and silicon are both in the third row with aluminum lying to the left, so silicon is smaller than aluminum ($Si < Al$) because its effective nuclear charge is greater. **B** Combining the two inequalities gives the overall order: $C < Si < Al$.

Exercise

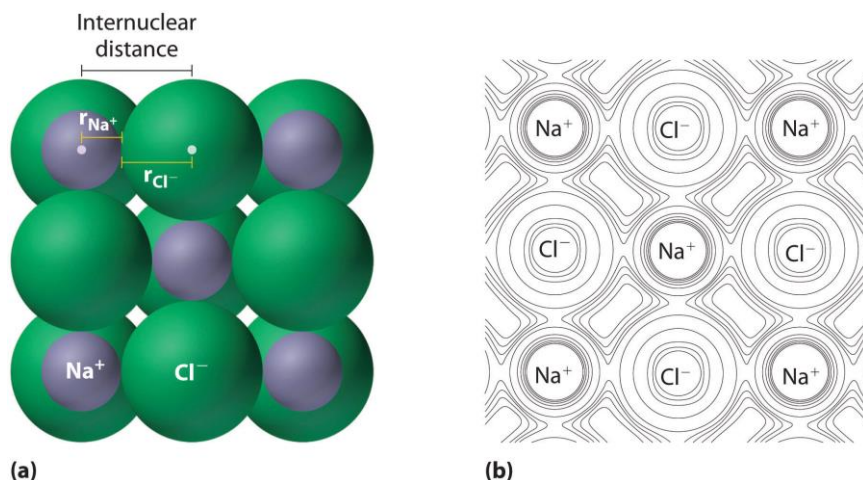
On the basis of their positions in the periodic table, arrange these elements in order of increasing size: oxygen, phosphorus, potassium, and sulfur.

Answer: $O < S < P < K$

Ionic Radii and Isoelectronic Series

As you learned in Chapter 2 "Molecules, Ions, and Chemical Formulas", ionic compounds consist of regular repeating arrays of alternating cations and anions. Although it is not possible to measure an ionic radius directly for the same reason it is not possible to directly measure an atom's radius, it is possible to measure the distance between the nuclei of a cation and an adjacent anion in an ionic compound to determine the ionic radius of one or both. As illustrated in Figure 7.8 "Definition of Ionic Radius", the internuclear distance corresponds to the *sum* of the radii of the cation and anion. A variety of methods have been developed to divide the experimentally measured distance proportionally between the smaller cation and larger anion. These methods produce sets of ionic radii that are internally consistent from one ionic compound to another, although each method gives slightly different values. For example, the radius of the Na^+ ion is essentially the same in $NaCl$ and Na_2S , as long as the same method is used to measure it. Thus despite minor differences due to methodology, certain trends can be observed.

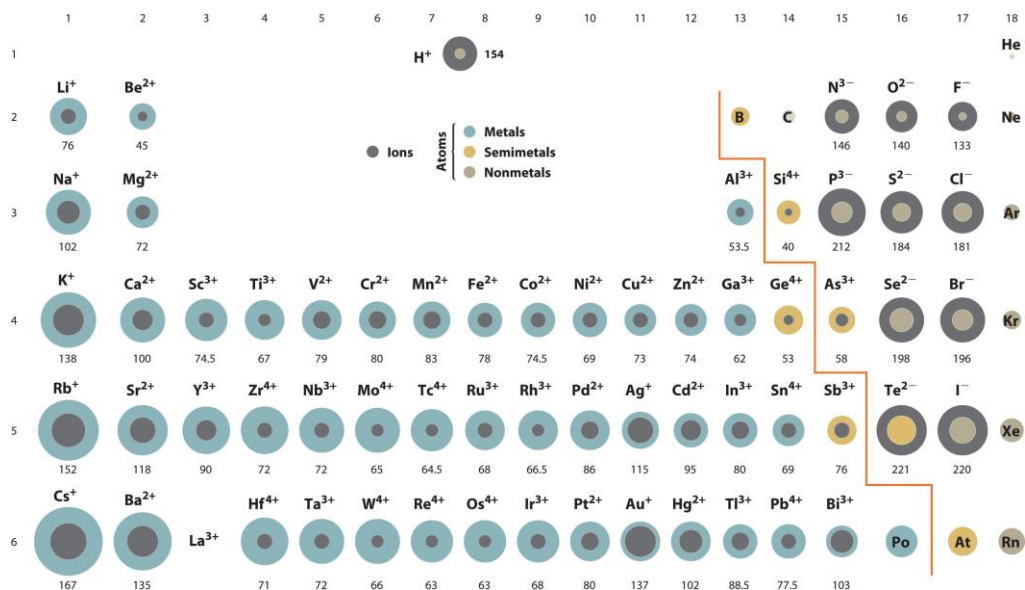
Figure 7.8 Definition of Ionic Radius



(a) The internuclear distance is apportioned between adjacent cations and anions in the ionic structure, as shown here for Na^+ and Cl^- in sodium chloride. (b) This depiction of electron density contours for a single plane of atoms in the NaCl structure shows how the lines connect points of equal electron density. Note the relative sizes of the electron density contour lines around Cl^- and Na^+ .

A comparison of ionic radii with atomic radii (Figure 7.9 "Ionic Radii (in Picometers) of the Most Common Oxidation States of the ") shows that a *cation is always smaller than its parent neutral atom, and an anion is always larger than the parent neutral atom*. When one or more electrons is removed from a neutral atom, two things happen: (1) repulsions between electrons in the same principal shell decrease because fewer electrons are present, and (2) the effective nuclear charge felt by the remaining electrons increases because there are fewer electrons to shield one another from the nucleus. Consequently, the size of the region of space occupied by electrons decreases (compare Li at 167 pm with Li^+ at 76 pm). If different numbers of electrons can be removed to produce ions with different charges, the ion with the greatest positive charge is the smallest (compare Fe^{2+} at 78 pm with Fe^{3+} at 64.5 pm). Conversely, adding one or more electrons to a neutral atom causes electron–electron repulsions to increase and the effective nuclear charge to decrease, so the size of the probability region increases (compare F at 42 pm with F^- at 133 pm).

Figure 7.9 *Ionic Radii (in Picometers) of the Most Common Oxidation States of the s-, p-, and d-Block Elements*



Gray circles indicate the sizes of the ions shown; colored circles indicate the sizes of the neutral atoms, previously shown in Figure 7.7 "Calculated Atomic Radii (in Picometers) of the".

Source: Ionic radius data from R. D. Shannon, "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides," *Acta Crystallographica* 32, no. 5 (1976): 751–767.

Note the Pattern

Cations are always smaller than the neutral atom, and anions are always larger.

Because most elements form either a cation or an anion but not both, there are few opportunities to compare the sizes of a cation and an anion derived from the same neutral atom. A few compounds of sodium, however, contain the Na^- ion, allowing comparison of its size with that of the far more familiar Na^+ ion, which is found in many compounds. The radius of sodium in each of its three known oxidation states is given in Table 7.2

"Experimentally Measured Values for the Radius of Sodium in Its Three Known Oxidation States". All three species have a nuclear charge of +11, but they contain 10 (Na^+), 11 (Na^0), and 12 (Na^-) electrons. The Na^+ ion is significantly smaller than the neutral Na atom because the $3s^1$ electron has been removed to give a closed shell with $n = 2$. The Na^- ion is larger than the parent Na atom because the additional electron produces a $3s^2$ valence electron configuration, while the nuclear charge remains the same.

Table 7.2 Experimentally Measured Values for the Radius of Sodium in Its Three Known Oxidation States

	Na^+	Na^0	Na^-
Electron Configuration	$1s^2 2s^2 2p^6$	$1s^2 2s^2 2p^6 3s^1$	$1s^2 2s^2 2p^6 3s^2$

	Na ⁺	Na ⁰	Na ⁻
Radius (pm)	102	154*	202 [†]
*The metallic radius measured for Na(s).			
[†] Source: M. J. Wagner and J. L. Dye, "Alkalides, Electrides, and Expanded Metals," <i>Annual Review of Materials Science</i> 23 (1993): 225–253.			

Ionic radii follow the same vertical trend as atomic radii; that is, for ions with the same charge, the ionic radius increases going down a column. The reason is the same as for atomic radii: shielding by filled inner shells produces little change in the effective nuclear charge felt by the outermost electrons. Again, principal shells with larger values of n lie at successively greater distances from the nucleus.

Because elements in different columns tend to form ions with different charges, it is not possible to compare ions of the same charge across a row of the periodic table. Instead, elements that are next to each other tend to form ions with the same number of electrons but with different overall charges because of their different atomic numbers. Such a set of species is known as an isoelectronic series. For example, the isoelectronic series of species with the neon closed-shell configuration ($1s^2 2s^2 2p^6$) is shown in Table 7.3 "Radius of Ions with the Neon Closed-Shell Electron Configuration". The sizes of the ions in this series decrease smoothly from N^{3-} to Al^{3+} . All six of the ions contain 10 electrons in the $1s$, $2s$, and $2p$ orbitals, but the nuclear charge varies from +7 (N) to +13 (Al). As the positive charge of the nucleus increases while the number of electrons remains the same, there is a greater electrostatic attraction between the electrons and the nucleus, which causes a decrease in radius. Consequently, the ion with the greatest nuclear charge (Al^{3+}) is the smallest, and the ion with the smallest nuclear charge (N^{3-}) is the largest. One member of this isoelectronic series is not listed in Table 7.3 "Radius of Ions with the Neon Closed-Shell Electron Configuration": the neon atom. Because neon forms no covalent or ionic compounds, its radius is difficult to measure.

Table 7.3 Radius of Ions with the Neon Closed-Shell Electron Configuration

Ion	Radius (pm)	Atomic Number
N^{3-}	146	7
O^{2-}	140	8
F^-	133	9
Na^+	102	11
Mg^{2+}	72	12
Al^{3+}	53.5	13

Source: R. D. Shannon, "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides," *Acta Crystallographica* 32, no. 5 (1976): 751–767.

EXAMPLE 3

Based on their positions in the periodic table, arrange these ions in order of increasing radius: Cl^- , K^+ , S^{2-} , and Se^{2-} .

Given: four ions

Asked for: order by increasing radius

Strategy:

A Determine which ions form an isoelectronic series. Of those ions, predict their relative sizes based on their nuclear charges. For ions that do not form an isoelectronic series, locate their positions in the periodic table.

B Determine the relative sizes of the ions based on their principal quantum numbers n and their locations within a row.

Solution:

A We see that S and Cl are at the right of the third row, while K and Se are at the far left and right ends of the fourth row, respectively. K^+ , Cl^- , and S^{2-} form an isoelectronic series with the [Ar] closed-shell electron configuration; that is, all three ions contain 18 electrons but have different nuclear charges. Because K^+ has the greatest nuclear charge ($Z = 19$), its radius is smallest, and S^{2-} with $Z = 16$ has the largest radius.

Because selenium is directly below sulfur, we expect the Se^{2-} ion to be even larger than S^{2-} . **B** The order must therefore be $\text{K}^+ < \text{Cl}^- < \text{S}^{2-} < \text{Se}^{2-}$.

Exercise

Based on their positions in the periodic table, arrange these ions in order of increasing size: Br^- , Ca^{2+} , Rb^+ , and Sr^{2+} .

Answer: $\text{Ca}^{2+} < \text{Sr}^{2+} < \text{Rb}^+ < \text{Br}^-$

Summary

A variety of methods have been established to measure the size of a single atom or ion. The **covalent atomic radius** (r_{cov}) is half the internuclear distance in a molecule with two identical atoms bonded to each other, whereas the **metallic atomic radius** (r_{met}) is defined as half the distance between the nuclei of two adjacent atoms in a metallic element. The **van der Waals radius** (r_{vdW}) of an element is

half the internuclear distance between two nonbonded atoms in a solid. Atomic radii decrease from left to right across a row because of the increase in effective nuclear charge due to poor electron screening by other electrons in the same principal shell. Moreover, atomic radii increase from top to bottom down a column because the effective nuclear charge remains relatively constant as the principal quantum number increases. The **ionic radii** of cations and anions are always smaller or larger, respectively, than the parent atom due to changes in electron–electron repulsions, and the trends in ionic radius parallel those in atomic size. A comparison of the dimensions of atoms or ions that have the same number of electrons but different nuclear charges, called an **isoelectronic series**, shows a clear correlation between increasing nuclear charge and decreasing size.

KEY TAKEAWAY

- Ionic radii share the same vertical trend as atomic radii, but the horizontal trends differ due to differences in ionic charges.

CONCEPTUAL PROBLEMS

1. The electrons of the 1s shell have a stronger electrostatic attraction to the nucleus than electrons in the 2s shell. Give two reasons for this.
2. Predict whether Na or Cl has the more stable $1s^2$ shell and explain your rationale.
3. Arrange K, F, Ba, Pb, B, and I in order of decreasing atomic radius.
4. Arrange Ag, Pt, Mg, C, Cu, and Si in order of increasing atomic radius.
5. Using the periodic table, arrange Li, Ga, Ba, Cl, and Ni in order of increasing atomic radius.
6. Element M is a metal that forms compounds of the type MX_2 , MX_3 , and MX_4 , where X is a halogen. What is the expected trend in the ionic radius of M in these compounds? Arrange these compounds in order of decreasing ionic radius of M.
7. The atomic radii of Na and Cl are 190 and 79 pm, respectively, but the distance between sodium and chlorine in NaCl is 282 pm. Explain this discrepancy.
8. Are shielding effects on the atomic radius more pronounced across a row or down a group? Why?
9. What two factors influence the size of an ion relative to the size of its parent atom? Would you expect the ionic radius of S^{2-} to be the same in both MgS and Na_2S ? Why or why not?
10. Arrange Br^- , Al^{3+} , Sr^{2+} , F^- , O^{2-} , and I^- in order of increasing ionic radius.
11. Arrange P^{3-} , N^{3-} , Cl^- , In^{3+} , and S^{2-} in order of decreasing ionic radius.

12. How is an isoelectronic series different from a series of ions with the same charge? Do the cations in magnesium, strontium, and potassium sulfate form an isoelectronic series? Why or why not?
13. What isoelectronic series arises from fluorine, nitrogen, magnesium, and carbon? Arrange the ions in this series by
 - a. increasing nuclear charge.
 - b. increasing size.
14. What would be the charge and electron configuration of an ion formed from calcium that is isoelectronic with
 - a. a chloride ion?
 - b. Ar^+ ?

ANSWERS

1. The 1s shell is closer to the nucleus and therefore experiences a greater electrostatic attraction. In addition, the electrons in the 2s subshell are shielded by the filled $1s^2$ shell, which further decreases the electrostatic attraction to the nucleus.
- 2.
3. $\text{Ba} > \text{K} > \text{Pb} > \text{I} > \text{B} > \text{F}$
- 4.
- 5.
- 6.
7. The sum of the calculated atomic radii of sodium and chlorine *atoms* is 253 pm. The sodium cation is significantly smaller than a neutral sodium atom (102 versus 154 pm), due to the loss of the single electron in the 3s orbital. Conversely, the chloride ion is much larger than a neutral chlorine atom (181 versus 99 pm), because the added electron results in greatly increased electron–electron repulsions within the filled $n = 3$ principal shell. Thus, transferring an electron from sodium to chlorine decreases the radius of sodium by about 50%, but causes the radius of chlorine to almost double. The net effect is that the distance between a sodium ion and a chloride ion in NaCl is *greater* than the sum of the atomic radii of the neutral atoms.
- 8.
- 9.
- 10.

11.

12.

13.

14.

NUMERICAL PROBLEMS

- Plot the ionic charge versus ionic radius using the following data for Mo: Mo^{3+} , 69 pm; Mo^{4+} , 65 pm; and Mo^{5+} , 61 pm. Then use this plot to predict the ionic radius of Mo^{6+} . Is the observed trend consistent with the general trends discussed in the chapter? Why or why not?
- Internuclear distances for selected ionic compounds are given in the following table.
 - If the ionic radius of Li^+ is 76 pm, what is the ionic radius of each of the anions?

	LiF	LiCl	LiBr	LiI
Distance (pm)	209	257	272	296

- What is the ionic radius of Na^+ ?

	NaF	NaCl	NaBr	NaI
Distance (pm)	235	282	298	322

- Arrange the gaseous species Mg^{2+} , P^{3-} , Br^- , S^{2-} , F^- , and N^{3-} in order of increasing radius and justify your decisions.

[1] Atomic radii are often measured in angstroms ($\text{\AA}$), a non-SI unit: $1 \text{ \AA} = 1 \times 10^{-10} \text{ m} = 100 \text{ pm}$.

[2] A similar approach for measuring the size of ions is discussed later in this section.

7.3 Energetics of Ion Formation

LEARNING OBJECTIVE

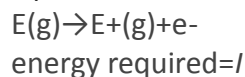
- To correlate ionization energies, electron affinities, and electronegativities with the chemistry of the elements.

We have seen that when elements react, they often gain or lose enough electrons to achieve the valence electron configuration of the nearest noble gas. In this section, we develop a more quantitative approach to predicting such reactions by examining periodic trends in the energy changes that accompany ion formation.

Ionization Energies

Because atoms do not spontaneously lose electrons, energy is required to remove an electron from an atom to form a cation. Chemists define the ionization energy(I) of an element as the amount of energy needed to remove an electron from the gaseous atom E in its ground state. I is therefore the energy required for the reaction

Equation 7.2



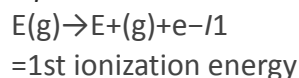
Because an input of energy is required, the ionization energy is always positive ($I > 0$) for the reaction as written in Equation 7.2. Larger values of I mean that the electron is more tightly bound to the atom and harder to remove.

Typical units for ionization energies are kilojoules/mole (kJ/mol) or electron volts (eV):

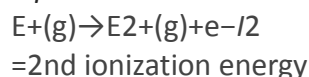
$$1 \text{ eV/atom} = 96.49 \text{ kJ/mol}$$

If an atom possesses more than one electron, the amount of energy needed to remove successive electrons increases steadily. We can define a first ionization energy (I_1), a second ionization energy (I_2), and in general an n th ionization energy (I_n) according to the following reactions:

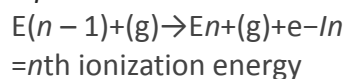
Equation 7.3



Equation 7.4



Equation 7.5



Values for the ionization energies of Li and Be listed in Table 7.4 "Ionization Energies (in kJ/mol) for Removing Successive Electrons from Li and Be" show that successive ionization energies for an element increase steadily; that is, it takes more energy to remove the second electron from an atom than the first, and so forth. There are two reasons for this trend. First, the second electron is being removed from a positively charged species rather than a neutral one, so in accordance with Coulomb's law, more energy is required. Second, removing the first electron reduces the

repulsive forces among the remaining electrons, so the attraction of the remaining electrons to the nucleus is stronger.

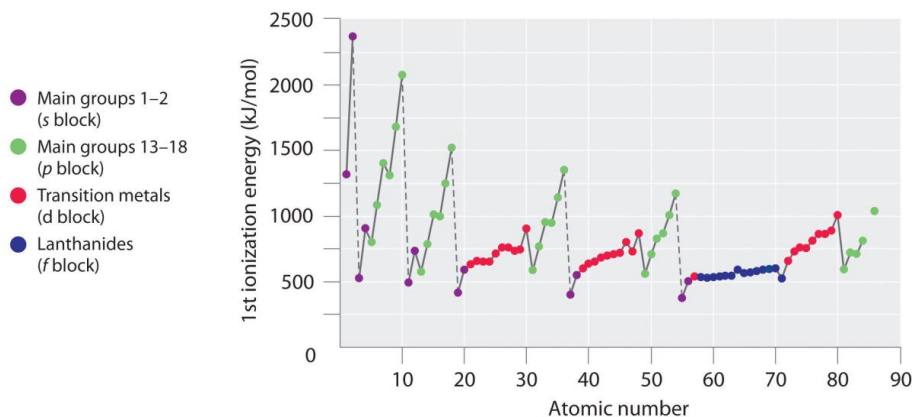
Note the Pattern

Successive ionization energies for an element increase steadily.

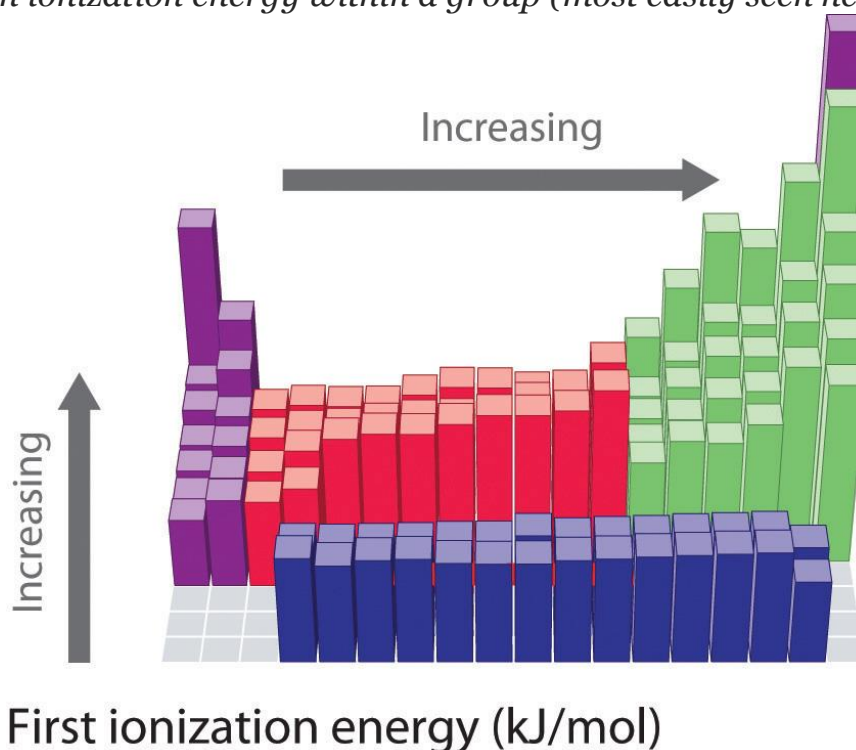
Table 7.4 Ionization Energies (in kJ/mol) for Removing Successive Electrons from Li and Be

Reaction	<i>I</i>	Reaction	<i>I</i>
$Li(g)1s22s1 \rightarrow Li + (g)1s2 + e^-$	$I_1 = 520.2$		$I_1 = 899.5$
$Li + (g)1s2 \rightarrow Li2 + (g)1s1 + e^-$	$I_2 = 7298.2$	$Be(g)1s22s2 \rightarrow Be + (g)1s22s1 + e^-$	$I_2 = 1757.1$
	$I_3 = 11,815.0$	$Li + (g)1s2 \rightarrow Li2 + (g)1s1 + e^-$	$I_3 = 14,848.8$
$Li + (g)1s2 \rightarrow Li2 + (g)1s1 + e^-$		$Be2 + (g)1s2 \rightarrow Be3 + (g)1s1 + e^-$ $Be3 + (g)1s1 \rightarrow Be4 + (g)1s0 + e^-$	$I_4 = 21,006.6$

Source: Data from *CRC Handbook of Chemistry and Physics* (2004).



There is a decrease in ionization energy within a group (most easily seen here



for groups 1 and 18). ■ s block ■ p block ■ d block ■ f block

The most important consequence of the values listed in Table 7.4 "Ionization Energies (in kJ/mol) for Removing Successive Electrons from Li and Be" is that the chemistry of Li is dominated by the Li^+ ion, while the chemistry of Be is dominated by the +2 oxidation state. The energy required to remove the *second* electron from Li

$$\text{Li}^+(\text{g}) \rightarrow \text{Li}^{2+}(\text{g}) + \text{e}^-$$

is more than 10 times greater than the energy needed to remove the first electron. Similarly, the energy required to remove the *third* electron from Be

$$\text{Be}^{2+}(\text{g}) \rightarrow \text{Be}^{3+}(\text{g}) + \text{e}^-$$

is about 15 times greater than the energy needed to remove the first electron and around 8 times greater than the energy required to remove the second electron. Both Li^+ and Be^{2+} have 1s^2 closed-shell configurations, and much more energy is required to remove an electron from the 1s^2 core than from the 2s valence orbital of the same element. The chemical consequences are enormous: lithium (and all the alkali metals) forms compounds with the $1+$ ion but not the $2+$ or $3+$ ions. Similarly, beryllium (and all the alkaline earth metals) forms compounds with the $2+$ ion but not the $3+$ or $4+$ ions. *The energy required to remove electrons from a filled core is prohibitively large and simply cannot be achieved in normal chemical reactions.*

Note the Pattern

The energy required to remove electrons from a filled core is prohibitively large under normal reaction conditions.

Ionization Energies of *s*- and *p*-Block Elements

Ionization energies of the elements in the third row of the periodic table exhibit the same pattern as those of Li and Be (Table 7.5 "Successive Ionization Energies (in kJ/mol) for the Elements in the Third Row of the Periodic Table"): successive ionization energies increase steadily as electrons are removed from the valence orbitals (*3s* or *3p*, in this case), followed by an especially large increase in ionization energy when electrons are removed from filled core levels as indicated by the bold diagonal line in Table 7.5 "Successive Ionization Energies (in kJ/mol) for the Elements in the Third Row of the Periodic Table". Thus in the third row of the periodic table, the largest increase in ionization energy corresponds to removing the fourth electron from Al, the fifth electron from Si, and so forth—that is, removing an electron from an ion that has the valence electron configuration of the preceding noble gas. This pattern explains why the chemistry of the elements normally involves only valence electrons. Too much energy is required to either remove or share the inner electrons.

Table 7.5 Successive Ionization Energies (in kJ/mol) for the Elements in the Third Row of the Periodic Table

Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Na	495.8	4562.4*	—	—	—	—	—
Mg	737.7	1450.7	7732.7	—	—	—	—
Al	577.5	1816.7	2744.8	11,577.5	—	—	—
Si	786.5	1577.1	3231.6	4355.5	16,090.6	—	—
P	1011.8	1907.5	2914.1	4963.6	6274.0	21,267.4	—
S	999.6	2251.8	3357	4556.2	7004.3	8495.8	27,107.4
Cl	1251.2	2297.7	3822	5158.6	6540	9362	11,018.2
Ar	1520.6	2665.9	3931	5771	7238	8781.0	11,995.3
*Inner-shell electron							

Source: Data from *CRC Handbook of Chemistry and Physics* (2004).

EXAMPLE 4

From their locations in the periodic table, predict which of these elements has the highest fourth ionization energy: B, C, or N.

Given: three elements

Asked for: element with highest fourth ionization energy

Strategy:

A List the electron configuration of each element.

B Determine whether electrons are being removed from a filled or partially filled valence shell. Predict which element has the highest fourth ionization energy, recognizing that the highest energy corresponds to the removal of electrons from a filled electron core.

Solution:

A These elements all lie in the second row of the periodic table and have the following electron configurations:

B: $[\text{He}]2s^22p^1$ C: $[\text{He}]2s^22p^2$ N: $[\text{He}]2s^22p^3$

B The fourth ionization energy of an element (I_4) is defined as the energy required to remove the fourth electron:



Because carbon and nitrogen have four and five valence electrons, respectively, their fourth ionization energies correspond to removing an electron from a partially filled valence shell. The fourth ionization energy for boron, however, corresponds to removing an electron from the filled $1s^2$ subshell. This should require much more energy. The actual values are as follows: B, 25,026 kJ/mol; C, 6223 kJ/mol; and N, 7475 kJ/mol.

Exercise

From their locations in the periodic table, predict which of these elements has the lowest second ionization energy: Sr, Rb, or Ar.

Answer: Sr

The first column of data in Table 7.5 "Successive Ionization Energies (in kJ/mol) for the Elements in the Third Row of the Periodic Table" shows that first ionization energies tend to increase across the third row of the periodic table. This is because the valence electrons do not screen each other very well, allowing the effective nuclear charge to increase steadily across the row. The valence electrons are therefore attracted more strongly to the nucleus, so atomic sizes decrease and ionization energies increase. These effects

represent two sides of the same coin: stronger electrostatic interactions between the electrons and the nucleus further increase the energy required to remove the electrons.

However, the first ionization energy decreases at Al ($[\text{Ne}]3s^23p^1$) and at S ($[\text{Ne}]3s^23p^4$). The electrons in aluminum's filled $3s^2$ subshell are better at screening the $3p^1$ electron than they are at screening each other from the nuclear charge, so the s electrons penetrate closer to the nucleus than the p electron does. The decrease at S occurs because the two electrons in the same p orbital repel each other. This makes the S atom slightly less stable than would otherwise be expected, as is true of all the group 16 elements.

The first ionization energies of the elements in the first six rows of the periodic table are plotted in Figure 7.10 "A Plot of Periodic Variation of First Ionization Energy with Atomic Number for the First Six Rows of the Periodic Table". They are presented numerically and graphically in Figure 7.11 "First Ionization Energies of the ". These figures illustrate three important trends:

1. The changes seen in the second (Li to Ne), fourth (K to Kr), fifth (Rb to Xe), and sixth (Cs to Rn) rows of the s and p blocks follow a pattern similar to the pattern described for the third row of the periodic table. The transition metals are included in the fourth, fifth, and sixth rows, however, and the lanthanides are included in the sixth row. The first ionization energies of the transition metals are somewhat similar to one another, as are those of the lanthanides. Ionization energies increase from left to right across each row, with discrepancies occurring at ns^2np^3 (group 13), ns^2np^4 (group 16), and $ns^2(n-1)d^{10}$ (group 12) electron configurations.
2. First ionization energies generally decrease down a column. Although the principal quantum number n increases down a column, filled inner shells are effective at screening the valence electrons, so there is a relatively small increase in the effective nuclear charge. Consequently, the atoms become larger as they acquire electrons. Valence electrons that are farther from the nucleus are less tightly bound, making them easier to remove, which causes ionization energies to decrease. *A larger radius corresponds to a lower ionization energy.*
3. Because of the first two trends, the elements that form positive ions most easily (have the lowest ionization energies) lie in the lower left corner of the periodic table, whereas those that are hardest to ionize lie in the upper right corner of the periodic table.

Consequently, ionization energies generally increase diagonally from lower left (Cs) to upper right (He).

Note the Pattern

Generally, I_1 increases diagonally from the lower left of the periodic table to the upper right.

Figure 7.10 A Plot of Periodic Variation of First Ionization Energy with Atomic Number for the First Six Rows of the Periodic Table

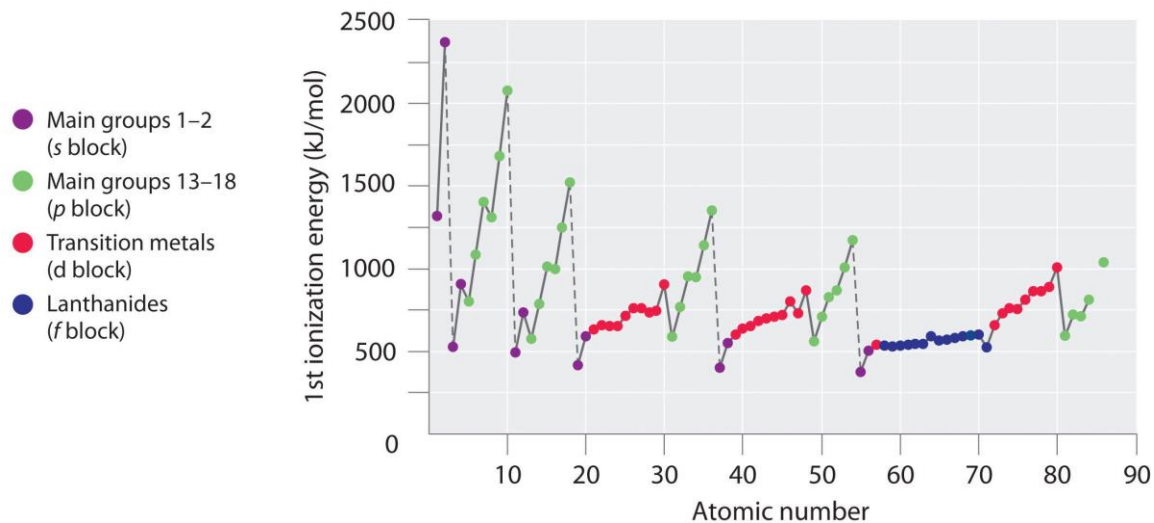
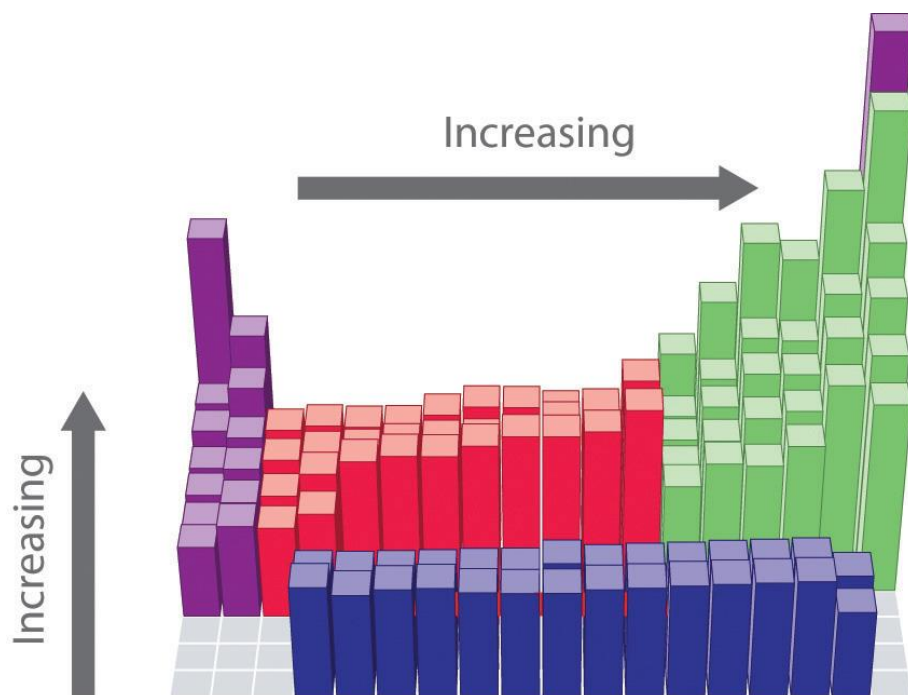


Figure 7.11 First Ionization Energies of the s-, p-, d-, and f-Block Elements



First ionization energy (kJ/mol)

■ s block
 ■ p block
 ■ d block
 ■ f block

1																	18	
1	H 1312.0	2	375.7 kJ/mol 2372.3 kJ/mol										13	14	15	16	17	He 2372.3
2	Li 520.2	Be 899.5											B 800.6	C 1086.5	N 1402.3	O 1313.9	F 1681.0	Ne 2080.7
3	Na 495.8	Mg 737.7	3	4	5	6	7	8	9	10	11	12	Al 577.5	Si 786.5	P 1011.8	S 999.6	Cl 1251.2	Ar 1520.6
4	K 418.8	Ca 589.8	Sc 633.1	Ti 658.8	V 650.9	Cr 652.9	Mn 717.3	Fe 762.5	Co 760.4	Ni 737.1	Cu 745.5	Zn 906.4	Ga 578.8	Ge 762.2	As 944.5	Se 941.0	Br 1139.9	Kr 1350.8
5	Rb 403.0	Sr 549.5	Y 599.9	Zr 640.1	Nb 652.1	Mo 684.3	Tc 702	Ru 710.2	Rh 719.7	Pd 804.4	Ag 731.0	Cd 867.8	In 558.3	Sn 708.6	Sb 830.6	Te 869.3	I 1008.4	Xe 1170.3
6	Cs 375.7	Ba 502.9	La 538.1	Hf 658.5	Ta 728.4	W 758.8	Re 755.8	Os 814.2	Ir 865.2	Pt 864.4	Au 890.1	Hg 1007.1	Tl 589.4	Pb 715.6	Bi 703.0	Po 812.1	At	Rn 1037.1
7	Fr 393.0	Ra 509.3	Ac 498.8	Rf 580	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup			
Lanthanides				Ce 534.4	Pr 528.1	Nd 533.1	Pm 538.6	Sm 544.5	Eu 547.1	Gd 593.4	Tb 565.8	Dy 573.0	Ho 581.0	Er 589.3	Tm 596.7	Yb 603.4	Lu 523.5	
Actinides				Th 608.5	Pa 568	U 597.6	Np 604.5	Pu 581.4	Am 576.4	Cm 578.1	Bk 598.0	Cf 606.1	Es 619	Fm 627	Md 635	No 642	Lr 472.8	

The darkness of the shading inside the cells of the table indicates the relative magnitudes of the ionization energies. Elements in gray have undetermined first ionization energies.

Source: Data from CRC Handbook of Chemistry and Physics (2004).

Gallium (Ga), which is the first element following the first row of transition metals, has the following electron configuration: $[\text{Ar}]4s^23d^{10}4p^1$. Its first ionization energy is significantly lower than that of the immediately preceding element, zinc, because the filled $3d^{10}$ subshell of gallium lies inside the $4p$ subshell, screening the single $4p$ electron from the nucleus. Experiments have revealed something of even greater interest: the second and third electrons that are removed when gallium is ionized come from the $4s^2$ orbital, *not* the $3d^{10}$ subshell. The chemistry of gallium is dominated by the resulting Ga^{3+} ion, with its $[\text{Ar}]3d^{10}$ electron configuration. This and similar electron configurations are particularly stable and are often encountered in the heavier p -block elements. They are sometimes referred to as pseudo noble gas configurations. In fact, for elements that exhibit these configurations, *no chemical compounds are known in which electrons are removed from the $(n - 1)d^{10}$ filled subshell.*

Ionization Energies of Transition Metals and Lanthanides

As we noted, the first ionization energies of the transition metals and the lanthanides change very little across each row. Differences in their second and third ionization energies are also rather small, in sharp contrast to the pattern seen with the s - and p -block elements. The reason for these similarities is that the transition metals and the lanthanides form cations by losing the ns electrons before the $(n - 1)d$ or $(n - 2)f$ electrons, respectively. This means that transition metal cations have $(n - 1)d^n$ valence electron configurations, and lanthanide cations have $(n - 2)f^n$ valence electron configurations. Because the $(n - 1)d$ and $(n - 2)f$ shells are closer to the nucleus than the ns shell, the $(n - 1)d$ and $(n - 2)f$ electrons screen the ns electrons quite effectively, reducing the effective nuclear charge felt by the ns electrons. As Z increases, the increasing positive charge is largely canceled by the electrons added to the $(n - 1)d$ or $(n - 2)f$ orbitals.

That the ns electrons are removed before the $(n - 1)d$ or $(n - 2)f$ electrons may surprise you because the orbitals were filled in the reverse order. (For more information on shell filling order, see Chapter 6 "The Structure of Atoms", Section 6.6 "Building Up the Periodic Table".) In fact, the ns , the $(n - 1)d$, and the $(n - 2)f$ orbitals are so close to one another in energy, and interpenetrate one another so extensively, that very small changes in the effective nuclear charge can change the order of their energy levels. As

the d orbitals are filled, the effective nuclear charge causes the $3d$ orbitals to be slightly lower in energy than the $4s$ orbitals. The $[\text{Ar}]3d^2$ electron configuration of Ti^{2+} tells us that the $4s$ electrons of titanium are lost before the $3d$ electrons; this is confirmed by experiment. A similar pattern is seen with the lanthanides, producing cations with an $(n - 2)f^n$ valence electron configuration. Because their first, second, and third ionization energies change so little across a row, these elements have important *horizontal* similarities in chemical properties in addition to the expected vertical similarities. For example, all the first-row transition metals except scandium form stable compounds as M^{2+} ions, whereas the lanthanides primarily form compounds in which they exist as M^{3+} ions.

EXAMPLE 5

Use their locations in the periodic table to predict which element has the lowest first ionization energy: Ca, K, Mg, Na, Rb, or Sr.

Given: six elements

Asked for: element with lowest first ionization energy

Strategy:

Locate the elements in the periodic table. Based on trends in ionization energies across a row and down a column, identify the element with the lowest first ionization energy.

Solution:

These six elements form a rectangle in the two far-left columns of the periodic table. Because we know that ionization energies increase from left to right in a row and from bottom to top of a column, we can predict that the element at the bottom left of the rectangle will have the lowest first ionization energy: Rb.

Exercise

Use their locations in the periodic table to predict which element has the highest first ionization energy:

As, Bi, Ge, Pb, Sb, or Sn.

Answer: As

Electron Affinities

The electron affinity (EA) of an element E is defined as the energy change that occurs when an electron is added to a gaseous atom:

Equation 7.6



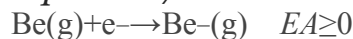
Unlike ionization energies, which are always positive for a neutral atom because energy is required to remove an electron, electron affinities can be negative (energy is released when an electron is added), positive (energy must be added to the system to produce an anion), or zero (the process is energetically neutral). This sign convention is consistent with our discussion of energy changes in Chapter 5 "Energy Changes in Chemical Reactions", where a negative value corresponded to the energy change for an exothermic process, which is one in which heat is released. Chlorine has the most negative electron affinity of any element, which means that more energy is released when an electron is added to a gaseous chlorine atom than to an atom of any other element:

Equation 7.7



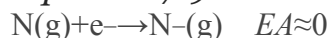
In contrast, beryllium does not form a stable anion, so its effective electron affinity is

Equation 7.8



Nitrogen is unique in that it has an electron affinity of approximately zero. Adding an electron neither releases nor requires a significant amount of energy:

Equation 7.9



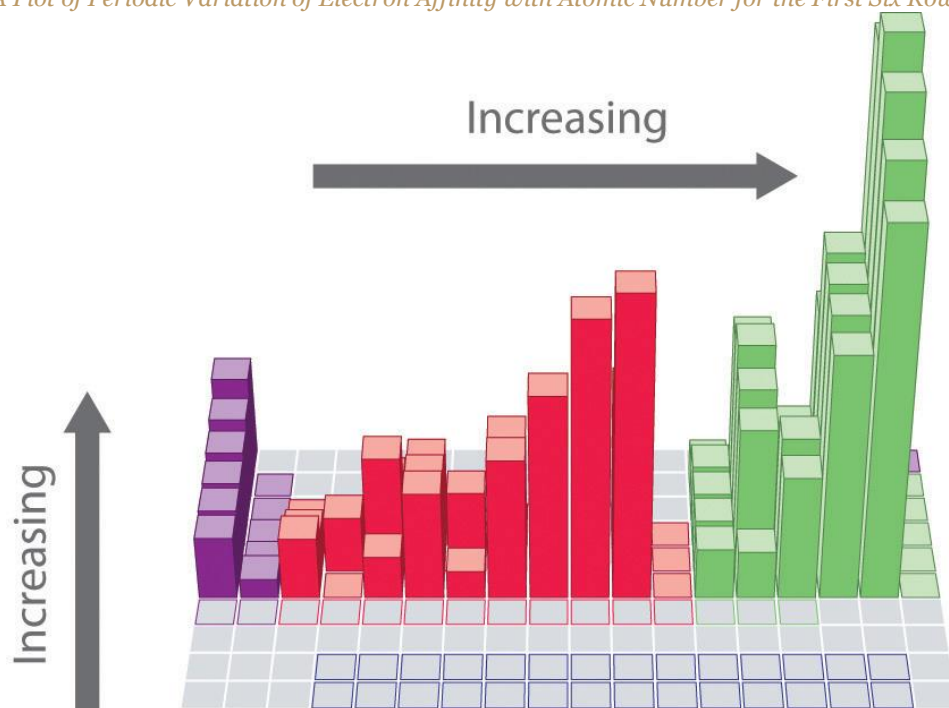
Electron affinities for the first six rows of the periodic table are plotted in Figure 7.12 "A Plot of Periodic Variation of Electron Affinity with Atomic Number for the First Six Rows of the Periodic Table" and presented numerically and graphically in Figure 7.13 "Electron Affinities (in kJ/mol) of the ". Both figures show that the halogens, with their ns^2np^5 valence electron configuration, have the most negative electron affinities. In general, electron affinities become more negative as we go across a row of the periodic table. This pattern corresponds to the increased effective nuclear charge felt by the valence electrons across a row, which leads to increased electrostatic attraction between the added electron and the nucleus (a more negative electron affinity). The trend, however, is not as uniform as the one observed for ionization energies. Some of the alkaline earths (group 2), the elements of group 12, and all the noble gases (group 18) have effective electron affinities that are greater than or equal to zero, while the electron affinities for

the elements of group 15 are usually less negative than those for the group 14 elements. These exceptions can be explained by the groups' electron configurations. Both the alkaline earth metals and the noble gases have valence electron shells with filled subshells (ns^2 and ns^2np^6 , respectively). In each case, the added electron must enter a higher-energy orbital, requiring an input of energy. All the group 15 elements have an ns^2np^3 valence electron configuration, in which each of the three p orbitals has a single electron, in accordance with Hund's rule; hence the added electron must enter an already occupied p orbital. The resulting electron–electron repulsions destabilize the anion, causing the electron affinities of these elements to be less negative than we would otherwise expect. In the case of nitrogen, the $2p$ orbital is quite small, and the electron–electron repulsions are so strong that nitrogen has approximately zero affinity for an extra electron. In the heavier elements, however, the effect is relatively small because they have larger valence p orbitals.

Note the Pattern

Generally, electron affinities become more negative across a row of the periodic table.

Figure 7.12 A Plot of Periodic Variation of Electron Affinity with Atomic Number for the First Six Rows of the



Magnitude of electron affinity (kJ/mol),
s-, p-, and d-block elements

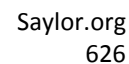
Periodic Table

■ s block

■ p block

■ d block

■ f block



largest radii, which have the lowest ionization energies (affinity for their own valence electrons), also have the lowest affinity for an added electron. There are, however, two major exceptions to this trend:

1. The electron affinities of elements B through F in the second row of the periodic table are *less* negative than those of the elements immediately below them in the third row. Apparently, the increased electron–electron repulsions experienced by electrons confined to the relatively small $2p$ orbitals overcome the increased electron–nucleus attraction at short nuclear distances. Fluorine, therefore, has a lower affinity for an added electron than does chlorine. Consequently, the elements of the *third* row ($n = 3$) have the most negative electron affinities. Farther down a column, the attraction for an added electron decreases because the electron is entering an orbital more distant from the nucleus. Electron–electron repulsions also decrease because the valence electrons occupy a greater volume of space. These effects tend to cancel one another, so the changes in electron affinity within a family are much smaller than the changes in ionization energy.
2. The electron affinities of the alkaline earth metals become more negative from Be to Ba. As you learned in Chapter 6 "The Structure of Atoms", the energy separation between the filled ns^2 and the empty np subshells decreases with increasing n , so that formation of an anion from the heavier elements becomes energetically more favorable.

Note the Pattern

In general, electron affinities become more negative across a row and less negative down a column.

The equations for second and higher electron affinities are analogous to those for second and higher ionization energies:

Equation 7.10



Equation 7.11



As we have seen, the first electron affinity can be greater than or equal to zero or negative, depending on the electron configuration of the atom. In contrast, the second electron affinity is *always* positive because the increased electron–

electron repulsions in a dianion are far greater than the attraction of the nucleus for the extra electrons. For example, the first electron affinity of oxygen is -141 kJ/mol , but the second electron affinity is $+744 \text{ kJ/mol}$:

Equation 7.12



Equation 7.13



Thus the formation of a gaseous oxide (O^{2-}) ion is energetically quite unfavorable:

Equation 7.14



Similarly, the formation of all common dianions (such as S^{2-}) or trianions (such as P^{3-}) is energetically unfavorable in the gas phase.

Note the Pattern

While first electron affinities can be negative, positive, or zero, second electron affinities are always positive.

If energy is required to form both positively charged ions and monatomic polyanions, why do ionic compounds such as MgO , Na_2S , and Na_3P form at all? The key factor in the formation of stable ionic compounds is the favorable electrostatic interactions between the cations and the anions *in the crystalline salt*. We will describe the energetics of ionic compounds in more detail in Chapter 8 "Ionic versus Covalent Bonding".

EXAMPLE 6

Based on their positions in the periodic table, which of Sb, Se, or Te would you predict to have the most negative electron affinity?

Given: three elements

Asked for: element with most negative electron affinity

Strategy:

A Locate the elements in the periodic table. Use the trends in electron affinities going down a column for elements in the same group. Similarly, use the trends in electron affinities from left to right for elements in the same row.

B Place the elements in order, listing the element with the most negative electron affinity first.

Solution:

A We know that electron affinities become less negative going down a column (except for the anomalously low electron affinities of the elements of the second row), so we can predict that the electron affinity of Se is more negative than that of Te. We also know that electron affinities become more negative from left to right across a row, and that the group 15 elements tend to have values that are less negative than expected. Because Sb is located to the left of Te and belongs to group 15, we predict that the electron affinity of Te is more negative than that of Sb. The overall order is $\text{Se} < \text{Te} < \text{Sb}$, so Se has the most negative electron affinity among the three elements.

Exercise

Based on their positions in the periodic table, which of Rb, Sr, or Xe would you predict to most likely form a gaseous anion?

Answer: Rb

Electronegativity

The elements with the highest ionization energies are generally those with the most negative electron affinities, which are located toward the upper right corner of the periodic table (compare Figure 7.11 "First Ionization Energies of the " and Figure 7.13 "Electron Affinities (in kJ/mol) of the "). Conversely, the elements with the lowest ionization energies are generally those with the least negative electron affinities and are located in the lower left corner of the periodic table.

Because the tendency of an element to gain or lose electrons is so important in determining its chemistry, various methods have been developed to quantitatively describe this tendency. The most important method uses a measurement called electronegativity (represented by the Greek letter *chi*, χ , pronounced “ky” as in “sky”), defined as the *relative* ability of an atom to attract electrons to itself *in a chemical compound*. Elements with high electronegativities tend to acquire electrons in chemical reactions and are

found in the upper right corner of the periodic table. Elements with low electronegativities tend to lose electrons in chemical reactions and are found in the lower left corner of the periodic table.

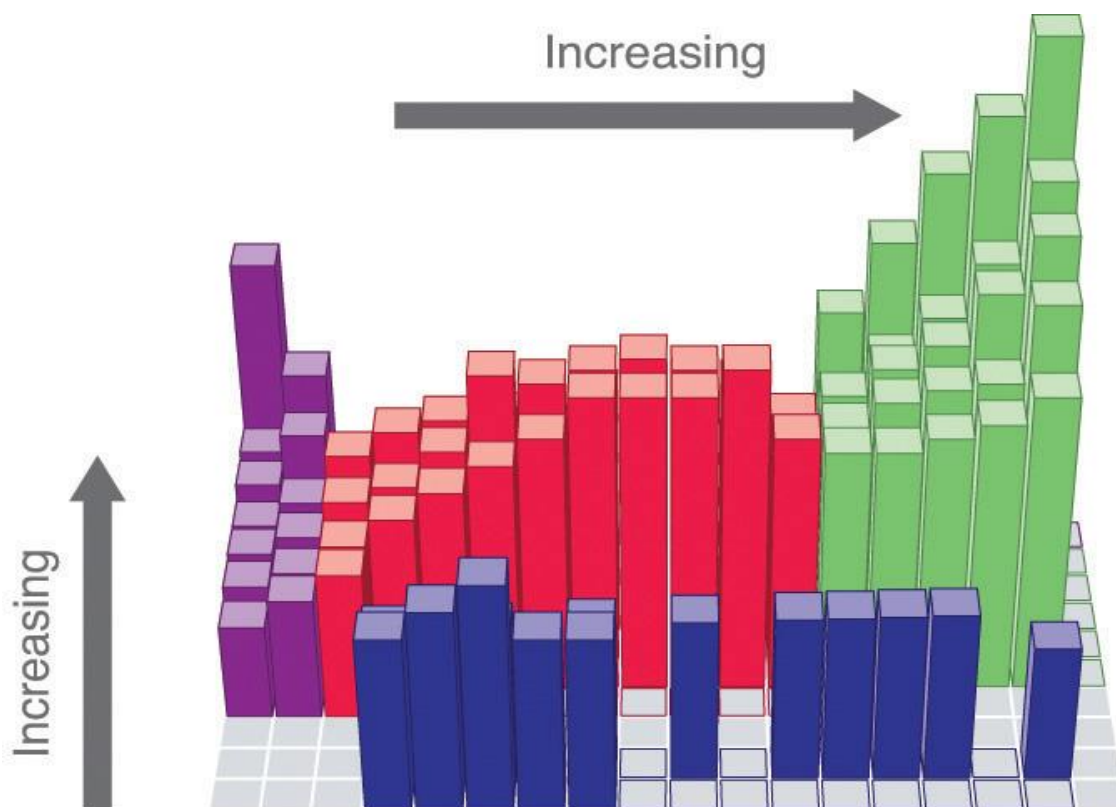
Unlike ionization energy or electron affinity, the electronegativity of an atom is not a simple, fixed property that can be directly measured in a single experiment. In fact, an atom's electronegativity should depend to some extent on its chemical environment because the properties of an atom are influenced by its neighbors in a chemical compound. Nevertheless, when different methods for measuring the electronegativity of an atom are compared, they all tend to assign similar relative values to a given element. For example, all scales predict that fluorine has the highest electronegativity and cesium the lowest of the stable elements, which suggests that all the methods are measuring the same fundamental property.

The Pauling Electronegativity Scale

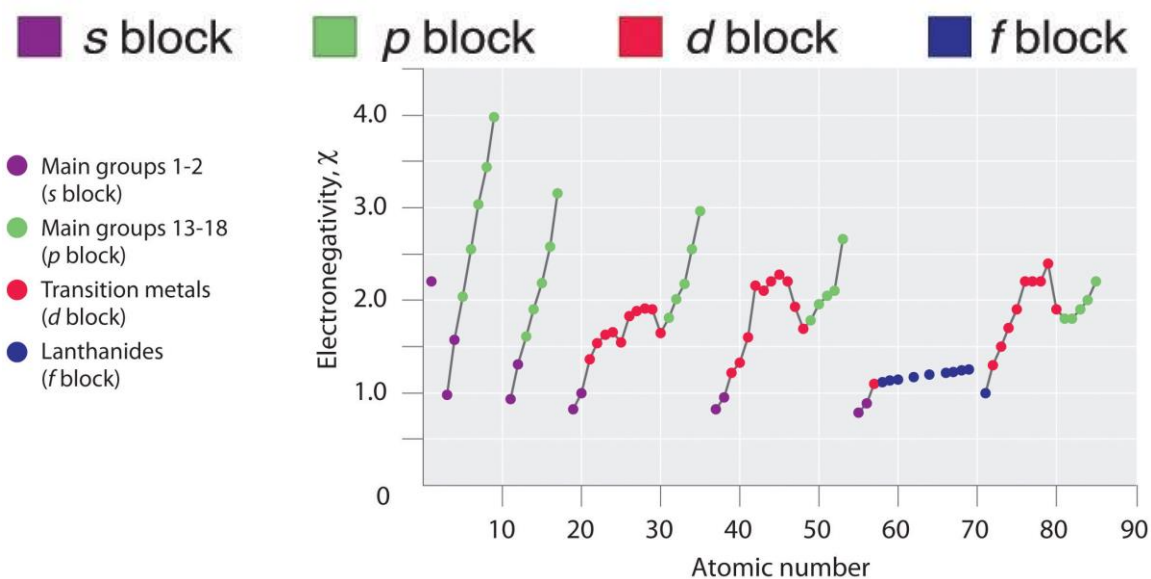
The original electronegativity scale, developed in the 1930s by Linus Pauling (1901– 1994) was based on measurements of the strengths of covalent bonds between different elements. Pauling arbitrarily set the electronegativity of fluorine at 4.0 (although today it has been refined to 3.98), thereby creating a scale in which all elements have values between 0 and 4.0.

Periodic variations in Pauling's electronegativity values are illustrated in Figure 7.14 "A Plot of Periodic Variation of Electronegativity with Atomic Number for the First Six Rows of the Periodic Table" and Figure 7.15 "Pauling Electronegativity Values of the ". If we ignore the inert gases and elements for which no stable isotopes are known, we see that fluorine ($\chi = 3.98$) is the most electronegative element and cesium is the least electronegative nonradioactive element ($\chi = 0.79$). Because electronegativities generally increase diagonally from the lower left to the upper right of the periodic table, elements lying on diagonal lines running from upper left to lower right tend to have comparable values (e.g., O and Cl and N, S, and Br).

Figure 7.14 A Plot of Periodic Variation of Electronegativity with Atomic Number for the First Six Rows of the Periodic Table



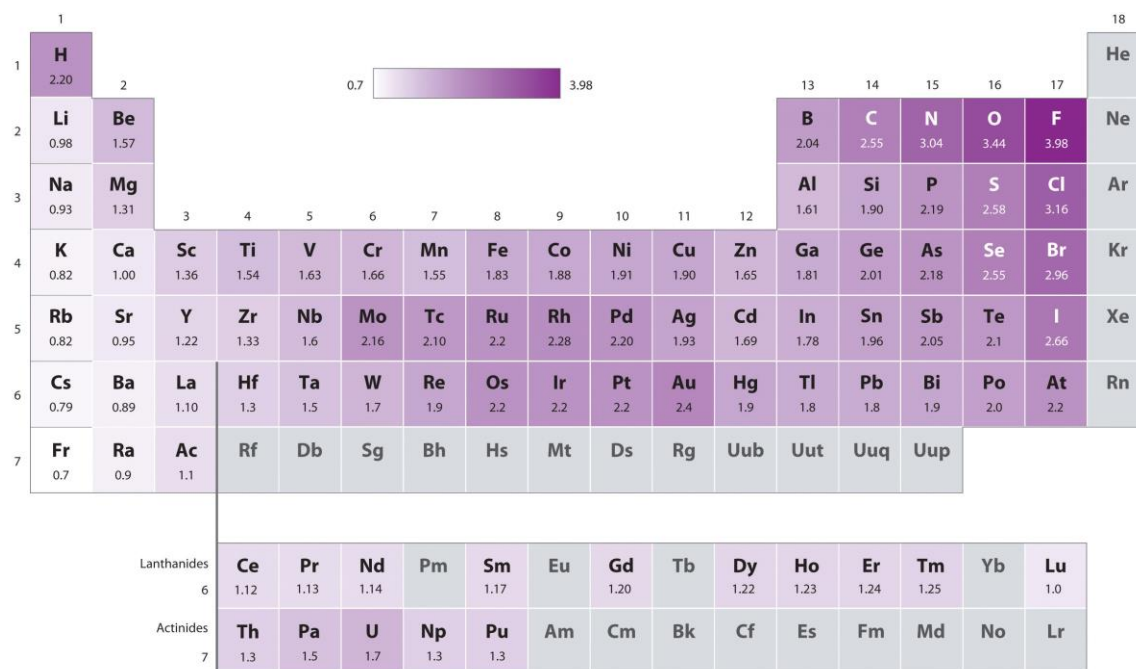
Electronegativity, χ



Linus Pauling (1901–1994)

Pauling won two Nobel Prizes, one for chemistry in 1954 and one for peace in 1962. When he was nine, Pauling's father died, and his mother tried to convince him to quit school to support the family. He did not quit school but was denied a high school degree because of his refusal to take a civics class.

Figure 7.15 Pauling Electronegativity Values of the s-, p-, d-, and f-Block Elements



Values for most of the actinides are approximate. Elements for which no data are available are shown in gray.

Source: Data from L. Pauling, *The Nature of the Chemical Bond*, 3rd ed. (1960).

Pauling's method is limited by the fact that many elements do not form stable covalent compounds with other elements; hence their electronegativities cannot be measured by his method. Other definitions have since been developed that address this problem.

The Mulliken Definition

An alternative method for measuring electronegativity was developed by Robert Mulliken (1896–1986; Nobel Prize in Chemistry 1966). Mulliken noticed that elements with large first ionization energies tend to have very negative electron affinities and gain electrons in chemical reactions. Conversely, elements with small first ionization energies tend to have slightly negative (or even positive) electron affinities and lose electrons in chemical reactions. Mulliken recognized that an atom's tendency to gain or lose electrons

could therefore be described quantitatively by the average of the values of its first ionization energy and the absolute value of its electron affinity. Using our definition of electron affinity, we can write Mulliken's original expression for electronegativity as follows:^[1]

Equation 7.15

$$X = (I + |EA|) / 2$$

Elements with a large first ionization energy and a very negative electron affinity have a large positive value in the numerator of Equation 7.15, so their electronegativity is high. Elements with a small first ionization energy and a small electron affinity have a small positive value for the numerator in Equation 7.15, so they have a low electronegativity.^[2]

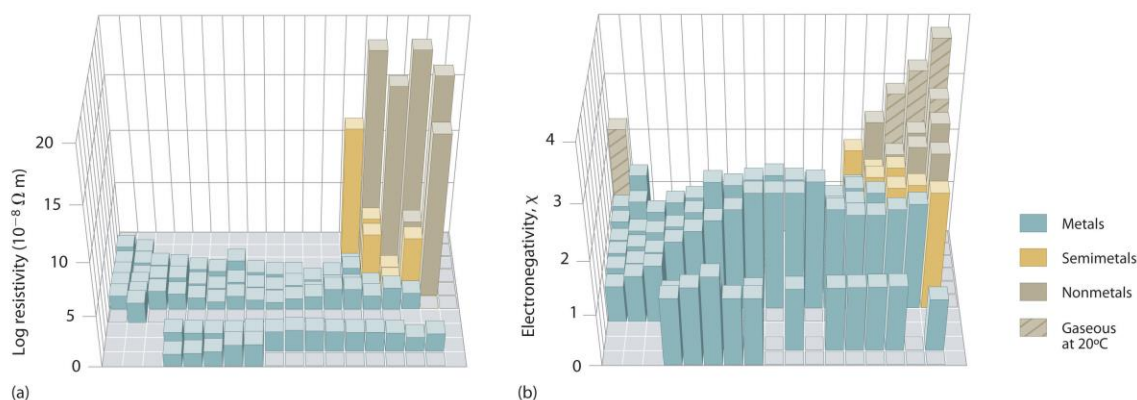
As noted previously, all electronegativity scales give essentially the same results for one element relative to another. Even though the Mulliken scale is based on the properties of individual *atoms* and the Pauling scale is based on the properties of atoms in *molecules*, they both apparently measure the same basic property of an element. In the following discussion, we will focus on the relationship between electronegativity and the tendency of *atoms* to form positive or negative ions. We will therefore be implicitly using the Mulliken definition of electronegativity. Because of the parallels between the Mulliken and Pauling definitions, however, the conclusions are likely to apply to atoms in molecules as well.

Electronegativity Differences between Metals and Nonmetals

An element's electronegativity provides us with a single value that we can use to characterize the chemistry of an element. Elements with a high electronegativity ($\chi \geq 2.2$ in Figure 7.15 "Pauling Electronegativity Values of the ") have very negative affinities and large ionization potentials, so they are generally nonmetals and electrical insulators that tend to gain electrons in chemical reactions (i.e., they are *oxidants*). In contrast, elements with a low electronegativity ($\chi \leq 1.8$) have electron affinities that have either positive or small negative values and small ionization potentials, so they are generally metals and good electrical conductors that tend to lose their valence electrons in chemical reactions (i.e., they are *reductants*). In between the metals and nonmetals, along the heavy diagonal line running from B to At in Figure 1.24 "The Periodic Table Showing the Elements in Order of Increasing ", is a group of elements with intermediate electronegativities ($\chi \sim 2.0$). These are the **semimetals**, elements that have some of the chemical properties of both nonmetals and metals. The distinction between metals and nonmetals is

one of the most fundamental we can make in categorizing the elements and predicting their chemical behavior. Figure 7.16 "Three-Dimensional Plots Demonstrating the Relationship between Electronegativity and the Metallic/Nonmetallic Character of the Elements" shows the strong correlation between electronegativity values, metallic versus nonmetallic character, and location in the periodic table.

Figure 7.16 Three-Dimensional Plots Demonstrating the Relationship between Electronegativity and the Metallic/Nonmetallic Character of the Elements



(a) A plot of electrical resistivity (measured resistivity to electron flow) at or near room temperature shows that substances with high resistivity (little to no measured electron flow) are electrical insulators, whereas substances with low resistivity (high measured electron flow) are metals. (b) A plot of Pauling electronegativities for a like set of elements shows that high electronegativity values ($\geq$ about 2.2) correlate with high electrical resistivities (insulators). Low electronegativity values ($\leq$ about 2.2) correlate with low resistivities (metals). Because electrical resistivity is typically measured only for solids and liquids, the gaseous elements do not appear in part (a).

The rules for assigning oxidation states that were introduced in Chapter 3 "Chemical Reactions" are based on the relative electronegativities of the elements; the more electronegative element in a binary compound is assigned a negative oxidation state. As we shall see, electronegativity values are also used to predict bond energies, bond polarities, and the kinds of reactions that compounds undergo.

EXAMPLE 7

On the basis of their positions in the periodic table, arrange Cl, Se, Si, and Sr in order of increasing electronegativity and classify each as a metal, a nonmetal, or a semimetal.

Given: four elements

Asked for: order by increasing electronegativity and classification

Strategy:

A Locate the elements in the periodic table. From their diagonal positions from lower left to upper right, predict their relative electronegativities.

B Arrange the elements in order of increasing electronegativity.

C Classify each element as a metal, a nonmetal, or a semimetal according to its location about the diagonal belt of semimetals running from B to At.

Solution:

A Electronegativity increases from lower left to upper right in the periodic table (Figure 7.15 "Pauling Electronegativity Values of the "). Because Sr lies far to the left of the other elements given, we can predict that it will have the lowest electronegativity. Because Cl lies above and to the right of Se, we can predict that $\chi_{\text{Cl}} > \chi_{\text{Se}}$. Because Si is located farther from the upper right corner than Se or Cl, its electronegativity should be lower than those of Se and Cl but greater than that of Sr. **B** The overall order is therefore

$$\chi_{\text{Sr}} < \chi_{\text{Si}} < \chi_{\text{Se}} < \chi_{\text{Cl}}.$$

C To classify the elements, we note that Sr lies well to the left of the diagonal belt of semimetals running from B to At; while Se and Cl lie to the right and Si lies in the middle. We can predict that Sr is a metal, Si is a semimetal, and Se and Cl are nonmetals.

Exercise

On the basis of their positions in the periodic table, arrange Ge, N, O, Rb, and Zr in order of increasing electronegativity and classify each as a metal, a nonmetal, or a semimetal.

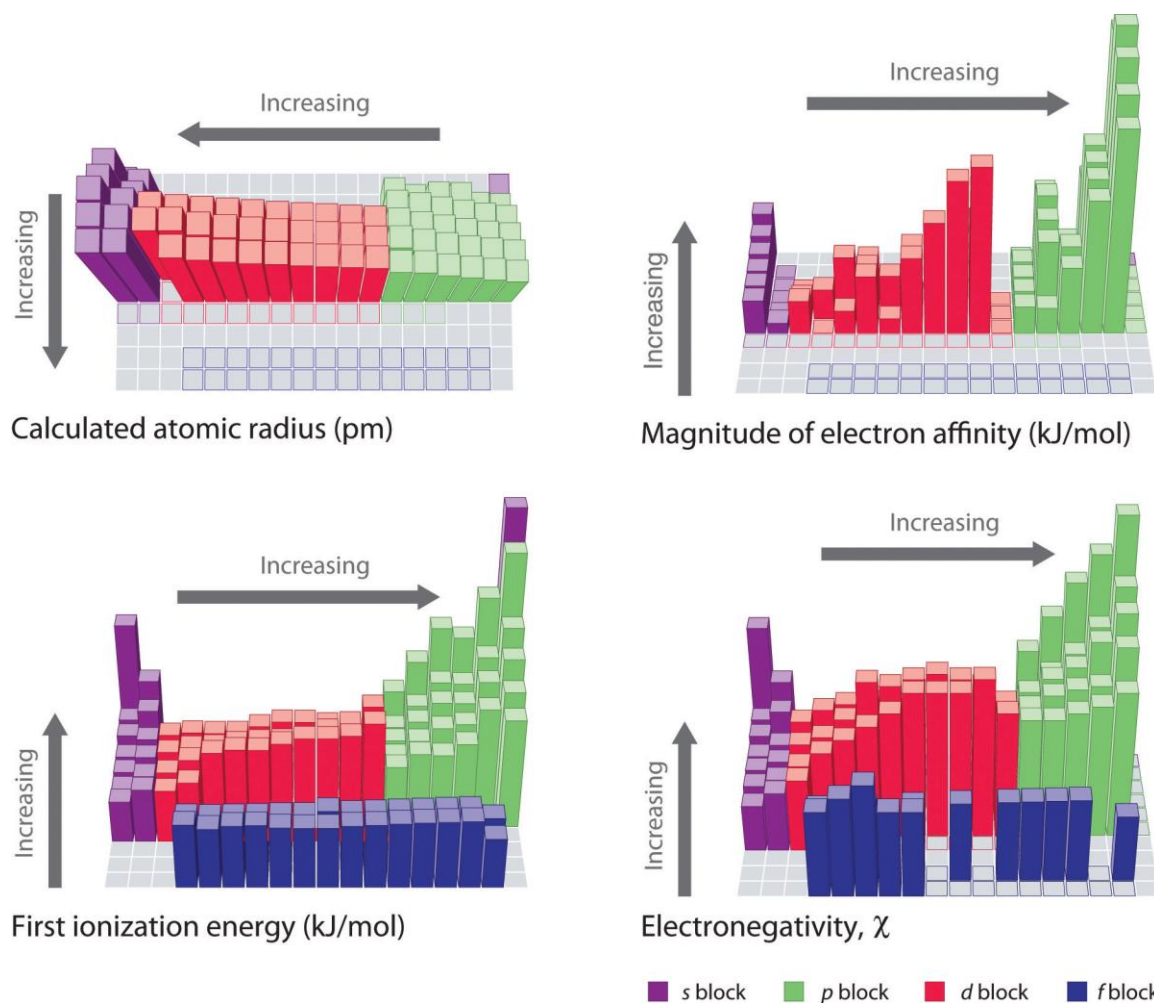
Answer: Rb < Zr < Ge < N < O; metals (Rb, Zr); semimetal (Ge); nonmetal (N, O)

Note the Pattern

Electronegativity values increase from lower left to upper right in the periodic table.

The trends in periodic properties are summarized in Figure 7.17 "Summary of Major Periodic Trends". As discussed, atomic radii decrease from lower left to upper right in the periodic table; ionization energies become more positive, electron affinities become more negative, and electronegativities increase from the lower left to the upper right.

Figure 7.17 Summary of Major Periodic Trends



The general trends for the first ionization energy, electron affinity, and electronegativity are opposite to the general trend for covalent atomic radius.

Summary

The tendency of an element to lose or gain electrons is one of the most important factors in determining the kind of compounds it forms. Periodic behavior is most evident for **ionization energy (I)**, the energy required to remove an electron from a gaseous atom. The energy required to remove successive electrons from an atom increases steadily, with a substantial increase occurring with the removal of an electron from a filled inner shell. Consequently, only valence electrons can be removed in chemical reactions, leaving the filled inner shell intact. Ionization energies explain the common oxidation states observed for the elements. Ionization energies increase diagonally from the lower left of the periodic table to the upper right. Minor deviations from this trend can be explained in terms of particularly stable electronic configurations, called **pseudo noble gas configurations**, in either the parent atom or the resulting

ion. The **electron affinity (EA)** of an element is the energy change that occurs when an electron is added to a gaseous atom to give an anion. In general, elements with the most negative electron affinities (the highest affinity for an added electron) are those with the smallest size and highest ionization energies and are located in the upper right corner of the periodic table. The **electronegativity (χ)** of an element is the relative ability of an atom to attract electrons to itself in a chemical compound and increases diagonally from the lower left of the periodic table to the upper right. The Pauling electronegativity scale is based on measurements of the strengths of covalent bonds between different atoms, whereas the Mulliken electronegativity of an element is the average of its first ionization energy and the absolute value of its electron affinity. Elements with a high electronegativity are generally nonmetals and electrical insulators and tend to behave as oxidants in chemical reactions. Conversely, elements with a low electronegativity are generally metals and good electrical conductors and tend to behave as reductants in chemical reactions.

KEY TAKEAWAY

- Generally, the first ionization energy and electronegativity values increase diagonally from the lower left of the periodic table to the upper right, and electron affinities become more negative across a row.

CONCEPTUAL PROBLEMS

1. Identify each statement as either true or false and explain your reasoning.
 - a. Ionization energies increase with atomic radius.
 - b. Ionization energies decrease down a group.
 - c. Ionization energies increase with an increase in the magnitude of the electron affinity.
 - d. Ionization energies decrease diagonally across the periodic table from He to Cs.
 - e. Ionization energies depend on electron configuration.
 - f. Ionization energies decrease across a row.
2. Based on electronic configurations, explain why the first ionization energies of the group 16 elements are lower than those of the group 15 elements, which is contrary to the general trend.
3. The first through third ionization energies do not vary greatly across the lanthanides. Why? How does the effective nuclear charge experienced by the ns electron change when going from left to right (with increasing atomic number) in this series?

- Most of the first row transition metals can form at least two stable cations, for example iron(II) and iron(III). In contrast, scandium and zinc each form only a single cation, the Sc^{3+} and Zn^{2+} ions, respectively. Use the electron configuration of these elements to provide an explanation.
- Of the elements Nd, Al, and Ar, which will readily form(s) +3 ions? Why?
- Orbital energies can reverse when an element is ionized. Of the ions B^{3+} , Ga^{3+} , Pr^{3+} , Cr^{3+} , and As^{3+} , in which would you expect this reversal to occur? Explain your reasoning.
- The periodic trends in electron affinities are not as regular as periodic trends in ionization energies, even though the processes are essentially the converse of one another. Why are there so many more exceptions to the trends in electron affinities compared to ionization energies?
- Elements lying on a lower right to upper left diagonal line cannot be arranged in order of increasing electronegativity according to where they occur in the periodic table. Why?
- Why do ionic compounds form, if energy is required to form gaseous cations?
- Why is Pauling's definition of electronegativity considered to be somewhat limited?
- Based on their positions in the periodic table, arrange Sb, O, P, Mo, K, and H in order of increasing electronegativity.
- Based on their positions in the periodic table, arrange V, F, B, In, Na, and S in order of decreasing electronegativity.

ANSWERS

5. Both Al and Nd will form a cation with a +3 charge. Aluminum is in Group 13, and loss of all three valence electrons will produce the Al^{3+} ion with a noble gas configuration. Neodymium is a lanthanide, and all of the lanthanides tend to form +3 ions because the ionization potentials do not vary greatly across the row, and a +3 charge can be achieved with many oxidants.

6. $\text{K} < \text{Mo} \approx \text{Sb} < \text{P} \approx \text{H} < \text{O}$

NUMERICAL PROBLEMS

- The following table gives values of the first and third ionization energies for selected elements:

Number of Electrons	Element	$I_1 (\text{E} \rightarrow \text{E}^+ + \text{e}^-, \text{ kJ/mol})$	Element	$I_3 (\text{E}^{2+} \rightarrow \text{E}^{3+} + \text{e}^-, \text{ kJ/mol})$

Number of Electrons	Element	I_1 ($E \rightarrow E^+ + e^-$, kJ/mol)	Element	I_3 ($E^{2+} \rightarrow E^{3+} + e^-$, kJ/mol)
11	Na	495.9	Al	2744.8
12	Mg	737.8	Si	3231.6
13	Al	577.6	P	2914.1
14	Si	786.6	S	3357
15	P	1011.9	Cl	3822
16	S	999.6	Ar	3931
17	Cl	1251.2	K	4419.6
18	Ar	1520.6	Ca	4912.4

- Plot the ionization energies versus number of electrons. Explain why the slopes of the I_1 and I_3 plots are different, even though the species in each row of the table have the same electron configurations.
- Would you expect the third ionization energy of iron, corresponding to the removal of an electron from a gaseous Fe^{2+} ion, to be larger or smaller than the fourth ionization energy, corresponding to removal of an electron from a gaseous Fe^{3+} ion? Why? How would these ionization energies compare to the first ionization energy of Ca?
- Which would you expect to have the highest first ionization energy: Mg, Al, or Si? Which would you expect to have the highest third ionization energy. Why?
- Use the values of the first ionization energies given in Figure 7.11 "First Ionization Energies of the " to construct plots of first ionization energy versus atomic number for (a) boron through oxygen in the second period; and (b) oxygen through tellurium in group 16. Which plot shows more variation? Explain the reason for the variation in first ionization energies for this group of elements.
- Arrange Ga, In, and Zn in order of increasing first ionization energies. Would the order be the same for second and third ionization energies? Explain your reasoning.
- Arrange each set of elements in order of increasing magnitude of electron affinity.
 - Pb, Bi, and Te
 - Na, K, and Rb
 - P, C, and Ge
- Arrange each set of elements in order of decreasing magnitude of electron affinity.

- As, Bi, and N
 - O, F, and Ar
 - Cs, Ba, and Rb
- Of the species F, O^- , Al^{3+} , and Li^+ , which has the highest electron affinity? Explain your reasoning.
 - Of the species O^- , N^{2-} , Hg^{2+} , and H^+ , which has the highest electron affinity? Which has the lowest electron affinity? Justify your answers.
 - The Mulliken electronegativity of element A is 542 kJ/mol. If the electron affinity of A is -72 kJ/mol, what is the first ionization energy of element A? Use the data in the following table as a guideline to decide if A is a metal, a nonmetal, or a semimetal. If 1 g of A contains 4.85×10^{21} molecules, what is the identity of element A?

	Na	Al	Si	S	Cl
EA (kJ/mol)	-59.6	-41.8	-134.1	-200.4	-348.6
I (kJ/mol)	495.8	577.5	786.5	999.6	1251.2

- Based on their valence electron configurations, classify the following elements as either electrical insulators, electrical conductors, or substances with intermediate conductivity: S, Ba, Fe, Al, Te, Be, O, C, P, Sc, W, Na, B, and Rb.
- Using the data in Problem 10, what conclusions can you draw with regard to the relationship between electronegativity and electrical properties? Estimate the approximate electronegativity of a pure element that is very dense, lustrous, and malleable.
- Of the elements Al, Mg, O_2 , Ti, I_2 , and H_2 , which, if any, would you expect to be a good reductant? Explain your reasoning.
- Of the elements Zn, B, Li, Se, Co, and Br_2 , which if any, would you expect to be a good oxidant? Explain your reasoning.
- Determine whether each species is a good oxidant, a good reductant, or neither.
 - Ba
 - Mo
 - Al
 - Ni
 - O_2

f. Xe

17. Determine whether each species is a good oxidant, a good reductant, or neither.

a. Ir

b. Cs

c. Be

d. B

e. N

f. Po

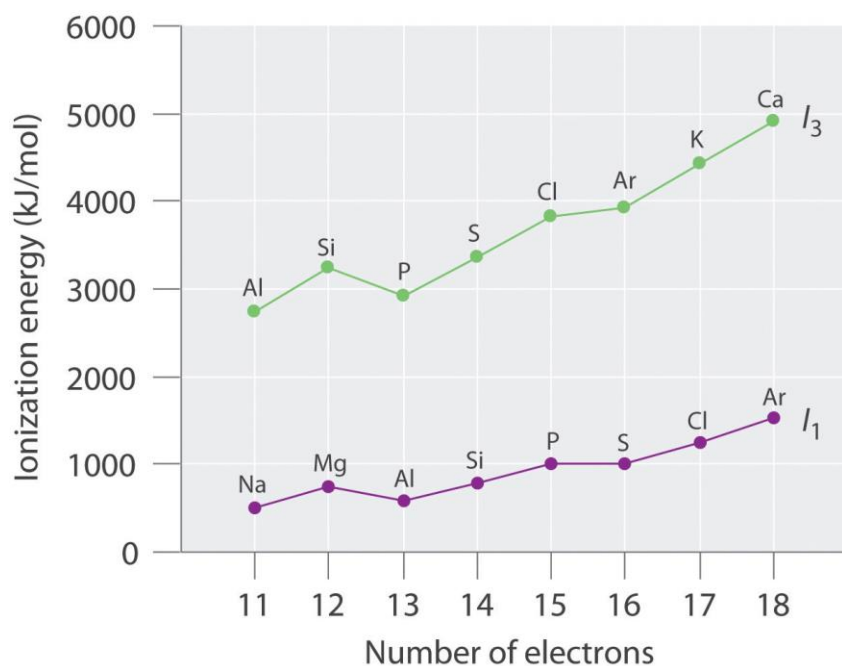
g. Ne

18. Of the species I_2 , O^- , Zn , Sn^{2+} , and K^+ , choose which you would expect to be a good oxidant. Then justify your answer.

19. Based on the valence electron configuration of the noble gases, would you expect them to have positive or negative electron affinities? What does this imply about their most likely oxidation states? their reactivity?

ANSWERS

1.



1. The general features of both plots are roughly the same, with a small peak at 12 electrons and an essentially level region from 15–16 electrons. The slope of the I_3 plot is about twice as large as the slope of the I_1 plot,

however, because the I_3 values correspond to removing an electron from an ion with a +2 charge rather than a neutral atom. The greater charge increases the effect of the steady rise in effective nuclear charge across the row.

2.

3. Electron configurations: Mg, $1s^2 2s^2 2p^6 3s^2$; Al, $1s^2 2s^2 2p^6 3s^2 3p^1$; Si, $1s^2 2s^2 2p^6 3s^2 3p^2$; First ionization energies increase across the row due to a steady increase in effective nuclear charge; thus, Si has the highest first ionization energy. The third ionization energy corresponds to removal of a 3s electron for Al and Si, but for Mg it involves removing a 2p electron from a filled inner shell; consequently, the third ionization energy of Mg is the highest.

4.

5.

6.

7.

- a. Bi > As > N
- b. F > O >> Ar
- c. Rb > Cs > Ba

8.

9. $\text{Hg}^{2+} > \text{H}^+ > \text{O}^- > \text{N}^{2-}$; Hg^{2+} has the highest positive charge plus a relatively low energy vacant set of orbitals (the 6p subshell) to accommodate an added electron, giving it the greatest electron affinity; N^{2-} has a greater negative charge than O^- , so electron–electron repulsions will cause its electron affinity to be even lower (more negative) than that of O^- .

10.

11. insulators: S, O, C (diamond), P; conductors: Ba, Fe, Al, C (graphite), Be, Sc, W, Na, Rb; Te and B are semimetals and semiconductors.

12.

13. Mg, Al, Ti, and H_2

14.

15.

- a. reductant

- b. neither
- c. reductant
- d. reductant
- e. oxidant
- f. neither

16.

17. I_2 is the best oxidant, with a moderately strong tendency to accept an electron to form the I^- ion, with a closed shell electron configuration. O^- would probably also be an oxidant, with a tendency to add an electron to form salts containing the oxide ion, O^{2-} . Zn and Sn^{2+} are all reductants, while K^+ has no tendency to act as an oxidant or a reductant.

[1] Mulliken's definition used the magnitude of the ionization energy and the electron affinity. By definition, the magnitude of a quantity is a positive number. Our definition of electron affinity produces negative values for the electron affinity for most elements, so vertical lines indicating absolute value are needed in Equation 7.15 to make sure that we are adding two positive numbers in the numerator.

[2] Inserting the appropriate data from Figure 7.11 "First Ionization Energies of the " and Figure 7.13 "Electron Affinities (in kJ/mol) of the " into Equation 7.15 gives a Mulliken electronegativity value for fluorine of 1004.6 kJ/mol. To compare Mulliken's electronegativity values with those obtained by Pauling, Mulliken's values are divided by 252.4 kJ/mol, which gives Pauling's value (3.98).

7.4 The Chemical Families

LEARNING OBJECTIVE

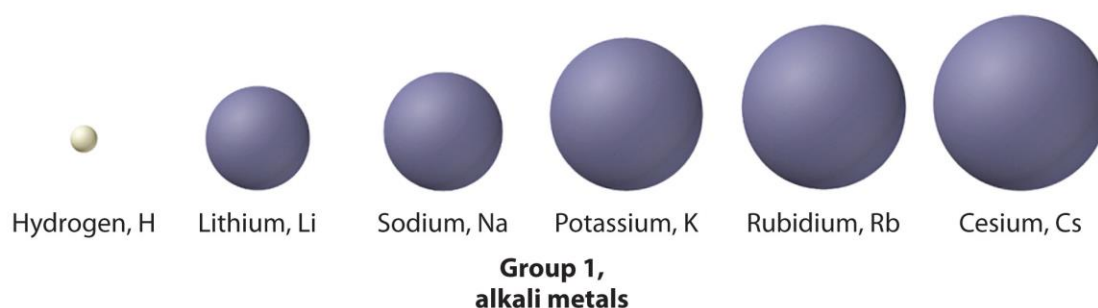
1. To understand the correlation between the chemical properties and the reactivity of the elements and their positions in the periodic table.

Periodic trends in properties such as atomic size and ionic size, ionization energy, electron affinity, and electronegativity illustrate the strong connection between the **chemical properties** and the reactivity of the elements and their positions in the periodic table. In this section, we explore that connection by focusing on two periodic properties that correlate strongly with the chemical behavior of the elements: valence electron configurations and Mulliken electronegativities.

The Main Group Elements

We have said that elements with the same valence electron configuration (i.e., elements in the same column of the periodic table) often have similar chemistry. This correlation is particularly evident for the elements of groups 1, 2, 3, 13, 16, 17, and 18. The intervening families in the *p* block (groups 14 and 15) straddle the diagonal line separating metals from nonmetals. The lightest members of these two families are nonmetals, so they react differently compared to the heaviest members, which are metals. We begin our survey with the alkali metals (group 1), which contain only a single electron outside a noble gas electron configuration, and end with the noble gases (group 18), which have full valence electron shells.

Group 1: The Alkali Metals

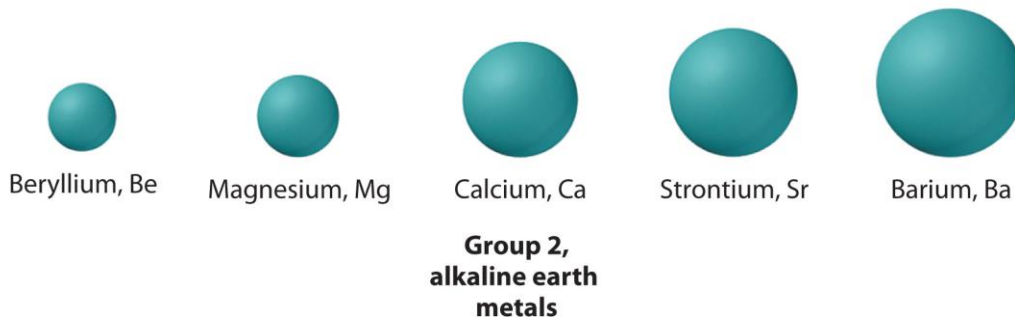


The elements of group 1 are called the *alkali metals*. *Alkali* (from the Arabic *al-qili*, meaning “ashes of the saltwort plant from salt marshes”) was a general term for substances derived from wood ashes, all of which possessed a bitter taste and were able to neutralize acids. Although oxides of both group 1 and group 2 elements were obtained from wood ashes, the alkali metals had lower melting points.

Potassium and sodium were first isolated in 1807 by the British chemist Sir Humphry Davy (1778–1829) by passing an electrical current through molten samples of potash (K_2CO_3) and soda ash (Na_2CO_3). The potassium burst into flames as soon as it was produced because it reacts readily with oxygen at the higher temperature. However, the group 1 elements, like the group 2 elements, become less reactive with air or water as their atomic number decreases. The heaviest element (francium) was not discovered until 1939. It is so radioactive that studying its chemistry is very difficult.

The alkali metals have ns^1 valence electron configurations and the lowest electronegativity of any group; hence they are often referred to as being *electropositive* elements. As a result, they have a strong tendency to lose their single valence electron to form compounds in the +1 oxidation state, producing the EX monohalides and the E_2O oxides. Because they are so reactive, pure group 1 elements are powerful reducing agents that are used in lithium batteries and cardiac pacemakers. Sodium salts such as common table salt (NaCl), baking soda (NaHCO_3), soda ash (Na_2CO_3),

and caustic soda (NaOH) are important industrial chemicals. Other compounds of the alkali metals are important in biology. For example, because potassium is required for plant growth, its compounds are used in fertilizers, and lithium salts are used to treat manic-depressive, or bipolar, disorders.



The elements of group 2 are collectively referred to as the *alkaline earth metals*, a name that originated in the Middle Ages, when an “earth” was defined as a substance that did not melt and was not transformed by fire. Alkalis that did not melt easily were called “alkaline earths.”

Recall that the trend in most groups is for the lightest member to have properties that are quite different from those of the heavier members. Consistent with this trend, the properties of the lightest element—in this case, beryllium—tend to be different from those of its heavier *congeners*, the other members of the group. Beryllium is relatively unreactive but forms many covalent compounds, whereas the other group members are much more reactive metals and form ionic compounds. As is the case with the alkali metals, the heaviest element, radium, is highly radioactive, making its size difficult to measure. Radium was discovered in 1902 by Marie Curie (1867–1934; Nobel Prize in Chemistry 1903 and Nobel Prize in Chemistry 1911), who, with her husband, Pierre, isolated 120 mg of radium chloride from tons of residues from uranium mining. (For more information about radioactivity, see Chapter 1 "Introduction to Chemistry", Section 1.5 "The Atom".)

All the alkaline earth metals have ns^2 valence electron configurations, and all have electronegativities less than 1.6. This means that they behave chemically as metals (although beryllium compounds are covalent) and lose the two valence electrons to form compounds in the +2 oxidation state. Examples include the dihalides (EX_2) and the oxides (EO).

Compounds of the group 2 elements have been commercially important since Egyptian and Roman times, when blocks of limestone or marble, which are both $CaCO_3$, were used as building materials, and gypsum ($CaSO_4 \cdot 2 H_2O$) or lime (CaO) was used as mortar. Calcium sulfate is still used in Portland cement and

plaster of Paris. Magnesium and beryllium form lightweight, high-strength alloys that are used in the aerospace, automotive, and other high-tech industries. As you learned in Chapter 6 "The Structure of Atoms", one of the most impressive uses of these elements is in fireworks; strontium and barium salts, for example, give red or green colors, respectively. Except for beryllium, which is highly toxic, the group 2 elements are also important biologically. Bone is largely hydroxyapatite $[\text{Ca}_5(\text{PO}_4)_3\text{OH}]$, mollusk shells are calcium carbonate, magnesium is part of the chlorophyll molecule in green plants, and calcium is important in hormonal and nerve signal transmission. Because BaSO_4 is so insoluble, it is used in "barium milk shakes" to obtain x-rays of the gastrointestinal tract.

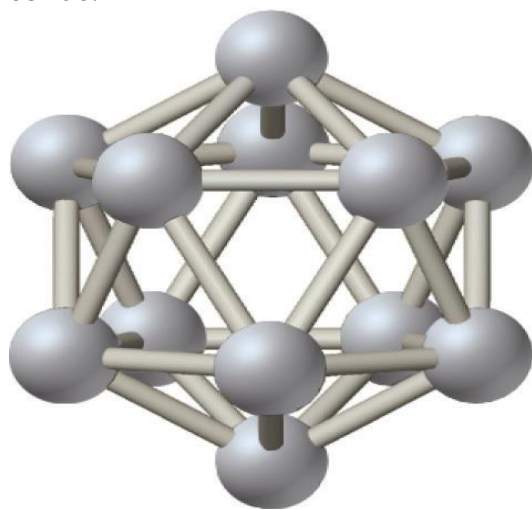
Group 13



Group 13

Of the

group 13 elements, only the lightest, boron, lies on the diagonal line that separates nonmetals and metals. Thus boron is a semimetal, whereas the rest of the group 13 elements are metals. Elemental boron has an unusual structure consisting of B_{12} icosahedra covalently bonded to one another; the other elements are typical metallic solids.



B_{12} icosahedron in elemental boron

No group 13 elements were known in ancient times, not

because they are scarce—Al is the third most abundant element in Earth's crust—but because they are

highly reactive and form extremely stable compounds with oxygen. To isolate the pure elements, potent reducing agents and careful handling were needed.

The elements of group 13 have ns^2np^1 valence electron configurations. Consequently, two oxidation states are important: +3, from losing three valence electrons to give the closed-shell electron configuration of the preceding noble gas; and +1, from losing the single electron in the np subshell. Because these elements have small, negative electron affinities (boron's is only -27.0 kJ/mol), they are unlikely to acquire five electrons to reach the next noble gas configuration. In fact, the chemistry of these elements is almost exclusively characterized by +3. Only the heaviest element (Tl) has extensive chemistry in the +1 oxidation state. It loses the single $6p$ electron to produce TlX monohalides and the oxide Tl_2O .

In the 19th century, aluminum was considered a precious metal. In fact, it was considered so precious that aluminum knives and forks were reserved for the French Emperor Louis Napoleon III, while his less important guests had to be content with gold or silver cutlery. Because of the metal's rarity the dedication of the Washington Monument in 1885 was celebrated by placing a 100 oz chunk of pure aluminum at the top. In contrast, today aluminum is used on an enormous scale in aircraft, automobile engines, armor, cookware, and beverage containers. It is valued for its combination of low density, high strength, and corrosion resistance. Aluminum is also found in compounds that are the active ingredients in most antiperspirant deodorants.

Compounds of boron, such as one form of BN, are hard, have a high melting point, and are resistant to corrosion. They are particularly useful in materials that are exposed to extreme conditions, such as aircraft turbines, brake linings, and polishing compounds. Boron is also a major component of many kinds of glasses, and sodium perborate $[Na_2B_2O_4(OH)_4]$ is the active ingredient in many so-called color-safe laundry bleaches.

Gallium, indium, and thallium are less widely used, but gallium arsenide is the red light-emitting diode (LED) in digital readouts in electronics, and $MgGa_2O_4$ produces the green light emitted in many xerographic machines. Compounds of thallium(I) are extremely toxic. Although Tl_2SO_4 is an excellent rat or ant poison, it is so toxic to humans that it is no longer used for this purpose.

Group 14



The

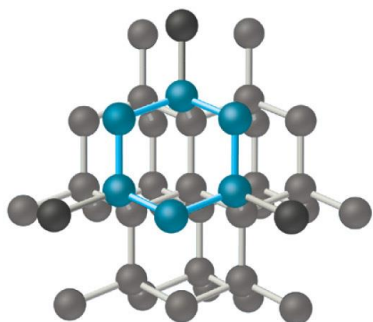
group 14 elements straddle the diagonal line that divides nonmetals from metals. Of the elements in this group, carbon is a nonmetal, silicon and germanium are semimetals, and tin and lead are metals. As a result of this diversity, the structures of the pure elements vary greatly.

The ns^2np^2 valence electron configurations of group 14 gives rise to three oxidation states: -4 , in which four electrons are added to achieve the closed-shell electron configuration of the next noble gas; $+4$, in which all four valence electrons are lost to give the closed-shell electron configuration of the preceding noble gas; and $+2$, in which the loss of two np^2 electrons gives a filled ns^2 subshell.

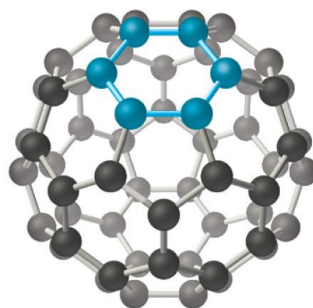
The electronegativity of carbon is only 2.5, placing it in the middle of the electronegativity range, so carbon forms covalent compounds with a wide variety of elements and is the basis of all organic compounds. All of the group 14 elements form compounds in the $+4$ oxidation state, so all of them are able to form dioxides (from CO_2 to PbO_2) and tetrachlorides (CCl_4 and PbCl_4). Only the two metallic elements, Sn and Pb, form an extensive series of compounds in the $+2$ oxidation state. Tin salts are sprayed onto glass to make an electrically conductive coating, and then the glass is used in the manufacture of frost-free windshields. Lead sulfate is formed when your car battery discharges.

Carbon has at least four allotropes (forms or crystal structures) that are stable at room temperature: graphite; diamond; a group of related cage structures called fullerenes (such as C_{60}); and nanotubes, which are cylinders of carbon atoms (Figure 7.18 "Four Allotropes of Carbon"). Graphite consists of extended planes of covalently bonded hexagonal rings. Because the planes are not linked by covalent bonds, they can slide across one another easily. This makes graphite ideally suited as a lubricant and as the "lead" in lead pencils. Graphite also provides the black color in inks and tires, and graphite fibers are used in high-tech items such as golf clubs, tennis rackets, airplanes, and sailboats because of their lightweight, strength, and stiffness.

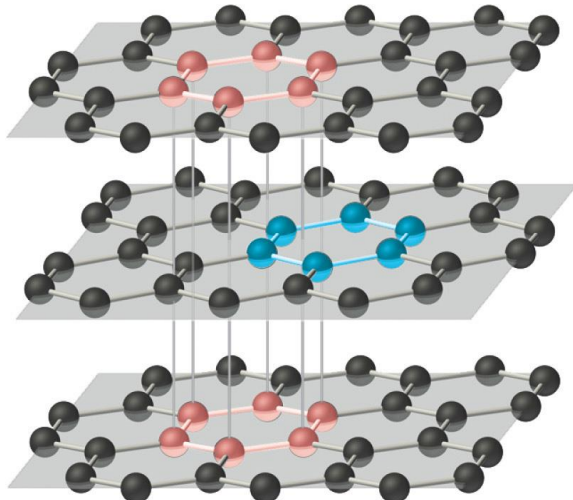
Figure 7.18 *Four Allotropes of Carbon*



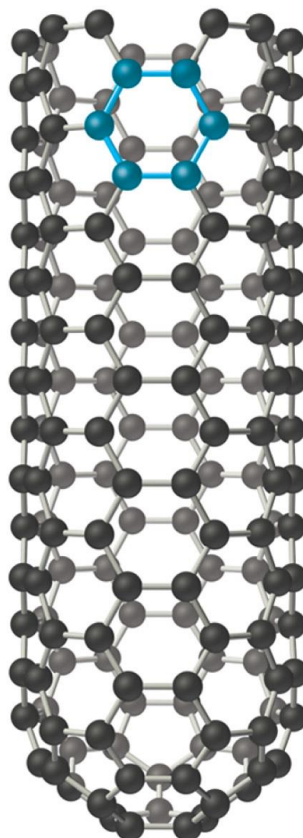
Diamond



Buckminsterfullerene, C₆₀



Graphite



Carbon nanotube

Diamond consists of a rigid three-dimensional array of carbon atoms, making it one of the hardest substances known. In contrast, graphite forms from extended planes of covalently bonded hexagonal rings of carbon atoms that can slide across one another easily. Fullerenes are spherical or ellipsoidal molecules with six- and five-membered rings of carbon atoms, and nanotubes are sheets of graphite rolled up into a cylinder.

In contrast to the layered structure of graphite, each carbon atom in diamond is bonded to four others to form a rigid three-dimensional array, making diamond one of the hardest substances known; consequently, it is used in industry as a cutting tool. Fullerenes, on the other hand, are spherical or ellipsoidal molecules with six- and five-membered rings of carbon atoms; they are volatile substances that dissolve in organic solvents. Fullerenes of extraterrestrial origin have been found in meteorites and have been discovered in a cloud of cosmic dust surrounding a distant star, which makes them the largest molecules ever seen in space. Carbon nanotubes, intermediate in structure between graphite and the fullerenes, can be described as sheets of graphite that have been rolled up into a cylinder or, alternatively, fullerene cages that have been stretched in one direction. Carbon nanotubes are being studied for use in the construction of molecular electronic devices and computers. For example, fabrics that are dipped in an ink of nanotubes and then pressed to thin out the coating are turned into batteries that maintain their flexibility. This creates “wearable electronics” and allows for the possibility of incorporating electronics into flexible surfaces. When applied to a t-shirt, for example, the t-shirt is converted into an “e-shirt.” Silicon is the second most abundant element in Earth’s crust. Both silicon and germanium have strong, three-dimensional network structures similar to that of diamond. Sand is primarily SiO_2 , which is used commercially to make glass and prevent caking in food products. Complex compounds of silicon and oxygen with elements such as aluminum are used in detergents and talcum powder and as industrial catalysts. Because silicon-chip technology laid the foundation for the modern electronics industry, the San Jose region of California, where many of the most important advances in electronics and computers were developed, has been nicknamed “Silicon Valley.”

Elemental tin and lead are metallic solids. Tin is primarily used to make alloys such as bronze, which consists of tin and copper; solder, which is tin and lead; and pewter, which is tin, antimony, and copper. In ancient times, lead was used for everything from pipes to cooking pots because it is easily hammered into different shapes. In fact, the term *plumbing* is derived from *plumbum*, the Latin name for lead. Lead compounds were used as pigments in paints, and tetraethyllead was an important antiknock agent in gasoline. Now, however, lead has been banned from many uses because of its toxicity, although it is still widely used in lead storage batteries for automobiles. In previous centuries, lead salts were frequently used as medicines. Evidence suggests, for example, that Beethoven’s death was caused by the application of various lead-containing medicines by his physician. Beethoven contracted pneumonia and was treated

with lead salts, but in addition, he suffered from a serious liver ailment. His physician treated the ailment by repeatedly puncturing his abdominal cavity and then sealing the wound with a lead-laced poultice. It seems that the repeated doses of lead compounds contributed to Beethoven's death.

Group 15: The Pnictogens



The group 15 elements are called the pnictogens—from the Greek *pnigein*, meaning “to choke,” and *genes*, meaning “producing”—ostensibly because of the noxious fumes that many nitrogen and phosphorus compounds produce. This family has five stable elements; one isotope of bismuth (^{209}Bi) is nonradioactive and is the heaviest nonradioactive isotope of any element. Once again, the lightest member of the family has unique properties. Although both nitrogen and phosphorus are nonmetals, nitrogen under standard conditions is a diatomic gas (N_2), whereas phosphorus consists of three allotropes: white, a volatile, low-melting solid consisting of P_4 tetrahedra; a red solid comprised of P_8 , P_9 , and P_{10} cages linked by P_2 units; and black layers of corrugated phosphorus sheets. The next two elements, arsenic and antimony, are semimetals with extended three-dimensional network structures, and bismuth is a silvery metal with a pink tint.

All of the pnictogens have ns^2np^3 valence electron configurations, leading to three common oxidation states: -3 , in which three electrons are added to give the closed-shell electron configuration of the next noble gas; $+5$, in which all five valence electrons are lost to give the closed-shell electron configuration of the preceding noble gas; and $+3$, in which only the three np electrons are lost to give a filled ns^2 subshell. Because the electronegativity of nitrogen is similar to that of chlorine, nitrogen accepts electrons from most elements to form compounds in the -3 oxidation state (such as in NH_3). Nitrogen has only positive oxidation states when combined with highly electronegative elements, such as oxygen and the halogens (e.g., HNO_3 , NF_3). Although phosphorus and arsenic can combine with active metals and hydrogen to produce compounds in which they have a -3 oxidation state (PH_3 , for example), they typically attain oxidation states of $+3$ and $+5$ when combined with more electronegative elements, such as PCl_3 and

H_3PO_4 . Antimony and bismuth are relatively unreactive metals, but form compounds with oxygen and the halogens in which their oxidation states are +3 and +5 (as in Bi_2O_3 and SbF_5).

Although it is present in most biological molecules, nitrogen was the last pnictogen to be discovered.

Nitrogen compounds such as ammonia, nitric acid, and their salts are used agriculturally in huge quantities; nitrates and nitrites are used as preservatives in meat products such as ham and bacon, and nitrogen is a component of nearly all explosives.

Phosphorus, too, is essential for life, and phosphate salts are used in fertilizers, toothpaste, and baking powder. One, phosphorus sulfide, P_4S_3 , is used to ignite modern safety matches. Arsenic, in contrast, is toxic; its compounds are used as pesticides and poisons. Antimony and bismuth are primarily used in metal alloys, but a bismuth compound is the active ingredient in the popular antacid medication Pepto-Bismol.

Group 16: The Chalcogens



The

group 16 elements are often referred to as the chalcogens—from the Greek *chalk*, meaning “copper,” and *genes*, meaning “producing”—because the most ancient copper ore, copper sulfide, is also rich in two other group 16 elements: selenium and tellurium. Once again, the lightest member of the family has unique properties. In its most common pure form, oxygen is a diatomic gas (O_2), whereas sulfur is a volatile solid with S_8 rings, selenium and tellurium are gray or silver solids that have chains of atoms, and polonium is a silvery metal with a regular array of atoms. Like astatine and radon, polonium is a highly radioactive metallic element.

All of the chalcogens have ns^2np^4 valence electron configurations. Their chemistry is dominated by three oxidation states: -2 , in which two electrons are added to achieve the closed-shell electron configuration of the *next* noble gas; $+6$, in which all six valence electrons are lost to give the closed-shell electron configuration of the *preceding* noble gas; and $+4$, in which only the four np electrons are lost to give a filled ns^2 subshell. Oxygen has the second highest electronegativity of any element; its chemistry is dominated by the -2 oxidation state (as in MgO and H_2O). No compounds of oxygen in the $+4$ or $+6$

oxidation state are known. In contrast, sulfur can form compounds in all three oxidation states. Sulfur accepts electrons from less electronegative elements to give H_2S and Na_2S , for example, and it donates electrons to more electronegative elements to give compounds such as SO_2 , SO_3 , and SF_6 . Selenium and tellurium, near the diagonal line in the periodic table, behave similarly to sulfur but are somewhat more likely to be found in positive oxidation states.

Oxygen, the second most electronegative element in the periodic table, was not discovered until the late 18th century, even though it constitutes 20% of the atmosphere and is the most abundant element in Earth's crust. Oxygen is essential for life; our metabolism is based on the oxidation of organic compounds by O_2 to produce CO_2 and H_2O . Commercially, oxygen is used in the conversion of pig iron to steel, as the oxidant in oxyacetylene torches for cutting steel, as a fuel for the US space shuttle, and in hospital respirators.

Sulfur is the brimstone in "fire and brimstone" from ancient times. Partly as a result of its long history, it is employed in a wide variety of commercial products and processes. In fact, as you learned in Chapter 2 "Molecules, Ions, and Chemical Formulas", more sulfuric acid is produced worldwide than any other compound. Sulfur is used to cross-link the polymers in rubber in a process called *vulcanization*, which was discovered by Charles Goodyear in the 1830s and commercialized by Benjamin Goodrich in the 1870s. Vulcanization gives rubber its unique combination of strength, elasticity, and stability.

Selenium, the only other commercially important chalcogen, was discovered in 1817, and today it is widely used in light-sensitive applications. For example, photocopying, or xerography, from the Greek *xèrós*, meaning "dry," and *graphia*, meaning "writing," uses selenium films to transfer an image from one piece of paper to another, while compounds such as cadmium selenide are used to measure light in photographic light meters and automatic streetlights.

Group 17: The Halogens



The

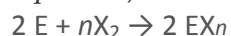
term *halogen*, derived from the Greek *hàls*, meaning "salt," and *genes*, meaning "producing," was first applied to chlorine because of its tendency to react with metals to form salts. All of the halogens have

an ns^2np^5 valence electron configuration, and all but astatine are diatomic molecules in which the two halogen atoms share a pair of electrons. Diatomic F_2 and Cl_2 are pale yellow-green and pale green gases, respectively, while Br_2 is a red liquid, and I_2 is a purple solid. The halogens were not isolated until the 18th and 19th centuries.

Because of their relatively high electronegativities, the halogens are nonmetallic and generally react by gaining one electron per atom to attain a noble gas electron configuration and an oxidation state of

−1. *Halides* are produced according to the following equation, in which X denotes a halogen:

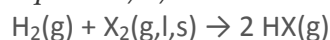
Equation 7.16



If the element E has a low electronegativity (as does Na), the product is typically an ionic halide (NaCl). If the element E is highly electronegative (as P is), the product is typically a covalent halide (PCl_5). Ionic halides tend to be nonvolatile substances with high melting points, whereas covalent halides tend to be volatile substances with low melting points. Fluorine is the most reactive of the halogens, and iodine the least, which is consistent with their relative electronegativities (Figure 7.15 "Pauling Electronegativity Values of the").^[1] In fact, fluorine reacts with nearly all elements at room temperature. Under more extreme conditions, it combines with all elements except helium, neon, and argon.

The halogens react with hydrogen to form the hydrogen halides (HX):

Equation 7.17



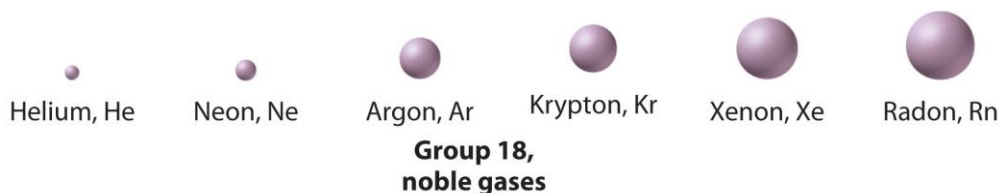
Fluorine is so reactive that any substance containing hydrogen, including coal, wood, and even water, will burst into flames if it comes into contact with pure F_2 .

Because it is the most electronegative element known, fluorine never has a positive oxidation state in any compound. In contrast, the other halogens (Cl, Br, I) form compounds in which their oxidation states are +1, +3, +5, and +7, as in the *oxoanions*, XO_n^- , where $n = 1-4$. Because oxygen has the second highest electronegativity of any element, it stabilizes the positive oxidation states of the halogens in these ions.

All of the halogens except astatine (which is radioactive) are commercially important. NaCl in salt water is purified for use as table salt. Chlorine and hypochlorite (OCl^-) salts are used to sanitize public water supplies, swimming pools, and wastewater, and hypochlorite salts are also used as bleaches because they oxidize colored organic molecules. Organochlorine compounds are used as drugs and pesticides. Fluoride (usually in the form of NaF) is added to many municipal water supplies to help prevent tooth decay, and

bromine (in AgBr) is a component of the light-sensitive coating on photographic film. Because iodine is essential to life—it is a key component of the hormone produced by the thyroid gland—small amounts of KI are added to table salt to produce “iodized salt,” which prevents thyroid hormone deficiencies.

Group 18: The Noble Gases



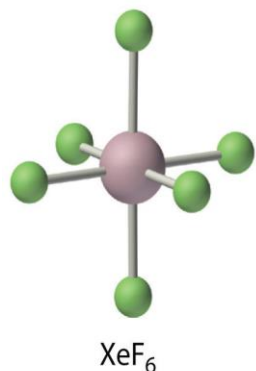
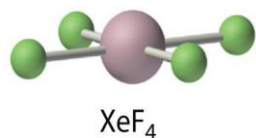
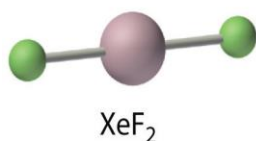
The

noble gases are helium, neon, argon, krypton, xenon, and radon. All have filled valence electron configurations and therefore are unreactive elements found in nature as monatomic gases. The noble gases were long referred to as either “rare gases” or “inert gases,” but they are neither rare nor inert. Argon constitutes about 1% of the atmosphere, which also contains small amounts of the lighter group 18 elements, and helium is found in large amounts in many natural gas deposits. The group’s perceived “rarity” stems in part from the fact that the noble gases were the last major family of elements to be discovered.

The noble gases have $EA \geq 0$, so they do not form compounds in which they have negative oxidation states. Because ionization energies decrease down the column, the only noble gases that form compounds in which they have positive oxidation states are Kr, Xe, and Rn. Of these three elements, only xenon forms an extensive series of compounds. The chemistry of radon is severely limited by its extreme radioactivity, and the chemistry of krypton is limited by its high ionization energy (1350.8 kJ/mol versus 1170.4 kJ/mol for xenon). In essentially all its compounds, xenon is bonded to highly electronegative atoms such as fluorine or oxygen. In fact, the only significant reaction of xenon is with elemental fluorine, which can give XeF_2 , XeF_4 , or XeF_6 . Oxides such as XeO_3 are produced when xenon fluorides react with water, and oxidation with ozone produces the perxenate ion $[\text{XeO}_6^{4-}]$, in which xenon acquires a +8 oxidation state by formally donating all eight of its valence electrons to the more electronegative oxygen atoms. In all of its stable compounds, xenon has a positive, even-numbered oxidation state: +2, +4, +6, or +8. The actual stability of these compounds varies greatly. For example, XeO_3 is a shock-sensitive, white crystalline solid with explosive power comparable to that of TNT (trinitrotoluene), whereas another compound, Na_2XeF_8 , is stable up to 300°C.

Although none of the noble gas compounds is commercially significant, the elements themselves have important applications. For example, argon is used in incandescent light bulbs, where it provides an inert atmosphere that protects the tungsten filament from oxidation, and in compact fluorescent light bulbs (CFLs). It is also used in arc

welding and in the manufacture of reactive elements, such as titanium, or of ultrapure products, such as the silicon used by the electronics industry. Helium, with a boiling point of only 4.2 K, is used as a liquid for studying the properties of substances at very low temperatures. It is also combined in an 80:20 mixture with oxygen used by scuba divers, rather than compressed air, when they descend to great depths. Because helium is less soluble in water than N_2 —a component of compressed air—replacing N_2 with He prevents the formation of bubbles in blood vessels, a condition called “the bends” that can occur during rapid ascents. Neon is familiar to all of us as the gas responsible for the red glow in neon lights.



The Transition Metals, the Lanthanides, and the Actinides

As expected for elements with the same valence electron configuration, the elements in each column of the d block have vertical similarities in chemical behavior. In contrast to the s - and p -block elements, however, elements in the d block also display strong *horizontal* similarities. The horizontal trends compete with the vertical trends. In further contrast to the p -block elements, which tend to have stable oxidation states that are separated by *two* electrons, the transition metals have multiple oxidation states that are separated by only *one* electron.

Note the Pattern

The p -block elements form stable compounds in oxidation states that tend to be separated by two electrons, whereas the transition metals have multiple oxidation states that are separated by one electron.

The group 6 elements, chromium, molybdenum, and tungsten, illustrate the competition that occurs between these horizontal and vertical trends. For example, the maximum oxidation state for all elements in group 6 is +6, achieved by losing all six valence electrons (recall that Cr has a $4s^1 3d^5$ valence electron configuration), yet nearly all the elements in the first row of the transition metals, including chromium, form compounds with the dication M^{2+} , and many also form the trication M^{3+} . As a result, the transition metals in group 6 have very different tendencies to achieve their maximum oxidation state. The most common oxidation state for chromium is +3, whereas the most common oxidation state for molybdenum and tungsten is +6.

Note the Pattern

The *d*-block elements display both strong vertical and horizontal similarities.

Groups 3 (scandium, lanthanum, actinium), 11 (copper, silver, gold), and 12 (zinc, cadmium, mercury) are the only transition metal groups in which the oxidation state predicted by the valence electron configuration dominates the chemistry of the group. The elements of group 3 have three valence electrons outside an inner closed shell, so their chemistry is almost exclusively that of the M^{3+} ions produced by losing all three valence electrons. The elements of group 11 have 11 valence electrons in $ans^1(n-1)d^{10}$ valence electron configuration, and so all three lose a single electron to form the monocation M^+ with a closed $(n-1)d^{10}$ electron configuration. Consequently, compounds of Cu^+ , Ag^+ , and Au^+ are very common, although there is also a great deal of chemistry involving Cu^{2+} . Similarly, the elements of group 12 all have $ans^2(n-1)d^{10}$ valence electron configuration, so they lose two electrons to form M^{2+} ions with an $(n-1)d^{10}$ electron configuration; indeed, the most important ions for these elements are Zn^{2+} , Cd^{2+} , and Hg^{2+} . Mercury, however, also forms the dimeric mercurous ion (Hg_2^{2+}) because of a subtle balance between the energies needed to remove additional electrons and the energy released when bonds are formed. The +3 oxidation state is the most important for the lanthanides and for most of the actinides.

EXAMPLE 8

Based on the following information, determine the most likely identities for elements D and E.

- Element D is a shiny gray solid that conducts electricity only moderately; it forms two oxides (DO_2 and DO_3).
- Element E is a reddish metallic substance that is an excellent conductor of electricity; it forms two oxides (EO and E_2O) and two chlorides (ECl and ECl_2).

Given: physical and chemical properties of two elements

Asked for: identities

Strategy:

A Based on the conductivity of the elements, determine whether each is a metal, a nonmetal, or a semimetal. Confirm your prediction from its physical appearance.

B From the compounds each element forms, determine its common oxidation states.

C If the element is a nonmetal, it must be located in the *p* block of the periodic table. If a semimetal, it must lie along the diagonal line of semimetals from B to At. Transition metals can have two oxidation states separated by one electron.

D From your classification, the oxidation states of the element, and its physical appearance, deduce its identity.

Solution:

a. **A** The moderate electrical conductivity of element D tells us that it is a semimetal. It must lie in the *p* block of the periodic table because all of the semimetals are located there. **B** The stoichiometry of the oxides tells us that two common oxidation states for D are +4 and +6. **C** Element D must be located in group 16 because the common oxidation states for the chalcogens (group 16) include +6 (by losing all six valence electrons) and +4 (by losing the four electrons from the *p* subshell). Thus D is likely to be Se or Te. **D** Additional information is needed to distinguish between the two.

b. **A** Element E is an excellent electrical conductor, so it is a metal. **B** The stoichiometry of the oxides and chlorides, however, tells us that common oxidation states for E are +2 and +1. **C** Metals that can have two oxidation states separated by one electron are usually transition metals. The +1 oxidation state is characteristic of only one group: group 11. Within group 11, copper is the only element with common oxidation states of +1 and +2. **D** Copper also has a reddish hue. Thus element E is probably copper.

Exercise

Based on the following information, determine the most likely identities for elements G and J.

a. Element G is a red liquid that does not conduct electricity. It forms three compounds with fluorine (GF , GF_3 , and GF_5) and one with sodium (NaG).

- a. Element J is a soft, dull gray solid that conducts electricity well and forms two oxides (JO and JO_2).

Answer:

- a. Br
b. Sn or Pb

Summary

The chemical families consist of elements that have the same valence electron configuration and tend to have similar chemistry. The alkali metals (group 1) have ns^1 valence electron configurations and form M^+ ions, while the alkaline earth metals (group 2) have ns^2 valence electron configurations and form M^{2+} ions. Group 13 elements have ns^2np^1 valence electron configurations and have an overwhelming tendency to form compounds in the +3 oxidation state. Elements in group 14 have ns^2np^2 valence electron configurations but exhibit a variety of chemical behaviors because they range from a nonmetal (carbon) to metals (tin/lead). Carbon, the basis of organic compounds, has at least four allotropes with distinct structures: diamond, graphite, **fullerenes**, and carbon **nanotubes**. The **pnictogens** (group 15) all have ns^2np^3 valence electron configurations; they form compounds in oxidation states ranging from -3 to $+5$. The **chalcogens** (group 16) have ns^2np^4 valence electron configurations and react chemically by either gaining two electrons or by formally losing four or six electrons. The halogens (group 17) all have ns^2np^5 valence electron configurations and are diatomic molecules that tend to react chemically by accepting a single electron. The noble gases (group 18) are monatomic gases that are chemically quite unreactive due to the presence of a filled shell of electrons. The **transition metals** (groups 3–10) contain partially filled sets of d orbitals, and the **lanthanides** and the **actinides** are those groups in which f orbitals are being filled. These groups exhibit strong horizontal similarities in behavior. Many of the transition metals form M^{2+} ions, whereas the chemistry of the lanthanides and actinides is dominated by M^{3+} ions.

KEY TAKEAWAY

- Periodic properties and the chemical behavior of the elements correlate strongly with valence electron configurations and Mulliken electronegativities.

CONCEPTUAL PROBLEMS

1. Of the group 1 elements, which would you expect to be the best reductant? Why? Would you expect boron to be a good reductant? Why or why not?
2. Classify each element as a metal, a nonmetal, or a semimetal: Hf, I, Tl, S, Si, He, Ti, Li, and Sb. Which would you expect to be good electrical conductors? Why?
3. Classify each element as a metal, a nonmetal, or a semimetal: Au, Bi, P, Kr, V, Na, and Po. Which would you expect to be good electrical insulators? Why?
4. Of the elements Kr, Xe, and Ar, why does only xenon form an extensive series of compounds? Would you expect Xe^{2+} to be a good oxidant? Why or why not?
5. Identify each statement about the halogens as either true or false and explain your reasoning.
 - a. Halogens have filled valence electron configurations.
 - b. Halogens tend to form salts with metals.
 - c. As the free elements, halogens are monatomic.
 - d. Halogens have appreciable nonmetallic character.
 - e. Halogens tend to have an oxidation state of -1 .
 - f. Halogens are good reductants.
6. Nitrogen forms compounds in the $+5$, $+4$, $+3$, $+2$, and -3 oxidation states, whereas Bi forms ions only in the $+5$ and $+3$ oxidation states. Propose an explanation for the differences in behavior.
7. Of the elements Mg, Al, O, P, and Ne, which would you expect to form covalent halides? Why? How do the melting points of covalent halides compare with those of ionic halides?
8. Of the elements Li, Ga, As, and Xe, would you expect to form ionic chlorides? Explain your reasoning. Which are usually more volatile—ionic or covalent halides? Why?
9. Predict the relationship between the oxidative strength of the oxoanions of bromine— BrO_n^- ($n = 1-4$)—and the number of oxygen atoms present (n). Explain your reasoning.
10. The stability of the binary hydrides of the chalcogens decreases in the order $\text{H}_2\text{O} > \text{H}_2\text{S} > \text{H}_2\text{Se} > \text{H}_2\text{Te}$. Why?
11. Of the elements O, Al, H, and Cl, which will form a compound with nitrogen in a positive oxidation state? Write a reasonable chemical formula for an example of a binary compound with each element.
12. How do you explain the differences in chemistry observed for the group 14 elements as you go down the column? Classify each group 14 element as a metal, a nonmetal, or a semimetal. Do you expect the group 14 elements to form covalent or ionic compounds? Explain your reasoning.

13. Why is the chemistry of the group 13 elements less varied than the chemistry of the group 15 elements? Would you expect the chemistry of the group 13 elements to be more or less varied than that of the group 17 elements? Explain your reasoning.
14. If you needed to design a substitute for BaSO_4 , the barium milkshake used to examine the large and small intestine by x-rays, would BeSO_4 be an inappropriate substitute? Explain your reasoning.
15. The alkali metals have an ns^1 valence electron configuration, and consequently they tend to lose an electron to form ions with +1 charge. Based on their valence electron configuration, what other kind of ion can the alkali metals form? Explain your answer.
16. Would Mo or W be the more appropriate biological substitute for Cr? Explain your reasoning.

ANSWER

11. Nitrogen will have a positive oxidation state in its compounds with O and Cl, because both O and Cl are more electronegative than N. Reasonable formulas for binary compounds are: N_2O_5 or N_2O_3 and NCl_3 .

NUMERICAL PROBLEMS

1. Write a balanced equation for formation of XeO_3 from elemental Xe and O_2 . What is the oxidation state of Xe in XeO_3 ? Would you expect Ar to undergo an analogous reaction? Why or why not?
2. Which of the p -block elements exhibit the greatest variation in oxidation states? Why? Based on their valence electron configurations, identify these oxidation states.
3. Based on its valence electron configuration, what are the three common oxidation states of selenium? In a binary compound, what atoms bonded to Se will stabilize the highest oxidation state? the lowest oxidation state?
4. Would you expect sulfur to be readily oxidized by HCl? Why or why not? Would you expect phosphorus to be readily oxidized by sulfur? Why or why not?
5. What are the most common oxidation states for the pnictogens? What factors determine the relative stabilities of these oxidation states for the lighter and the heavier pnictogens? What is likely to be the most common oxidation state for phosphorus and arsenic? Why?
6. Of the compounds NF_3 , NCl_3 , and NI_3 , which would be the least stable? Explain your answer. Of the ions BrO^- , ClO^- , or FO^- , which would be the least stable? Explain your answer.

7. In an attempt to explore the chemistry of the superheavy element ununquadium, $Z = 114$, you isolated two distinct salts by exhaustively oxidizing metal samples with chlorine gas. These salts are found to have the formulas MCl_2 and MCl_4 . What would be the name of ununquadium using Mendeleev's *eka*-notation?
8. Would you expect the compound CCl_2 to be stable? $SnCl_2$? Why or why not?
9. A newly discovered element (Z) is a good conductor of electricity and reacts only slowly with oxygen. Reaction of 1 g of Z with oxygen under three different sets of conditions gives products with masses of 1.333 g, 1.668 g, and 1.501 g, respectively. To what family of elements does Z belong? What is the atomic mass of the element?
10. An unknown element (Z) is a dull, brittle powder that reacts with oxygen at high temperatures. Reaction of 0.665 gram of Z with oxygen under two different sets of conditions forms gaseous products with masses of 1.328 g and 1.660 g. To which family of elements does Z belong? What is the atomic mass of the element?
11. Why are the alkali metals such powerful reductants? Would you expect Li to be able to reduce H_2 ? Would Li reduce V? Why or why not?
12. What do you predict to be the most common oxidation state for Au, Sc, Ag, and Zn? Give the valence electron configuration for each element in its most stable oxidation state.
13. Complete the following table.

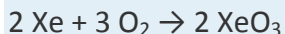
	Mg	C	Ne	Fe	Br
Valence Electron Configuration					
Common Oxidation States					
Oxidizing Strength					

14. Use the following information to identify elements T, X, D, and Z. Element T reacts with oxygen to form at least three compounds: TO , T_2O_3 , and TO_2 . Element X reacts with oxygen to form XO_2 , but X is also known to form compounds in the +2 oxidation state. Element D forms D_2O_3 , and element Z reacts vigorously and forms Z_2O . Electrical conductivity measurements showed that element X exhibited electrical conductivity intermediate between metals and insulators, while elements T, D, and Z were good conductors of electricity. Element T is a hard, lustrous, silvery metal, element X is a blue-gray metal, element D is a light, silvery metal, and element Z is a soft, low-melting metal.
15. Predict whether Cs, F_2 , Al, and He will react with oxygen. If a reaction will occur, identify the products.
16. Predict whether K, Ar, O, and Al will react with Cl_2 . If a reaction will occur, identify the products.

17. Use the following information to identify elements X, T, and Z.
- Element X is a soft, silvery-white metal that is flammable in air and reacts vigorously with water. Its first ionization energy is less than 500 kJ/mol, but the second ionization energy is greater than 3000 kJ/mol.
 - Element T is a gas that reacts with F_2 to form a series of fluorides ranging from TF_2 to TF_6 . It is inert to most other chemicals.
 - Element Z is a deep red liquid that reacts with fluorine to form ZF_3 and with chlorine to form ZCl and ZCl_3 , and with iodine to form ZI . Element Z also reacts with the alkali metals and alkaline earth metals.
18. Adding a reactive metal to water in the presence of oxygen results in a fire. In the absence of oxygen, the addition of 551 mg of the metal to water produces 6.4 mg of hydrogen gas. Treatment of 2.00 g of this metal with 6.3 g of Br_2 results in the formation of 3.86 g of an ionic solid. To which chemical family does this element belong? What is the identity of the element? Write and balance the chemical equation for the reaction of water with the metal to form hydrogen gas.

ANSWERS

1.



The oxidation state of xenon in XeO_3 is +6. No, Ar is much more difficult to oxidize than Xe.

2.

3. The valence electron configuration of Se is $[\text{Ar}]4s^23d^{10}4p^4$. Its common oxidation states are: +6, due to loss of all six electrons in the 4s and 4p subshells; +4, due to loss of only the four 4p electrons; and -2, due to addition of two electrons to give an $[\text{Ar}]4s^23d^{10}4p^6$ electron configuration, which is isoelectronic with the following noble gas, Kr. The highest oxidation state (+6) will be stabilized by bonds to highly electronegative atoms such as F (SeF_6) and O (SeO_3), while the lowest oxidation state will be stabilized in covalent compounds by bonds to less electronegative atoms such as H (H_2Se) or C $[(\text{CH}_3)_2\text{Se}]$, or in ionic compounds with cations of electropositive metals (Na_2Se).

4.

5. All of the pnictogens have ns^2np^3 valence electron configurations. The pnictogens therefore tend to form compounds in three oxidation states: +5, due to loss of all five valence electrons; +3, due to loss of the

three np^3 electrons; and -3 , due to addition of three electrons to give a closed shell electron configuration.

Bonds to highly electronegative atoms such as F and O will stabilize the higher oxidation states, while bonds to less electronegative atoms such as H and C will stabilize the lowest oxidation state, as will formation of an ionic compound with the cations of electropositive metals. The most common oxidation state for phosphorus and arsenic is $+5$.

6.

7. Uuq = *eka*-lead

8.

9. The ratios of the masses of the element to the mass of oxygen give empirical formulas of ZO , Z_2O_3 , and ZO_2 .

The high electrical conductivity of the element immediately identifies it as a metal, and the existence of three oxides of the element with oxidation states separated by only one electron identifies it as a transition metal.

If 1 g of Z reacts with 0.33 g O_2 to give ZO , the balanced equation for the reaction must be $2Z + O_2 \rightarrow 2ZO$.

Using M to represent molar mass, the ratio of the molar masses of ZO and Z is therefore:

$$M_{ZO}:M_Z = (M_Z + M_O):M_Z = (M_Z + 16.0):M_Z = 1.33:1 = 1.33.$$

Solving for M_Z gives a molar mass of 48 g/mol and an atomic mass of 48 amu for Z, which identifies it as titanium.

10.

11. Alkali metals are powerful reductants because they have a strong tendency to lose their ns^1 valence electron, as reflected in their low first ionization energies and electronegativities. Lithium has a more positive electron affinity than hydrogen and a substantially lower first ionization energy, so we expect lithium to reduce hydrogen. Transition metals have low electron affinities and do not normally form compounds in negative oxidation states. Therefore, we do not expect lithium to reduce vanadium.

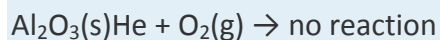
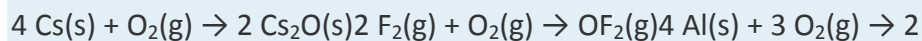
12.

13.

	Mg	C	Ne	Fe	Br
Valence Electron Configuration	$3s^2$	$2s^2 2p^2$	$2s^2 2p^6$	$4s^2 3d^6$	$4s^2 4p^5$
Common Oxidation States	+2	$-4, +4$	0	+2, +3	$-1, +1, +3, +5, +7$
Oxidizing Strength	None	Weak	None	None	Strong

14.

15.



16.

17.

- a. sodium or potassium
- b. xenon
- c. bromine

[1] As we shall see in subsequent chapters, however, factors such as bond strengths are also important in dictating the reactivities of these elements.

7.5 Trace Elements in Biological Systems

LEARNING OBJECTIVE

1. To describe some of the roles of trace elements in biological systems.

Of the more than 100 known elements, approximately 28 are known to be **essential** for the growth of at least one biological species, and only 19 are essential to humans. (For more information on essential elements, see **Chapter 1** "Introduction to Chemistry", Section 1.8 "Essential Elements for Life", and Figure 1.26 "The Essential Elements in the Periodic Table".) What makes some elements essential to an organism and the rest nonessential? There are at least two reasons:

1. The element must have some unique chemical property that an organism can use to its advantage and without which it cannot survive.
2. Adequate amounts of the element must be available in the environment in an easily accessible form.

As you can see in Table 7.6 "Relative Abundance of Some Essential Elements in Earth's Crust and Oceans", many of the elements that are abundant in Earth's crust are nevertheless not found in an easily accessible form (e.g., as ions dissolved in seawater). Instead, they tend to form insoluble oxides, hydroxides, or carbonate salts. Although silicon is the second most abundant element in Earth's crust, SiO_2 and many silicate minerals are insoluble, so they are not easily absorbed by living tissues. This is also the case for iron and aluminum, which form insoluble hydroxides. Many organisms have therefore developed elaborate strategies to obtain iron from their environment. In contrast, molybdenum and iodine, though not particularly abundant, are highly soluble—molybdenum as molybdate (MoO_4^{2-})

and iodine as iodide (I^-) and iodate (IO_3^-)—and thus are more abundant in seawater than iron. Not surprisingly, both molybdenum and iodine are used by many organisms.

Table 7.6 Relative Abundance of Some Essential Elements in Earth's Crust and Oceans

Element*	Crust (ppm; average)	Seawater (mg/L = ppm)
O	461,000	857,000
Si	282,000	2.2
Al	82,300	0.002
Fe	56,300	0.002
Ca	41,500	412
Na	23,600	10,800
Mg	23,300	1290
K	20,900	399
H	1400	108,000
P	1050	0.06
Mn	950	0.0002
F	585	1.3
S	350	905
C	200	28
Cl	145	19,400
V	120	0.0025
Cr	102	0.0003
Ni	84	0.00056
Zn	70	0.0049
Cu	60	0.00025
Co	25	0.00002
Li	20	0.18
N	19	0.5
Br	2.4	67.3
Mo	1.2	0.01
I	0.45	0.06
Se	0.05	0.0002

Element*	Crust (ppm; average)	Seawater (mg/L = ppm)
*Elements in boldface are known to be essential to humans.		

Source: Data from *CRC Handbook of Chemistry and Physics* (2004).

Fortunately, many of the elements essential to life are necessary in only small amounts. (Table 1.6 "Approximate Elemental Composition of a Typical 70 kg Human" lists trace elements in humans.) Even so, elements that are present in trace amounts can exert large effects on the health of an organism. Such elements function as part of an amplification mechanism, in which a molecule containing a trace element is an essential part of a larger molecule that acts in turn to regulate the concentrations of other molecules, and so forth. The amplification mechanism enables small variations in the concentration of the trace element to have large biochemical effects. Essential trace elements in mammals can have four general roles: (1) they can behave as macrominerals, (2) they can participate in the catalysis of group-transfer reactions, (3) they can participate in oxidation–reduction reactions, or (4) they can serve as structural components.

Macrominerals

The macrominerals—Na, Mg, K, Ca, Cl, and P—are found in large amounts in biological tissues and are present as inorganic compounds, either dissolved or precipitated. All form monatomic ions (Na^+ , Mg^{2+} , K^+ , Ca^{2+} , Cl^-) except for phosphorus, which is found as the phosphate ion (PO_4^{3-}). Recall that calcium salts are used by many organisms as structural materials, such as in bone [hydroxyapatite, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$]; calcium salts are also in sea shells and egg shells (CaCO_3), and they serve as a repository for Ca^{2+} in plants (calcium oxalate).

The body fluids of all multicellular organisms contain relatively high concentrations of these ions. Some ions (Na^+ , Ca^{2+} , and Cl^-) are located primarily in *extracellular* fluids such as blood plasma, whereas K^+ , Mg^{2+} , and phosphate are located primarily in *intracellular* fluids. Substantial amounts of energy are required to selectively transport these ions across cell membranes. The selectivity of these ion pumps is based on differences in ionic radius (Section 7.2 "Sizes of Atoms and Ions") and ionic charge.

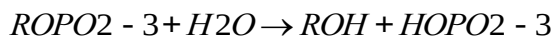
Maintaining optimum levels of macrominerals is important because temporary changes in their concentration within a cell affect biological functions. For example, nerve impulse transmission requires a sudden, reversible increase in the amount of Na^+ that flows into the nerve cell. Similarly, when hormones bind to a cell, they can cause Ca^{2+} ions to enter that cell. In a complex series of reactions, the Ca^{2+} ions trigger events such as muscle contraction, the release of neurotransmitters, or the secretion of hormones.

When people who exercise vigorously for long periods of time overhydrate with water, low blood salt levels can result in a condition known as *hyponatremia*, which causes nausea, fatigue, weakness, seizures, and even death. For this reason, athletes should hydrate with a sports drink containing salts, not just water.

Group-Transfer Reactions

Trace metal ions also play crucial roles in many biological group-transfer reactions. In these reactions, a recognizable functional group, such as a phosphoryl unit ($-\text{PO}_3^-$), is transferred from one molecule to another. In this example,

Equation 7.18



a unit is transferred from an alkoxide (RO^-) to hydroxide (OH^-). To neutralize the negative charge on the molecule that is undergoing the reaction, many biological reactions of this type require the presence of metal ions, such as Zn^{2+} , Mn^{2+} , Ca^{2+} , or Mg^{2+} and occasionally Ni^{2+} or Fe^{3+} . The effectiveness of the metal ion depends largely on its charge and radius.

Zinc is an important component of enzymes that catalyze the hydrolysis of proteins, the addition of water to CO_2 to produce HCO_3^- and H^+ , and most of the reactions involved in DNA (deoxyribonucleic acid) and RNA (ribonucleic acid) synthesis, repair, and replication. Consequently, zinc deficiency has serious adverse effects, including abnormal growth and sexual development and a loss of the sense of taste.

Biological Oxidation–Reduction Reactions

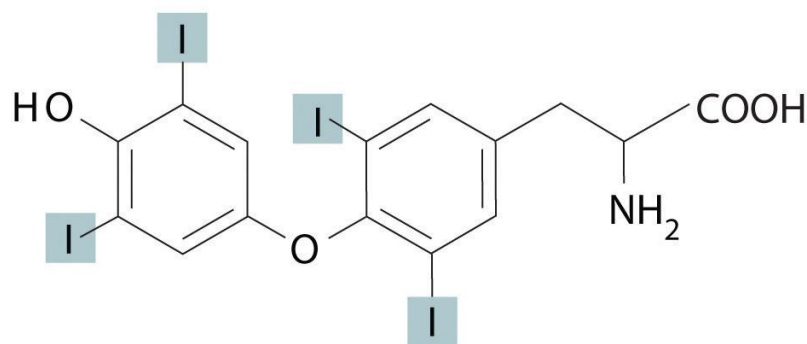
A third important role of trace elements is to transfer electrons in biological oxidation–reduction reactions. Iron and copper, for example, are found in proteins and enzymes that participate in O_2 transport, the reduction of O_2 , the oxidation of organic molecules, and the conversion of atmospheric N_2 to NH_3 . These metals usually transfer one electron per metal ion by alternating between oxidation states, such as $3+/2+$ (Fe) or $2+/1+$ (Cu).

Because most transition metals have multiple oxidation states separated by only one electron, they are uniquely suited to transfer multiple electrons one at a time. Examples include molybdenum ($+6/+5/+4$), which is widely used for two-electron oxidation–reduction reactions, and cobalt ($+3/+2/+1$), which is found in vitamin B_{12} . In contrast, many of the *p*-block elements are well suited for transferring *two* electrons at once. Selenium ($+4/+2$), for example, is found in the enzyme that catalyzes

the oxidation of glutathione (GSH) to its disulfide form (GSSG): $2 \text{ GSH} + \text{H}_2\text{O}_2 \rightarrow 2 \text{ H}_2\text{O} + \text{GSSG}$. (For more information about glutathione and its disulfide form, see Chapter 4 "Reactions in Aqueous Solution", Section 4.9 "Quantitative Analysis Using Titrations", Example 20.)

Structural Components

Trace elements also act as essential structural components of biological tissues or molecules. In many systems where trace elements do not change oxidation states or otherwise participate directly in biochemical reactions, it is often assumed, though frequently with no direct evidence, that the element stabilizes a particular three-dimensional structure of the biomolecule in which it is found. One example is a sugar-binding protein containing Mn^{2+} and Ca^{2+} that is a part of the biological defense system of certain plants. Other examples include enzymes that require Zn^{2+} at one site for activity to occur at a different site on the molecule. Some nonmetallic elements, such as F^- , also appear to have structural roles. Fluoride, for example, displaces the hydroxide ion from hydroxyapatite in bone and teeth to form fluoroapatite $[\text{Ca}_5(\text{PO}_4)_3\text{F}]$. Fluoroapatite is less soluble in acid and provides increased resistance to tooth decay. Another example of a nonmetal that plays a structural role is iodine, which in humans is found in only one molecule, the thyroid hormone *thyroxine*. When a person's diet does not contain sufficient iodine, the thyroid glands in their neck become greatly enlarged, leading to a condition called *goiter*. Because iodine is found primarily in ocean fish and seaweed, many of the original settlers of the American Midwest developed goiter due to the lack of seafood in their diet. Today most table salt contains small amounts of iodine [actually potassium iodide (KI)] to prevent this problem.



Thyroxine

EXAMPLE 9

There is some evidence that tin is an essential element in mammals. Based solely on what you know about the chemistry of tin and its position in the periodic table, predict a likely biological function for tin.

Given: element and data in Table 1.6 "Approximate Elemental Composition of a Typical 70 kg Human"

Asked for: likely biological function

Strategy:

From the position of tin in the periodic table, its common oxidation states, and the data in Table 1.6 "Approximate Elemental Composition of a Typical 70 kg Human", predict a likely biological function for the element.

Solution:

From its position in the lower part of group 14, we know that tin is a metallic element whose most common oxidation states are +4 and +2. Given the low levels of tin in mammals (140 mg/70 kg human), tin is unlikely to function as a macromineral. Although a role in catalyzing group-transfer reactions or as an essential structural component cannot be ruled out, the most likely role for tin would be in catalyzing oxidation–reduction reactions that involve two-electron transfers. This would take advantage of the ability of tin to have two oxidation states separated by two electrons.

Exercise

Based solely on what you know about the chemistry of vanadium and its position in the periodic table, predict a likely biological function for vanadium.

Answer: Vanadium likely catalyzes oxidation–reduction reactions because it is a first-row transition metal and is likely to have multiple oxidation states.

Summary

Many of the elements in the periodic table are **essential trace elements** that are required for the growth of most organisms. Although they are present in only small quantities, they have important biological effects because of their participation in an **amplification mechanism**. **Macrominerals** are present in larger amounts and play structural roles or act as electrolytes whose distribution in cells is tightly controlled. These ions are selectively transported across cell membranes by **ion pumps**. Other trace elements catalyze **group-transfer reactions** or biological oxidation–reduction reactions, while others yet are essential structural components of biological molecules.

KEY TAKEAWAY

- Essential trace elements in mammals have four general roles: as macrominerals, as catalysts in group-transfer reactions or redox reactions, or as structural components.

CONCEPTUAL PROBLEMS

1. Give at least one criterion for essential elements involved in biological oxidation–reduction reactions. Which region of the periodic table contains elements that are very well suited for this role? Explain your reasoning.
2. What are the general biological roles of trace elements that do not have two or more accessible oxidation states?

7.6 End-of-Chapter Material

APPLICATION PROBLEMS

Problems marked with a ♦ involve multiple concepts.

1. ♦ Most plants, animals, and bacteria use oxygen as the terminal oxidant in their respiration process. In a few locations, however, whole ecosystems have developed in the absence of oxygen, containing creatures that can use sulfur compounds instead of oxygen. List the common oxidation states of sulfur, provide an example of any oxoanions containing sulfur in these oxidation states, and name the ions. Which ion would be the best oxidant?
2. Titanium is currently used in the aircraft industry and is now used in ships, which operate in a highly corrosive environment. Interest in this metal is due to the fact that titanium is strong, light, and corrosion resistant. The densities of selected elements are given in the following table. Why can an element with an even lower density such as calcium not be used to produce an even lighter structural material?

Element	Density (g/cm ³)	Element	Density (g/cm ³)
K	0.865	Cr	7.140
Ca	1.550	Mn	7.470
Sc	2.985	Fe	7.874
Ti	4.507	Co	8.900
V	6.110	Ni	8.908

3. ♦ The compound Fe₃O₄ was called lodestone in ancient times because it responds to Earth's magnetic field and can be used to construct a primitive compass. Today Fe₃O₄ is commonly called magnetite because it contains both Fe²⁺ and Fe³⁺, and the unpaired electrons on these ions align to form tiny magnets. How many unpaired electrons does each ion have? Would you expect to observe magnetic behavior in compounds

containing Zn^{2+} ? Why or why not? Would you expect Fe or Zn to have the lower third ionization energy? Why?

4. ♦ Understanding trends in periodic properties allows us to predict the properties of individual elements. For example, if we need to know whether francium is a liquid at room temperature (approximately 20°C), we could obtain this information by plotting the melting points of the other alkali metals versus atomic number. Based on the data in the following table, would you predict francium to be a solid, a liquid, or a gas at 20°C ?

	Li	Na	K	Rb	Cs
Melting Point ($^\circ\text{C}$)	180	97.8	63.7	39.0	28.5

5. Francium is found in minute traces in uranium ores. Is this consistent with your conclusion? Why or why not? Why would francium be found in these ores, but only in small quantities?

ANSWERS

- Due to its $3s^2 3p^4$ electron configuration, sulfur has three common oxidation states: +6, +4, and -2. Examples of each are: -2 oxidation state, the sulfide anion, S^{2-} or hydrogen sulfide, H_2S ; +4 oxidation state, the sulfite ion, SO_3^{2-} ; +6 oxidation state, the sulfate ion, SO_4^{2-} . The sulfate ion would be the best biological oxidant, because it can accept the greatest number of electrons.
-
- Iron(II) has four unpaired electrons, and iron(III) has five unpaired electrons. Compounds of Zn^{2+} do not exhibit magnetic behavior, because the Zn^{2+} ion has no unpaired electrons. The third ionization potential of zinc is larger than that of iron, because removing a third electron from zinc requires breaking into the closed $3d^{10}$ subshell.

Chapter 8 Ionic versus Covalent Bonding

In Chapter 7 "The Periodic Table and Periodic Trends", we described the relationship between the chemical properties and reactivity of an element and its position in the periodic table. In this chapter and Chapter 9 "Molecular Geometry and Covalent Bonding Models", we describe the interactions that hold atoms together in chemical substances, and we examine the factors that determine how the atoms of a substance are arranged in space. Our goal is to understand how the properties of the component atoms in a chemical compound determine the structure and reactivity of the compound.

The properties described in Chapter 6 "The Structure of Atoms" and Chapter 7 "The Periodic Table and Periodic Trends" were properties of isolated atoms, yet most of the substances in our world consist of atoms held together in molecules, ionic compounds, or metallic solids. The properties of these substances depend on not only the characteristics of the component atoms but also how those atoms are bonded to one another.

Carbon and silicon bonding. *Both the group 14 elements carbon and silicon form bonds with oxygen, but how they form those bonds results in a vast difference in physical properties. Because of its simple molecular bond, carbon dioxide is a gas that exists as a volatile molecular solid, known as "dry ice," at temperatures of -78°C and below. Silicon dioxide is a giant covalent structure, whose strong bonds in three dimensions make it a hard, high-melting-point solid, such as quartz.*

What you learn in this chapter about chemical bonding and molecular structure will help you understand how different substances with the same atoms can have vastly different physical and chemical properties. For example, oxygen gas (O_2) is essential for life, yet ozone (O_3) is toxic to cells, although as you learned in Chapter 3 "Chemical Reactions", ozone in the upper atmosphere shields us from harmful ultraviolet light. Moreover, you saw in Chapter 7 "The Periodic Table and Periodic Trends" that diamond is a hard, transparent solid that is a gemstone; graphite is a soft, black solid that is a lubricant; and fullerenes are molecular species with carbon cage structures—yet all of these are composed of carbon. As you learn about bonding, you will also discover why, although carbon and silicon both have ns^2np^2 valence electron configurations and form dioxides, CO_2 is normally a gas that condenses into the volatile molecular solid known as dry ice, whereas SiO_2 is a nonvolatile solid with a network structure that can take several forms, including beach sand and quartz crystals.

8.1 An Overview of Chemical Bonding

LEARNING OBJECTIVE

1. To present three common features of chemical bonding.

In Chapter 2 "Molecules, Ions, and Chemical Formulas", we defined a **chemical bond** as the force that holds atoms together in a chemical compound. We also introduced two idealized types of bonding: covalent bonding, in which electrons are shared between atoms in a molecule or polyatomic ion, and ionic bonding, in which positively and negatively charged ions are held together by electrostatic forces. The concepts of covalent and ionic bonding were developed to explain the properties of different kinds of chemical substances. Ionic compounds, for example, typically dissolve in water to form aqueous solutions that conduct electricity. (For more information about solution conductivity, see Chapter 4 "Reactions in Aqueous Solution", Section 4.1 "Aqueous Solutions".) In contrast, most

covalent compounds that dissolve in water form solutions that do not conduct electricity. Furthermore, many covalent compounds are volatile, whereas ionic compounds are not.

Despite the differences in the distribution of electrons between these two idealized types of bonding, all models of chemical bonding have three features in common:

1. Atoms interact with one another to form aggregates such as molecules, compounds, and crystals because doing so lowers the total energy of the system; that is, the aggregates are more stable than the isolated atoms.
2. Energy is required to dissociate bonded atoms or ions into isolated atoms or ions. For ionic solids, in which the ions form a three-dimensional array called a *lattice*, this energy is called the lattice energy (U), the enthalpy change that occurs when a solid ionic compound is transformed into gaseous ions. For covalent compounds, this energy is called the bond energy, which is the enthalpy change that occurs when a given bond in a gaseous molecule is broken.
3. Each chemical bond is characterized by a particular optimal internuclear distance called the bond distance(r_o).

Note the Pattern

Energy is required to dissociate bonded atoms or ions.

We explore these characteristics further, after briefly describing the energetic factors involved in the formation of an ionic bond.

Summary

Chemical bonding is the general term used to describe the forces that hold atoms together in molecules and ions. Two idealized types of bonding are **ionic bonding**, in which positively and negatively charged ions are held together by electrostatic forces, and **covalent bonding**, in which electron pairs are shared between atoms. All models of chemical bonding have three common features: atoms form bonds because the products are more stable than the isolated atoms; bonding interactions are characterized by a particular energy (the **bond energy** or **lattice energy**), which is the amount of energy required to dissociate the substance into its components; and bonding interactions have an optimal internuclear distance, the **bond distance**.

KEY TAKEAWAY

- Forming bonds lowers the total energy of the system, energy is required to dissociate bonded atoms or ions, and there is an optimal bond distance.

CONCEPTUAL PROBLEMS

- Describe the differences between covalent bonding and ionic bonding. Which best describes the bonding in MgCl_2 and PF_5 ?
- What three features do all chemical bonds have in common?

8.2 Ionic Bonding

LEARNING OBJECTIVE

- To quantitatively describe the energetic factors involved in the formation of an ionic bond.

Chapter 2 "Molecules, Ions, and Chemical Formulas" explained that ionic bonds are formed when positively and negatively charged ions are held together by electrostatic forces. You learned that the energy of the electrostatic attraction (E), a measure of the force's strength, is inversely proportional to the internuclear distance between the charged particles (r):

Equation 8.1

$$E \propto \frac{Q_1 Q_2}{r} \quad E = k \frac{Q_1 Q_2}{r}$$

where each ion's charge is represented by the symbol Q . The proportionality constant k is equal to

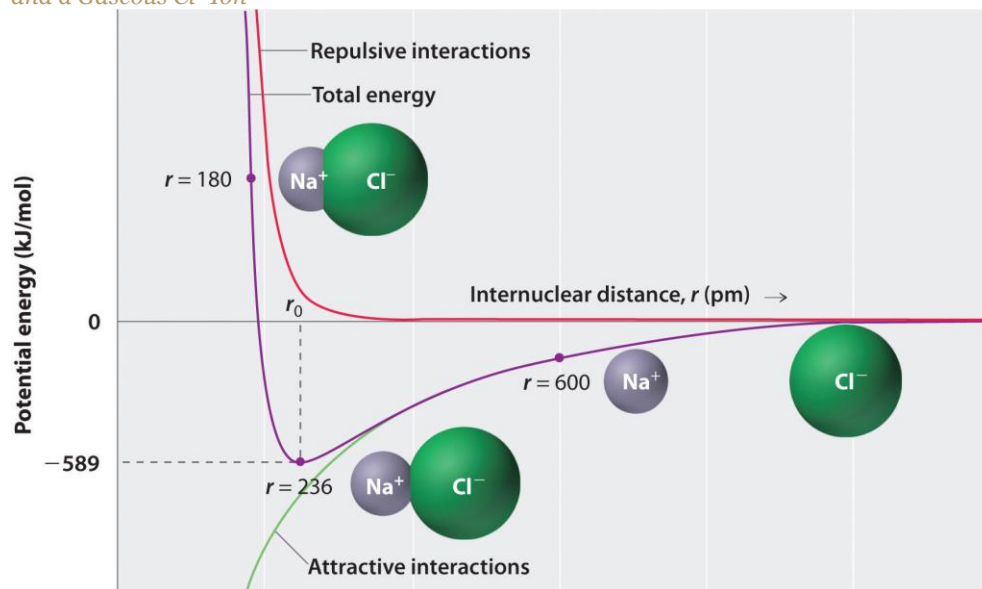
$2.31 \times 10^{-28} \text{ J} \cdot \text{m}$.^[1] If Q_1 and Q_2 have opposite signs (as in NaCl , for example, where Q_1 is $+1$ for Na^+ and Q_2 is -1 for Cl^-), then E is negative, which means that energy is released when oppositely charged ions are brought together from an infinite distance to form an isolated ion pair. As shown by the green curve in the lower half of Figure 8.1 "A Plot of Potential Energy versus Internuclear Distance for the Interaction between a Gaseous Na", Equation 8.1 predicts that the maximum energy is released when the ions are infinitely close to each other, at $r = 0$. Because ions occupy space, however, they cannot be infinitely close together. At very short distances, repulsive electron–electron interactions between electrons on adjacent ions become stronger than the attractive interactions between ions with opposite charges, as shown by the red curve in the upper half of Figure 8.1 "A Plot of Potential Energy versus Internuclear Distance for the Interaction between a Gaseous Na". The total energy of the system is a balance between the attractive and repulsive interactions. The purple curve in Figure 8.1 "A Plot of Potential Energy versus Internuclear Distance for the Interaction between a Gaseous Na" shows that the total energy of the system reaches a minimum at r_0 , the point

where the electrostatic repulsions and attractions are exactly balanced. This distance is the same as the experimentally measured bond distance.

Note the Pattern

Energy is released when a bond is formed.

Figure 8.1 A Plot of Potential Energy versus Internuclear Distance for the Interaction between a Gaseous Na^+ Ion and a Gaseous Cl^- Ion



The energy of the system reaches a minimum at a particular distance (r_0) when the attractive and repulsive interactions are balanced.

Let's consider the energy released when a gaseous Na^+ ion and a gaseous Cl^- ion are brought together from $r = \infty$ to $r = r_0$. Given that the observed gas-phase internuclear distance is 236 pm, the energy change associated with the formation of an ion pair from an $\text{Na}^+(\text{g})$ ion and a $\text{Cl}^-(\text{g})$ ion is as follows:

Equation 8.2

$$= -9.79 \times 10^{-19} \text{ J/ion pair}$$

The negative value indicates that energy is released. To calculate the energy change in the formation of a mole of NaCl pairs, we need to multiply the energy per ion pair by Avogadro's number:

Equation 8.3

$$E = -589 \text{ kJ/mol}$$

This is the energy released when 1 mol of gaseous ion pairs is formed, *not* when 1 mol of positive and negative ions condenses to form a crystalline lattice. Because of long-range interactions in the lattice structure, this energy does not

correspond directly to the lattice energy of the crystalline solid. However, the large negative value indicates that bringing positive and negative ions together is energetically very favorable, whether an ion pair or a crystalline lattice is formed.

We summarize the important points about ionic bonding:

- At r_0 , the ions are more stable (have a lower potential energy) than they are at an infinite internuclear distance. When oppositely charged ions are brought together from $r = \infty$ to $r = r_0$, the energy of the system is lowered (energy is released).
- Because of the low potential energy at r_0 , energy must be added to the system to separate the ions. The amount of energy needed is the bond energy.
- The energy of the system reaches a minimum at a particular internuclear distance (the bond distance).

EXAMPLE 1

Calculate the amount of energy released when 1 mol of gaseous Li^+F^- ion pairs is formed from the separated ions. The observed internuclear distance in the gas phase is 156 pm.

Given: cation and anion, amount, and internuclear distance

Asked for: energy released from formation of gaseous ion pairs

Strategy:

Substitute the appropriate values into Equation 8.1 to obtain the energy released in the formation of a single ion pair and then multiply this value by Avogadro's number to obtain the energy released per mole.

Solution:

Inserting the values for Li^+F^- into Equation 8.1 (where $Q_1 = +1$, $Q_2 = -1$, and $r = 156$ pm), we find that the

energy associated with the formation of a single pair of Li^+F^- ions is

$$E = kQ_1Q_2/r_0 = (2.31 \times 10^{-28} \text{ J}\cdot\text{m}) / (+1)(-1)(156 \text{ pm} \times 10^{-12} \text{ m/pm}) \\ = -1.48 \times 10^{-18} \text{ J/ion pair}$$

Then the energy released per mole of Li^+F^- ion pairs is

$$E = (-1.48 \times 10^{-18} \text{ J/ion pair})(6.022 \times 10^{23} \text{ ion pair/mol}) = -891 \text{ kJ/mol}$$

Because Li^+ and F^- are smaller than Na^+ and Cl^- (see Figure 7.9 "Ionic Radii (in Picometers) of the Most Common Oxidation States of the"), the internuclear distance in LiF is shorter than in NaCl . Consequently, in accordance with Equation 8.1, much more energy is released when 1 mol of gaseous Li^+F^- ion pairs is formed (-891 kJ/mol) than when 1 mol of gaseous Na^+Cl^- ion pairs is formed (-589 kJ/mol).

Exercise

Calculate the amount of energy released when 1 mol of gaseous MgO ion pairs is formed from the separated ions. The internuclear distance in the gas phase is 175 pm.

Answer: $-3180 \text{ kJ/mol} = -3.18 \times 10^3 \text{ kJ/mol}$

Summary

The strength of the electrostatic attraction between ions with opposite charges is directly proportional to the magnitude of the charges on the ions and inversely proportional to the internuclear distance. The total energy of the system is a balance between the repulsive interactions between electrons on adjacent ions and the attractive interactions between ions with opposite charges.

KEY TAKEAWAY

- The amount of energy needed to separate a gaseous ion pair is its bond energy.

CONCEPTUAL PROBLEMS

1. Describe the differences in behavior between NaOH and CH₃OH in aqueous solution. Which solution would be a better conductor of electricity? Explain your reasoning.
2. What is the relationship between the strength of the electrostatic attraction between oppositely charged ions and the distance between the ions? How does the strength of the electrostatic interactions change as the size of the ions increases?
3. Which will result in the release of more energy: the interaction of a gaseous sodium ion with a gaseous oxide ion or the interaction of a gaseous sodium ion with a gaseous bromide ion? Why?
4. Which will result in the release of more energy: the interaction of a gaseous chloride ion with a gaseous sodium ion or a gaseous potassium ion? Explain your answer.
5. What are the predominant interactions when oppositely charged ions are
 - a. far apart?
 - b. at internuclear distances close to r_0 ?
 - c. very close together (at a distance that is less than the sum of the ionic radii)?
6. Several factors contribute to the stability of ionic compounds. Describe one type of interaction that *destabilizes* ionic compounds. Describe the interactions that *stabilize* ionic compounds.
7. What is the relationship between the electrostatic attractive energy between charged particles and the distance between the particles?

ANSWER

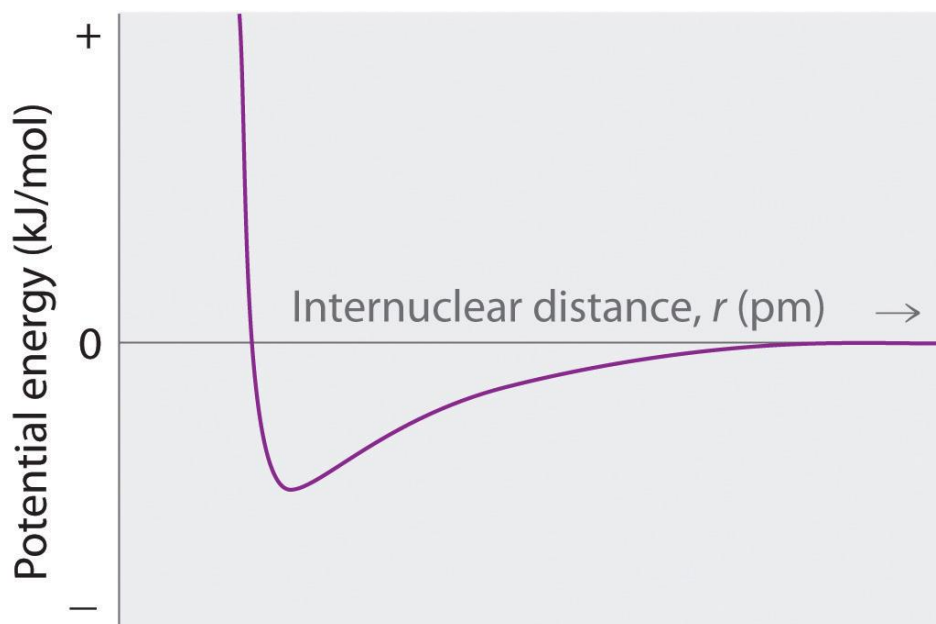
- 1.
- 2.
3. The interaction of a sodium ion and an oxide ion. The electrostatic attraction energy between ions of opposite charge is directly proportional to the charge on each ion (Q_1 and Q_2 in Equation 8.1). Thus, more energy is released as the charge on the ions increases (assuming the internuclear distance does not increase substantially). A sodium ion has a +1 charge; an oxide ion, a -2 charge; and a bromide ion, a -1 charge. For the interaction of a sodium ion with an oxide ion, $Q_1 = +1$ and $Q_2 = -2$, whereas for the interaction of a sodium ion with a bromide ion, $Q_1 = +1$ and $Q_2 = -1$. The larger value of $Q_1 \times Q_2$ for the sodium ion–oxide ion interaction means it will release more energy.

NUMERICAL PROBLEMS

1. How does the energy of the electrostatic interaction between ions with charges +1 and -1 compare to the interaction between ions with charges +3 and -1 if the distance between the ions is the same in both cases? How does this compare with the magnitude of the interaction between ions with +3 and -3 charges?
2. How many grams of gaseous MgCl_2 are needed to give the same electrostatic attractive energy as 0.5 mol of gaseous LiCl ? The ionic radii are $\text{Li}^+ = 76 \text{ pm}$, $\text{Mg}^{+2} = 72 \text{ pm}$, and $\text{Cl}^- = 181 \text{ pm}$.
3. Sketch a diagram showing the relationship between potential energy and internuclear distance (from $r = \infty$ to $r = 0$) for the interaction of a bromide ion and a potassium ion to form gaseous KBr . Explain why the energy of the system increases as the distance between the ions decreases from $r = r_0$ to $r = 0$.
4. Calculate the magnitude of the electrostatic attractive energy (E , in kilojoules) for 85.0 g of gaseous SrS ion pairs. The observed internuclear distance in the gas phase is 244.05 pm.
5. What is the electrostatic attractive energy (E , in kilojoules) for 130 g of gaseous HgI_2 ? The internuclear distance is 255.3 pm.

ANSWERS

1. According to Equation 8.1, in the first case $Q_1Q_2 = (+1)(-1) = -1$; in the second case, $Q_1Q_2 = (+3)(-1) = -3$. Thus, E will be three times larger for the +3/-1 ions. For +3/-3 ions, $Q_1Q_2 = (+3)(-3) = -9$, so E will be nine times larger than for the +1/-1 ions.



At $r < r_0$, the energy of the system increases due to electron–electron repulsions between the overlapping electron distributions on *adjacent* ions. At very short internuclear distances, electrostatic repulsions between adjacent *nuclei* also become important.

[1] This value of k includes the charge of a single electron (1.6022×10^{-19} C) for each ion. The equation can also be written using the charge of each ion, expressed in coulombs (C), incorporated in the constant. In this case, the proportionality constant, k , equals 8.999×10^9 J·m/C². In the example given, $Q_1 = +1(1.6022 \times 10^{-19}$ C) and $Q_2 = -1(1.6022 \times 10^{-19}$ C).

8.3 Lattice Energies in Ionic Solids

LEARNING OBJECTIVES

1. To understand the relationship between the lattice energy and physical properties of an ionic compound.
2. To use the Born–Haber cycle to calculate lattice energies.

Recall from Chapter 2 "Molecules, Ions, and Chemical Formulas" that the reaction of a metal with a nonmetal usually produces an ionic compound; that is, electrons are transferred from the metal (the *reductant*) to the nonmetal (the *oxidant*). Ionic compounds are usually rigid, brittle, crystalline substances with flat surfaces that intersect at characteristic angles. They are not easily deformed, and they melt at relatively high temperatures. NaCl, for example, melts at 801°C. These properties result from the regular arrangement of the ions in the crystalline lattice and from the strong electrostatic attractive forces between ions with opposite charges.

While Equation 8.1 has demonstrated that the formation of ion pairs from isolated ions releases large amounts of energy, even more energy is released when these ion pairs condense to form an ordered three-dimensional array (Figure 7.8 "Definition of Ionic Radius"). In such an arrangement each cation in the lattice is surrounded by more than one anion (typically four, six, or eight) and vice versa, so it is more stable than a system consisting of separate pairs of ions, in which there is only one cation–anion interaction in each pair. Note that r_0 may differ between the gas-phase dimer and the lattice.

Note the Pattern

An ionic lattice is more stable than a system consisting of separate ion pairs.

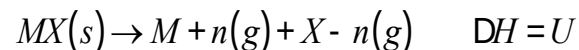
Calculating Lattice Energies

The lattice energy of nearly any ionic solid can be calculated rather accurately using a modified form of Equation 8.1:

Equation 8.4

$U = -k' \frac{Q_1 Q_2}{r_0}$, where $U > 0$. U , which is always a positive number, represents the amount of energy required to dissociate 1 mol of an ionic solid into the gaseous ions. If we assume that $\Delta V = 0$, then the lattice energy, U , is approximately equal to the change in enthalpy, ΔH (see Chapter 5 "Energy Changes in Chemical Reactions", Section 5.2 "Enthalpy"):

Equation 8.5



As before, Q_1 and Q_2 are the charges on the ions and r_0 is the internuclear distance. We see from Equation 8.4 that lattice energy is directly related to the product of the ion charges and inversely related to the internuclear distance. The value of the constant k' depends on the specific arrangement of ions in the solid lattice and their valence electron configurations, topics that will be discussed in more detail in Chapter 12 "Solids". Representative values for calculated lattice energies, which range from about 600 to 10,000 kJ/mol, are listed in Table 8.1 "Representative Calculated Lattice Energies". Energies of this magnitude can be decisive in determining the chemistry of the elements.

Table 8.1 Representative Calculated Lattice Energies

Substance	U (kJ/mol)
NaI	682
CaI ₂	1971

Substance	U (kJ/mol)
MgI ₂	2293
NaOH	887
Na ₂ O	2481
NaNO ₃	755
Ca ₃ (PO ₄) ₂	10,602
CaCO ₃	2804

Source: Data from *CRC Handbook of Chemistry and Physics* (2004).

Because the lattice energy depends on the *product* of the charges of the ions, a salt having a metal cation with a +2 charge (M^{2+}) and a nonmetal anion with a -2 charge (X^{2-}) will have a lattice energy four times greater than one with M^+ and X^- , assuming the ions are of comparable size (and have similar internuclear distances). For example, the calculated value of U for NaF is 910 kJ/mol, whereas U for MgO (containing Mg^{2+} and O^{2-} ions) is 3795 kJ/mol.

Because lattice energy is *inversely* related to the internuclear distance, it is also inversely proportional to the size of the ions. This effect is illustrated in Figure 8.2 "A Plot of Lattice Energy versus the Identity of the Halide for the Lithium, Sodium, and Potassium Halides", which shows that lattice energy decreases for the series LiX, NaX, and KX as the radius of X^- increases. Because r_0 in Equation 8.4 is the sum of the ionic radii of the cation and the anion ($r_0 = r^+ + r^-$), r_0 increases as the cation becomes larger in the series, so the magnitude of U decreases. A similar effect is seen when the anion becomes larger in a series of compounds with the same cation.

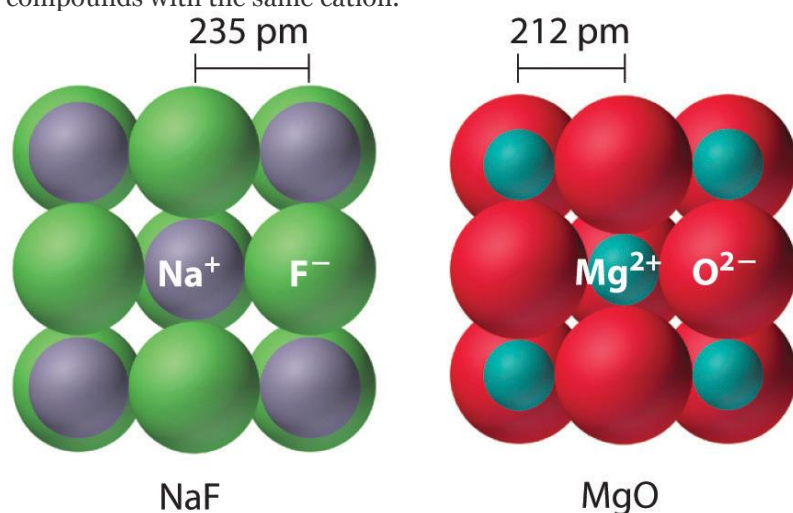
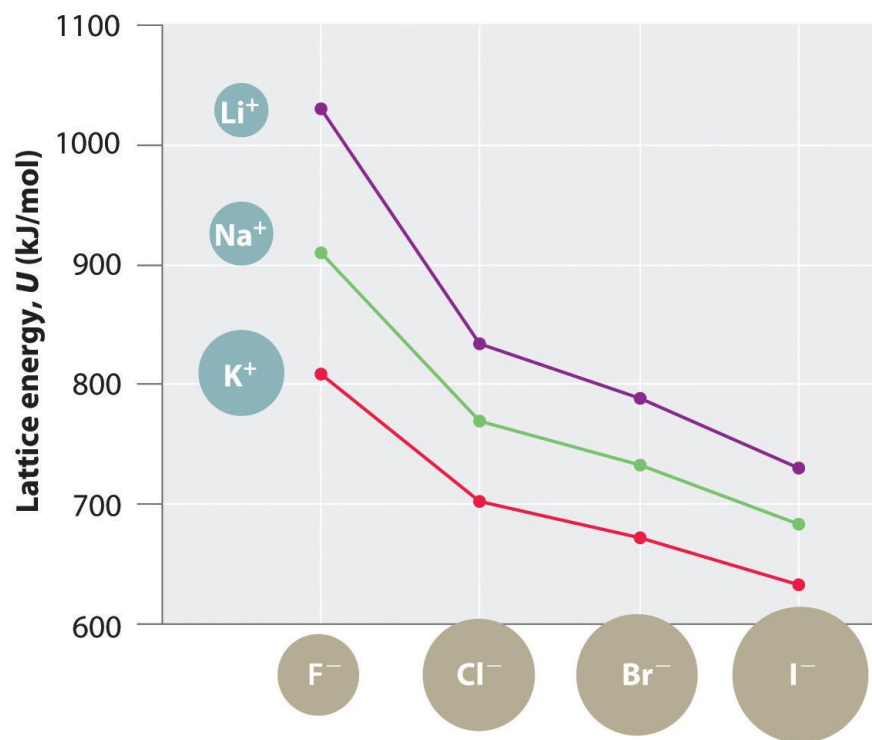


Figure 8.2 A Plot of Lattice Energy versus the Identity of the Halide for the Lithium, Sodium, and Potassium Halides



Because the ionic radii of the cations decrease in the order $K^+ > Na^+ > Li^+$ for a given halide ion, the lattice energy decreases smoothly from Li^+ to K^+ . Conversely, for a given alkali metal ion, the fluoride salt always has the highest lattice energy and the iodide salt the lowest.

Note the Pattern

Lattice energies are highest for substances with small, highly charged ions.

EXAMPLE 2

Arrange GaP, BaS, CaO, and RbCl in order of increasing lattice energy.

Given: four compounds

Asked for: order of increasing lattice energy

Strategy:

Using Equation 8.4, predict the order of the lattice energies based on the charges on the ions. For compounds with ions with the same charge, use the relative sizes of the ions to make this prediction.

Solution:

The compound GaP, which is used in semiconductor electronics, contains Ga^{3+} and P^{3-} ions; the compound BaS contains Ba^{2+} and S^{2-} ions; the compound CaO contains Ca^{2+} and O^{2-} ions; and the compound RbCl has Rb^+ and Cl^- ions. We know from Equation 8.4 that lattice energy is directly proportional to the product of the ionic charges. Consequently, we expect RbCl, with a $(-1)(+1)$ term in the numerator, to have the

lowest lattice energy, and GaP, with a $(+3)(-3)$ term, the highest. To decide whether BaS or CaO has the greater lattice energy, we need to consider the relative sizes of the ions because both compounds contain a +2 metal ion and a -2 chalcogenide ion. Because Ba^{2+} lies below Ca^{2+} in the periodic table, Ba^{2+} is larger than Ca^{2+} . Similarly, S^{2-} is larger than O^{2-} . Because the cation and the anion in BaS are both larger than the corresponding ions in CaO, the internuclear distance is greater in BaS and its lattice energy will be lower than that of CaO. The order of increasing lattice energy is $\text{RbCl} < \text{BaS} < \text{CaO} < \text{GaP}$.

Exercise

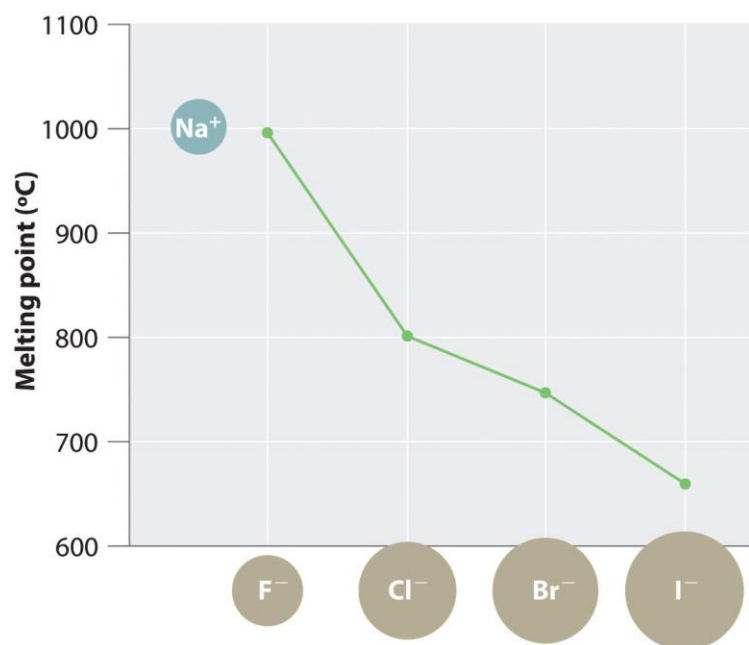
Arrange InAs, KBr, LiCl, SrSe, and ZnS in order of decreasing lattice energy.

Answer: $\text{InAs} > \text{ZnS} > \text{SrSe} > \text{LiCl} > \text{KBr}$

The Relationship between Lattice Energies and Physical Properties

The magnitude of the forces that hold an ionic substance together has a dramatic effect on many of its properties. The melting point, for example, is the temperature at which the individual ions have enough kinetic energy to overcome the attractive forces that hold them in place. At the melting point, the ions can move freely, and the substance becomes a liquid. Thus melting points vary with lattice energies for ionic substances that have similar structures. The melting points of the sodium halides (Figure 8.3 "A Plot of Melting Point versus the Identity of the Halide for the Sodium Halides"), for example, decrease smoothly from NaF to NaI, following the same trend as seen for their lattice energies (Figure 8.2 "A Plot of Lattice Energy versus the Identity of the Halide for the Lithium, Sodium, and Potassium Halides"). Similarly, the melting point of MgO is 2825°C , compared with 996°C for NaF, reflecting the higher lattice energies associated with higher charges on the ions. In fact, because of its high melting point, MgO is used as an electrical insulator in heating elements for electric stoves.

Figure 8.3 A Plot of Melting Point versus the Identity of the Halide for the Sodium Halides



The melting points follow the same trend as the magnitude of the lattice energies in Figure 8.2 "A Plot of Lattice Energy versus the Identity of the Halide for the Lithium, Sodium, and Potassium Halides".

The hardness of ionic materials—that is, their resistance to scratching or abrasion—is also related to their lattice energies. Hardness is directly related to how tightly the ions are held together electrostatically, which, as we saw, is also reflected in the lattice energy. As an example, MgO is harder than NaF, which is consistent with its higher lattice energy.

In addition to determining melting point and hardness, lattice energies affect the solubilities of ionic substances in water. In general, *the higher the lattice energy, the less soluble a compound is in water*. For example, the solubility of NaF in water at 25°C is 4.13 g/100 mL, but under the same conditions, the solubility of MgO is only 0.65 mg/100 mL, meaning that it is essentially insoluble.

Note the Pattern

High lattice energies lead to hard, insoluble compounds with high melting points.

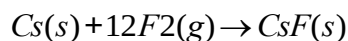
The Born–Haber Cycle

In principle, lattice energies could be measured by combining gaseous cations and anions to form an ionic solid and then measuring the heat evolved. Unfortunately, measurable quantities of gaseous ions have never been obtained under conditions where heat flow can be measured. Instead, lattice energies are found using the experimentally determined enthalpy changes for other chemical processes, Hess's law,

and a *thermochemical cycle* called the Born–Haber cycle, similar to those introduced in Chapter 5 "Energy Changes in Chemical Reactions". Developed by Max Born and Fritz Haber in 1919, the Born–Haber cycle describes a process in which an ionic solid is conceptually formed from its component elements in a stepwise manner.

Let's use the Born–Haber cycle to determine the lattice energy of CsF(s). CsF is a nearly ideal ionic compound because Cs is the least electronegative element that is not radioactive and F is the most electronegative element. To construct a thermochemical cycle for the formation of CsF, we need to know its enthalpy of formation, ΔH_f , which is defined by the following chemical reaction:

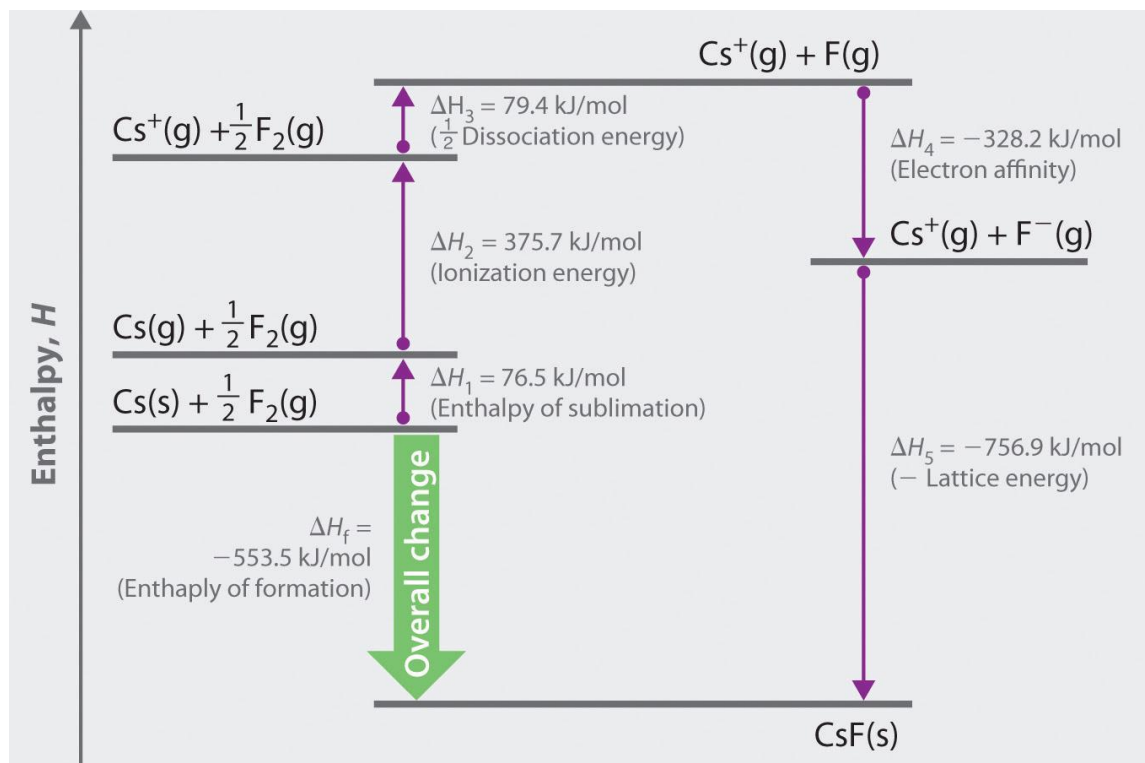
Equation 8.6



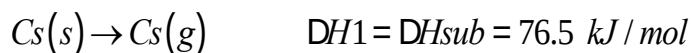
Because enthalpy is a state function, the overall ΔH for a series of reactions is the sum of the values of ΔH for the individual reactions. (For more information about state functions and Hess's law, see Chapter 5 "Energy Changes in Chemical Reactions", Section 5.2 "Enthalpy".) We can therefore use a thermochemical cycle to determine the enthalpy change that accompanies the formation of solid CsF from the parent *elements* (not ions).

The Born–Haber cycle for calculating the lattice energy of cesium fluoride is shown in Figure 8.4 "The Born–Haber Cycle Illustrating the Enthalpy Changes Involved in the Formation of Solid Cesium Fluoride from Its Elements". This particular cycle consists of six reactions, Equation 8.6 plus the following five reactions:

Figure 8.4 The Born–Haber Cycle Illustrating the Enthalpy Changes Involved in the Formation of Solid Cesium Fluoride from Its Elements



Reaction 1



This equation describes the sublimation of elemental cesium, the conversion of the solid directly to a gas.

The accompanying enthalpy change is called the enthalpy of sublimation (ΔH_{sub}) (Table 8.2 "Selected Enthalpies of Sublimation at 298 K") and is *always* positive because energy is required to sublime a solid.

Table 8.2 Selected Enthalpies of Sublimation at 298 K

Substance	ΔH_{sub} (kJ/mol)
Li	159.3
Na	107.5
K	89.0
Rb	80.9
Cs	76.5
Be	324.0
Mg	147.1
Ca	177.8
Sr	164.4
Ba	180.0

Source: Data from *CRC Handbook of Chemistry and Physics* (2004).

Reaction 2



This equation describes the ionization of cesium, so the enthalpy change is the first ionization energy of cesium. Recall from Chapter 7 "The Periodic Table and Periodic Trends" that energy is needed to ionize any neutral atom. Hence, regardless of the compound, the enthalpy change for this portion of the Born–Haber cycle is always positive.

Reaction 3



This equation describes the dissociation of fluorine molecules into fluorine atoms, where D is the energy required for dissociation to occur. ΔH for this reaction, too, is always positive because energy is required to dissociate any stable diatomic molecule into the component atoms.

Table 8.3 Selected Bond Dissociation Enthalpies at 298 K

Substance	D (kJ/mol)
$\text{H}_2(g)$	436.0
$\text{N}_2(g)$	945.3
$\text{O}_2(g)$	498.4
$\text{F}_2(g)$	158.8
$\text{Cl}_2(g)$	242.6
$\text{Br}_2(g)$	192.8
$\text{I}_2(g)$	151.1

Source: Data from *CRC Handbook of Chemistry and Physics* (2004).

Reaction 4



This equation describes the formation of a gaseous fluoride ion from a fluorine atom; the enthalpy change is the electron affinity of fluorine. Recall from Chapter 7 "The Periodic Table and Periodic Trends" that electron affinities can be positive, negative, or zero. In this case, ΔH is negative because of the highly negative electron affinity of fluorine.

Reaction 5



This equation describes the formation of the ionic solid from the gaseous ions. Because Reaction 5 is the reverse of the equation used to define lattice energy and U is defined to be a *positive* number, ΔH_5 is always *negative*, as it should be in a step that forms bonds.

If the enthalpy of formation of CsF from the elements is known ($\Delta H_f = -553.5$ kJ/mol at 298 K), then the thermochemical cycle shown in Figure 8.4 "The Born–Haber Cycle Illustrating the Enthalpy Changes Involved in the Formation of Solid Cesium Fluoride from Its Elements" has only one unknown, the quantity $\Delta H_5 = -U$. From Hess's law, we can write

Equation 8.7

$$\Delta H_f = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5$$

We can rearrange Equation 8.7 to give

Equation 8.8

$$-\Delta H_5 = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 - \Delta H_f$$

Substituting for the individual ΔH s, we obtain



Substituting the appropriate values into this equation gives

Equation 8.9

$$U = 76.5 \text{ kJ/mol} + 375.7 \text{ kJ/mol} + 79.4 \text{ kJ/mol} + (-328.2 \text{ kJ/mole}) - (-553.5 \text{ kJ/mol}) = 756.9 \text{ kJ/mol}$$

U is larger in magnitude than any of the other quantities in Equation 8.9. The process we have used to arrive at this value is summarized in Table 8.4 "Summary of Reactions in the Born–Haber Cycle for the Formation of CsF(s)".

Table 8.4 Summary of Reactions in the Born–Haber Cycle for the Formation of CsF(s)

	Reaction	Enthalpy Change (kJ/mol)
(1)	$\text{Cs}(\text{s}) \rightarrow \text{Cs}(\text{g})$	$\Delta H_{\text{sub}} = 76.5$
(2)	$\text{Cs}(\text{g}) \rightarrow \text{Cs} + (\text{g}) + \text{e}^-$	$I_1 = 375.7$
(3)	$\frac{1}{2}\text{F}_2(\text{g}) \rightarrow \text{F}(\text{g})$	$\frac{1}{2}D = 79.4$
(4)	$\text{F}(\text{g}) + \text{e}^- \rightarrow \text{F}^-(\text{g})$	$EA = -328.2$
(5)	$\text{Cs} + (\text{g}) + \text{F}^-(\text{g}) \rightarrow \text{CsF}(\text{s})$	$-U = -756.9$
	$\text{Cs}(\text{s}) + \frac{1}{2}\text{F}_2(\text{g}) \rightarrow \text{CsF}(\text{s})$	$\Delta H_f = -553.5$

Predicting the Stability of Ionic Compounds

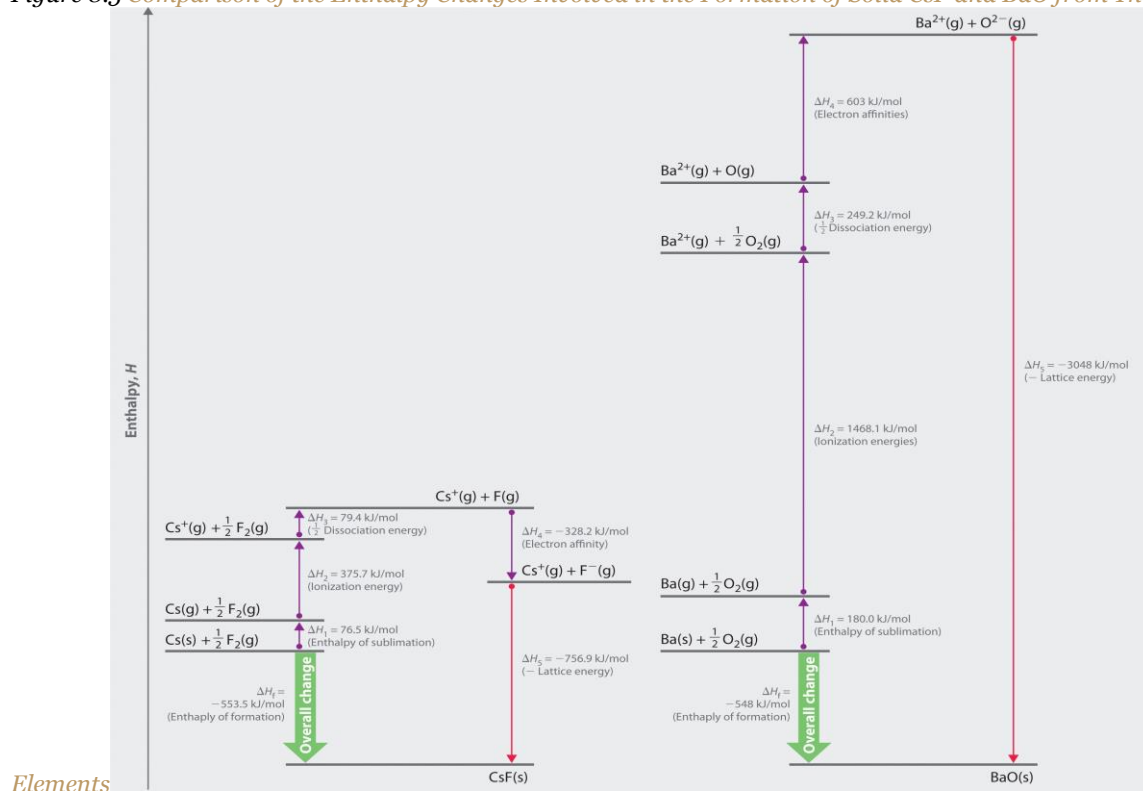
Equation 8.7 may be used as a tool for predicting which ionic compounds are likely to form from particular elements. As we have noted, ΔH_1 (ΔH_{sub}), ΔH_2 (I), and ΔH_3 (D) are always positive numbers, and ΔH_2 can be quite large. In contrast, ΔH_4 (EA) is comparatively small and can be positive, negative, or zero. Thus the first three terms in Equation 8.7 make the formation of an ionic substance energetically unfavorable, and the fourth term contributes little either way. The formation of an ionic compound will be exothermic ($\Delta H_f < 0$) if and only if ΔH_5 ($-U$) is a large negative number. This means that *lattice energy is the most important factor in determining the stability of an ionic compound*. Another example is the formation of BaO:

Equation 8.10



whose Born–Haber cycle is compared with that for the formation of CsF in Figure 8.5 "Comparison of the Enthalpy Changes Involved in the Formation of Solid CsF and BaO from Their Elements".

Figure 8.5 Comparison of the Enthalpy Changes Involved in the Formation of Solid CsF and BaO from Their



The lattice energy of BaO, with a dipositive cation and a dinegative anion, dominates the Born–Haber cycle.

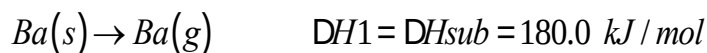
Reaction 1

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More than twice as much energy is required to sublime barium metal (180.0 kJ/mol) as is required to sublime cesium (76.5 kJ/mol).

Reaction 2



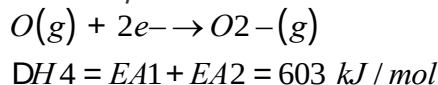
Nearly four times the energy is needed to form Ba^{2+} ions ($I_1 = 502.9 \text{ kJ/mol}$, $I_2 = 965.2 \text{ kJ/mol}$, $I_1 + I_2 = 1468.1 \text{ kJ/mol}$) as Cs^{+} ions ($I_1 = 375.7 \text{ kJ/mol}$).

Reaction 3



Because the bond energy of $\text{O}_2(g)$ is 498.4 kJ/mol compared with 158.8 kJ/mol for $\text{F}_2(g)$, more than three times the energy is needed to form oxygen atoms from O_2 molecules as is required to form fluorine atoms from F_2 .

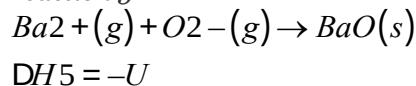
Reaction 4



Forming gaseous oxide (O^{2-}) ions is energetically unfavorable. Even though adding one electron to an oxygen atom is exothermic ($\text{EA}_1 = -141 \text{ kJ/mol}$), adding a second electron to an $\text{O}^{-}(g)$ ion is energetically unfavorable ($\text{EA}_2 = +744 \text{ kJ/mol}$)—so much so that the overall cost of forming $\text{O}^{2-}(g)$ from $\text{O}(g)$ is energetically prohibitive ($\text{EA}_1 + \text{EA}_2 = +603 \text{ kJ/mol}$).

If the first four terms in the Born–Haber cycle are all substantially more positive for BaO than for CsF, why does BaO even form? The answer is the formation of the ionic solid from the gaseous ions (Reaction 5):

Reaction 5



Although the internuclear distances are not significantly different for BaO and CsF (275 and 300 pm, respectively), the larger ionic charges in BaO produce a much higher lattice energy. Substituting values for BaO ($\Delta H_f = -548.0$

kJ/mol) into the equation and solving for U gives

$$\begin{aligned} U &= \text{DH}_{\text{sub}}(\text{Ba}) + [I_1(\text{Ba}) + I_2(\text{Ba})] \\ &+ 12D(\text{O}_2) + [\text{EA}_1(\text{O}) + \text{EA}_2(\text{O})] \\ &- \text{DH}_f(\text{BaO}) = 180.0 \text{ kJ/mol} + 1468.1 \text{ kJ/mol} \\ &+ 249.2 \text{ kJ/mol} \\ &+ 603 \text{ kJ/mol} - (-548.0 \text{ kJ/mol}) = 3048 \text{ kJ/mol} \end{aligned}$$

Thus U for BaO is slightly more than four times greater than U for CsF. The extra energy released when BaO forms from its ions more than compensates for the additional energy required to form $\text{Ba}^{2+}(\text{g})$ and $\text{O}^{2-}(\text{g})$ ions from Ba(s) and $1/2\text{O}_2(\text{g})$.

If the formation of ionic lattices containing multiply charged ions is so energetically favorable, why does CsF contain Cs^+ and F^- ions rather than Cs^{2+} and F^{2-} ions? If we assume that U for a $\text{Cs}^{2+}\text{F}^{2-}$ salt would be approximately the same as U for BaO, the formation of a lattice containing Cs^{2+} and F^{2-} ions would release 2291 kJ/mol (3048 kJ/mol – 756.9 kJ/mol) more energy than one containing Cs^+ and F^- ions. To form the Cs^{2+} ion from Cs^+ , however, would require removing a $5p$ electron from a filled inner shell, which calls for a great deal of energy: $I_2 = 2234.4$ kJ/mol for Cs. Furthermore, forming an F^{2-} ion is expected to be even more energetically unfavorable than forming an O^{2-} ion. Not only is an electron being added to an already negatively charged ion, but because the F^- ion has a filled $2p$ subshell, the added electron would have to occupy an empty high-energy $3s$ orbital. Cesium fluoride, therefore, is not $\text{Cs}^{2+}\text{F}^{2-}$ because the energy cost of forming the doubly charged ions would be greater than the additional lattice energy that would be gained.

Note the Pattern

Lattice energy is usually the most important energy factor in determining the stability of an ionic compound.

EXAMPLE 3

Use data from Figure 7.13 "Electron Affinities (in kJ/mol) of the ", Table 7.5 "Successive Ionization Energies (in kJ/mol) for the Elements in the Third Row of the Periodic Table", Table 8.2 "Selected Enthalpies of Sublimation at 298 K", Table 8.3 "Selected Bond Dissociation Enthalpies at 298 K", and Chapter 25 "Appendix A: Standard Thermodynamic Quantities for Chemical Substances at 25°C" to calculate the lattice energy of MgH_2 .

Given: chemical compound and data from figures and tables

Asked for: lattice energy

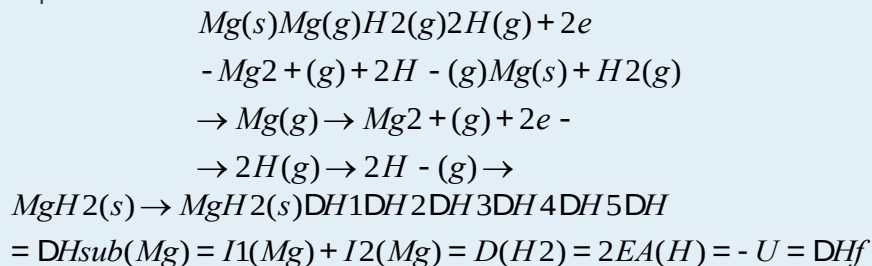
Strategy:

A Write a series of stepwise reactions for forming MgH_2 from its elements via the gaseous ions.

B Use Hess's law and data from the specified figures and tables to calculate the lattice energy.

Solution:

A Hess's law allows us to use a thermochemical cycle (the Born–Haber cycle) to calculate the lattice energy for a given compound. We begin by writing reactions in which we form the component ions from the elements in a stepwise manner and then assemble the ionic solid:



B Table 7.5 "Successive Ionization Energies (in kJ/mol) for the Elements in the Third Row of the Periodic Table" lists the first and second ionization energies for the period 3 elements [$I_1(\text{Mg}) = 737.7$

kJ/mol, $I_2(\text{Mg}) = 1450.7$ kJ/mol]. First electron affinities for all elements are given in Figure 7.13 "Electron Affinities (in kJ/mol) of the "[$EA(\text{H}) = -72.8$ kJ/mol]. Table 8.2 "Selected Enthalpies of Sublimation at 298 K" lists selected enthalpies of sublimation [$\Delta H_{\text{sub}}(\text{Mg}) = 147.1$ kJ/mol]. Table 8.3 "Selected Bond Dissociation Enthalpies at 298 K" lists selected bond dissociation energies [$D(\text{H}_2) = 436.0$ kJ/mol].

Enthalpies of formation ($\Delta H_f = -75.3$ kJ/mol for MgH_2) are listed in Chapter 25 "Appendix A: Standard Thermodynamic Quantities for Chemical Substances at 25°C". From Hess's law, ΔH_f is equal to the sum of the enthalpy changes for Reactions 1–5:

$$\begin{aligned}
 \Delta H_f &= \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 \\
 &= \Delta H_{\text{sub}}(\text{Mg}) + [I_1(\text{Mg}) + I_2(\text{Mg})] + D(\text{H}_2) + 2EA(\text{H}) - U
 \end{aligned}$$

For MgH_2 , $U = 2701.2$ kJ/mol. Once again, lattice energy provides the driving force for forming this compound because ΔH_1 , ΔH_2 , $\Delta H_3 > 0$. When solving this type of problem, be sure to write the chemical equation for each step and double-check that the enthalpy value used for each step has the correct sign for the reaction in the direction it is written.

$$\begin{aligned}
 & 7 \text{ kJ/mol} + 1450.7 \text{ kJ/mol} \\
 & + 436.0 \text{ kJ/mol} + 2(-72.8 \text{ kJ/mol}) - U \\
 & = 2701.2 \text{ kJ/mol}
 \end{aligned}$$

see Equation 7.13).

Answer: 2809 kJ/mol

Summary

Ionic compounds have strong electrostatic attractions between oppositely charged ions in a regular array. The lattice energy (U) of an ionic substance is defined as the energy required to dissociate the solid into gaseous ions; U can be calculated from the charges on the ions, the arrangement of the ions in the solid, and the internuclear distance. Because U depends on the product of the ionic charges, substances with di- or tripositive cations and/or di- or trinegative anions tend to have higher lattice energies than their singly charged counterparts. Higher lattice energies typically result in higher **melting points** and increased **hardness** because more thermal energy is needed to overcome the forces that hold the ions together. Lattice energies cannot be measured directly but are obtained from a thermochemical cycle called the **Born–Haber cycle**, in which Hess’s law is used to calculate the lattice energy from the measured enthalpy of formation of the ionic compound, along with other thermochemical data. The Born–Haber cycle can be used to predict which ionic compounds are likely to form. **Sublimation**, the conversion of a solid directly to a gas, has an accompanying enthalpy change called the **enthalpy of sublimation**.

KEY TAKEAWAY

- The lattice energy is usually the most important energy factor in determining the stability of an ionic compound.

KEY EQUATION

Lattice energy

Equation 8.4:
$$U = -k \frac{Q_1 Q_2}{r_0}$$

CONCEPTUAL PROBLEMS

1. If a great deal of energy is required to form gaseous ions, why do ionic compounds form at all?
2. What are the general physical characteristics of ionic compounds?
3. Ionic compounds consist of crystalline lattices rather than discrete ion pairs. Why?
4. What factors affect the magnitude of the lattice energy of an ionic compound? What is the relationship between ionic size and lattice energy?
5. Which would have the larger lattice energy—an ionic compound consisting of a large cation and a large anion or one consisting of a large anion and a small cation? Explain your answer and any assumptions you made.

6. How would the lattice energy of an ionic compound consisting of a monovalent cation and a divalent anion compare with the lattice energy of an ionic compound containing a monovalent cation and a monovalent anion, if the internuclear distance was the same in both compounds? Explain your answer.
7. Which would have the larger lattice energy— CrCl_2 or CrCl_3 —assuming similar arrangements of ions in the lattice? Explain your answer.
8. Which cation in each pair would be expected to form a chloride salt with the larger lattice energy, assuming similar arrangements of ions in the lattice? Explain your reasoning.
 - a. Na^+ , Mg^{2+}
 - b. Li^+ , Cs^+
 - c. Cu^+ , Cu^{2+}
9. Which cation in each pair would be expected to form an oxide with the higher melting point, assuming similar arrangements of ions in the lattice? Explain your reasoning.
 - a. Mg^{2+} , Sr^{2+}
 - b. Cs^+ , Ba^{2+}
 - c. Fe^{2+} , Fe^{3+}
10. How can a thermochemical cycle be used to determine lattice energies? Which steps in such a cycle require an input of energy?
11. Although NaOH and CH_3OH have similar formulas and molecular masses, the compounds have radically different properties. One has a high melting point, and the other is a liquid at room temperature. Which compound is which and why?

NUMERICAL PROBLEMS

1. Arrange SrO , PbS , and PrI_3 in order of decreasing lattice energy.
2. Compare BaO and MgO with respect to each of the following properties.
 - a. enthalpy of sublimation
 - b. ionization energy of the metal
 - c. lattice energy
 - d. enthalpy of formation
3. Use a thermochemical cycle and data from Figure 7.13 "Electron Affinities (in kJ/mol) of the ", Table 7.5 "Successive Ionization Energies (in kJ/mol) for the Elements in the Third Row of the Periodic Table", Table 8.2

"Selected Enthalpies of Sublimation at 298 K", Table 8.3 "Selected Bond Dissociation Enthalpies at 298 K", and Chapter 25 "Appendix A: Standard Thermodynamic Quantities for Chemical Substances at 25°C" to calculate the lattice energy (U) of magnesium chloride (MgCl_2).

4. Would you expect the formation of SrO from its component elements to be exothermic or endothermic? Why or why not? How does the valence electron configuration of the component elements help you determine this?
5. Using the information in Problem 4 and Problem 5, predict whether CaO or MgCl_2 will have the higher melting point.
6. Use a thermochemical cycle and data from Table 8.2 "Selected Enthalpies of Sublimation at 298 K", Table 8.3 "Selected Bond Dissociation Enthalpies at 298 K", and Chapter 25 "Appendix A: Standard Thermodynamic Quantities for Chemical Substances at 25°C" to calculate the lattice energy of calcium oxide. The first and second ionization energies of calcium are 589.8 kJ/mol and 1145.4 kJ/mol.

ANSWERS

1. Lattice energy is directly proportional to the product of the ionic charges and inversely proportional to the internuclear distance. Therefore, $\text{PbI}_3 > \text{SrO} > \text{PbS}$.
- 2.
3. $U = 2522.2 \text{ kJ/mol}$
- 4.
5. Despite the fact that Mg^{2+} is smaller than Ca^{2+} , the higher charge of O^{2-} versus Cl^- gives CaO a larger lattice energy than MgCl_2 . Consequently, we expect CaO to have the higher melting point.

8.4 Lewis Electron Dot Symbols

LEARNING OBJECTIVE

1. To use Lewis electron dot symbols to predict the number of bonds an element will form.

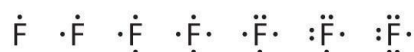
At the beginning of the 20th century, the American chemist G. N. Lewis (1875–1946) devised a system of symbols—now called Lewis electron dot symbols, often shortened to *Lewis dot symbols*—that can be used for predicting the number of bonds formed by most elements in their compounds (Figure 8.6 "G. N. Lewis and the Octet Rule").

Each Lewis dot symbol consists of the chemical symbol for an element surrounded by dots that represent its valence electrons. Cesium, for example, has the electron configuration $[\text{Xe}]6s^1$, which indicates one valence electron outside a closed shell. In the Lewis dot symbol, this single electron is represented as a single dot:



Creating a Lewis Dot Symbol

To write an element's Lewis dot symbol, we place dots representing its valence electrons, one at a time, around the element's chemical symbol. Up to four dots are placed above, below, to the left, and to the right of the symbol (in any order, as long as elements with four or fewer valence electrons have no more than one dot in each position). The next dots, for elements with more than four valence electrons, are again distributed one at a time, each paired with one of the first four. Fluorine, for example, with the electron configuration $[\text{He}]2s^22p^5$, has seven valence electrons, so its Lewis dot symbol is constructed as follows:



The

number of dots in the Lewis dot symbol is the same as the number of valence electrons, which is the same as the last digit of the element's group number in the periodic table. Lewis dot symbols for the elements in period 2 are given in Figure 8.7 "Lewis Dot Symbols for the Elements in Period 2".

Lewis used the unpaired dots to predict the number of bonds that an element will form in a compound. Consider the symbol for nitrogen in Figure 8.7 "Lewis Dot Symbols for the Elements in Period 2". The Lewis dot symbol explains why nitrogen, with three unpaired valence electrons, tends to form compounds in which it shares the unpaired electrons to form three bonds. Boron, which also has three unpaired valence electrons in its Lewis dot symbol, also tends to form compounds with three bonds, whereas carbon, with four unpaired valence electrons in its Lewis dot symbol, tends to share all of its unpaired valence electrons by forming compounds in which it has four bonds.

Figure 8.7 *Lewis Dot Symbols for the Elements in Period 2*

Group	1	2	13	14	15	16	17	18
Electron Configuration	$[\text{He}]2s^1$	$[\text{He}]2s^2$	$[\text{He}]2s^22p^1$	$[\text{He}]2s^22p^2$	$[\text{He}]2s^22p^3$	$[\text{He}]2s^22p^4$	$[\text{He}]2s^22p^5$	$[\text{He}]2s^22p^6$
Lewis Dot Symbol	$\text{Li}\cdot$	$\cdot\text{Be}\cdot$	$\cdot\ddot{\text{B}}\cdot$	$\cdot\ddot{\text{C}}\cdot$	$\cdot\ddot{\text{N}}\cdot$	$:\ddot{\text{O}}\cdot$	$:\ddot{\text{F}}\cdot$	$:\ddot{\text{Ne}}:$

The Octet Rule

Lewis's major contribution to bonding theory was to recognize that atoms tend to lose, gain, or share electrons to reach a total of eight valence electrons, called an *octet*. This so-called octet rule explains the stoichiometry of most compounds in the *s* and *p* blocks of the periodic table. We now know from quantum mechanics that the number eight corresponds to one *ns* and three *np* valence orbitals, which together can accommodate a total of eight electrons. Remarkably, though, Lewis's insight was made nearly a decade before Rutherford proposed the nuclear model of the

atom. An exception to the octet rule is helium, whose $1s^2$ electron configuration gives it a full $n = 1$ shell, and hydrogen, which tends to gain or share its one electron to achieve the electron configuration of helium.

Lewis dot symbols can also be used to represent the ions in ionic compounds. The reaction of cesium with fluorine, for example, to produce the ionic compound CsF can be written as follows:



No dots are shown on Cs^+ in the product because cesium has lost its single valence electron to fluorine. The transfer of this electron produces the Cs^+ ion, which has the valence electron configuration of Xe, and the F^- ion, which has a total of eight valence electrons (an octet) and the Ne electron configuration. This description is consistent with the statement in Chapter 7 "The Periodic Table and Periodic Trends" that among the main group elements, ions in simple binary ionic compounds generally have the electron configurations of the nearest noble gas. The charge of each ion is written in the product, and the anion and its electrons are enclosed in brackets. This notation emphasizes that the ions are associated electrostatically; no electrons are shared between the two elements.

As you might expect for such a qualitative approach to bonding, there are exceptions to the octet rule, which we describe in Section 8.6 "Exceptions to the Octet Rule". These include molecules in which one or more atoms contain fewer or more than eight electrons. In Section 8.5 "Lewis Structures and Covalent Bonding", however, we explain how to form molecular compounds by completing octets.

Summary

One convenient way to predict the number and basic arrangement of bonds in compounds is by using **Lewis electron dot symbols**, which consist of the chemical symbol for an element surrounded by dots that represent its valence electrons, grouped into pairs often placed above, below, and to the left and right of the symbol. The structures reflect the fact that the elements in period 2 and beyond tend to gain, lose, or share electrons to reach a total of eight valence electrons in their compounds, the so-called **octet rule**. Hydrogen, with only two valence electrons, does not obey the octet rule.

KEY TAKEAWAY

- Lewis dot symbols can be used to predict the number of bonds formed by most elements in their compounds.

CONCEPTUAL PROBLEMS

1. The Lewis electron system is a simplified approach for understanding bonding in covalent and ionic compounds. Why do chemists still find it useful?

2. Is a Lewis dot symbol an exact representation of the valence electrons in an atom or ion? Explain your answer.
3. How can the Lewis electron dot system help to predict the stoichiometry of a compound and its chemical and physical properties?
4. How is a Lewis dot symbol consistent with the quantum mechanical model of the atom described in Chapter 6 "The Structure of Atoms"? How is it different?

ANSWER

3. Lewis dot symbols allow us to predict the number of bonds atoms will form, and therefore the stoichiometry of a compound. The Lewis structure of a compound also indicates the presence or absence of lone pairs of electrons, which provides information on the compound's chemical reactivity and physical properties.

8.5 Lewis Structures and Covalent Bonding

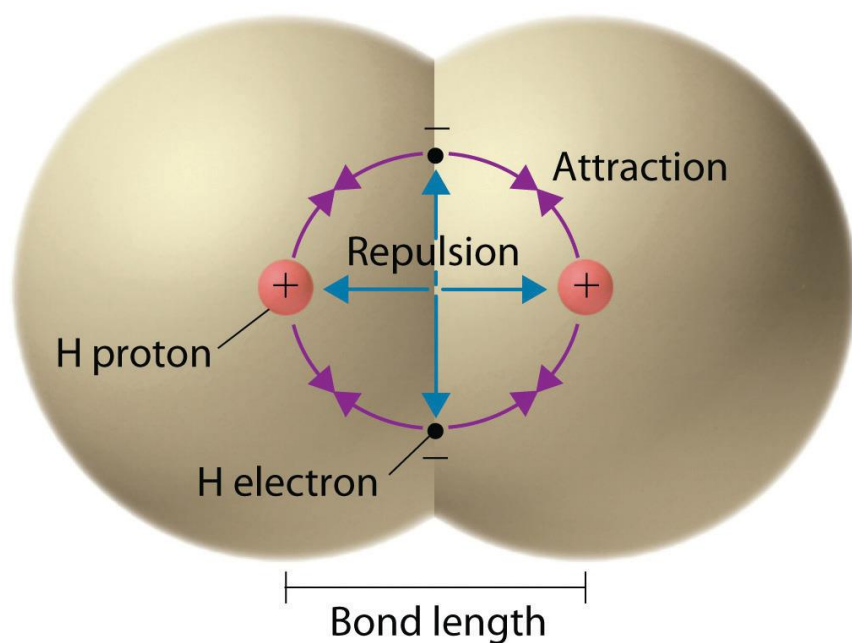
LEARNING OBJECTIVES

1. To use Lewis dot symbols to explain the stoichiometry of a compound.
2. To understand the concept of resonance.

We begin our discussion of the relationship between structure and bonding in covalent compounds by describing the interaction between two identical neutral atoms—for example, the H_2 molecule, which contains a purely covalent bond. Each hydrogen atom in H_2 contains one electron and one proton, with the electron attracted to the proton by electrostatic forces. As the two hydrogen atoms are brought together, additional interactions must be considered (Figure 8.8 "Attractive and Repulsive Interactions between Electrons and Nuclei in the Hydrogen Molecule"):

- The electrons in the two atoms repel each other because they have the same charge ($E > 0$).
- Similarly, the protons in adjacent atoms repel each other ($E > 0$).
- The electron in one atom is attracted to the oppositely charged proton in the other atom and vice versa ($E < 0$).^[1]

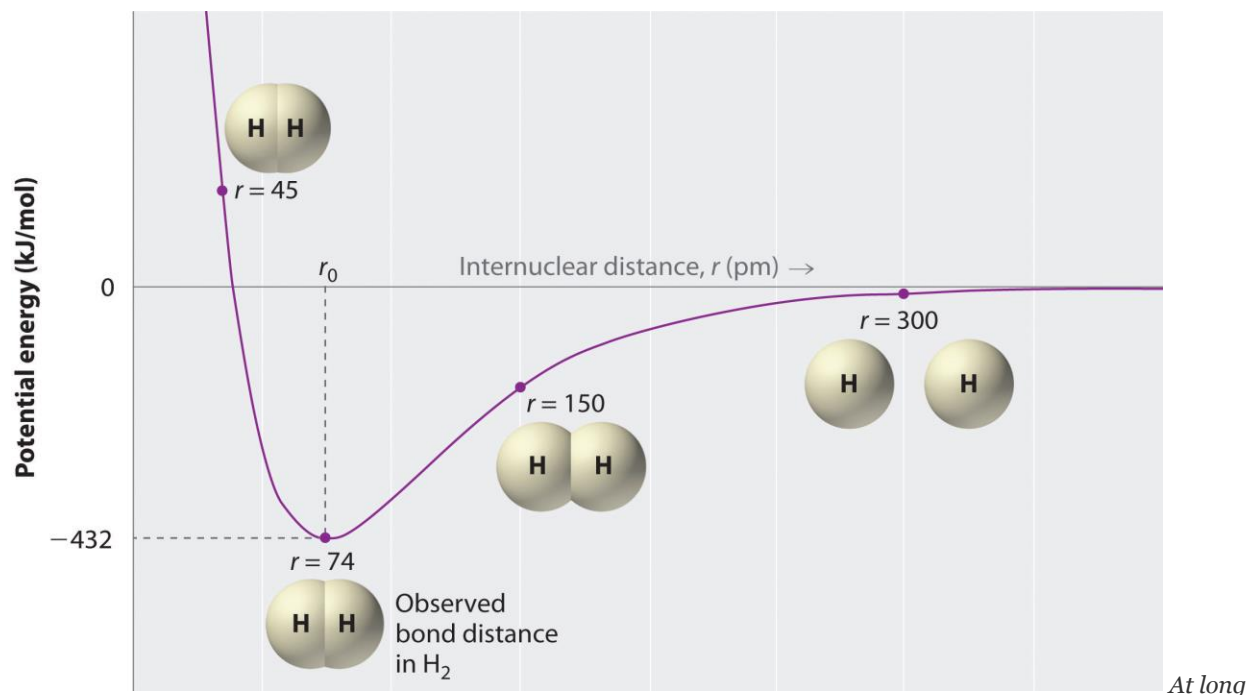
Figure 8.8 Attractive and Repulsive Interactions between Electrons and Nuclei in the Hydrogen Molecule



Electron–electron and proton–proton interactions are repulsive; electron–proton interactions are attractive. At the observed bond distance, the repulsive and attractive interactions are balanced.

A plot of the potential energy of the system as a function of the internuclear distance (Figure 8.9 "A Plot of Potential Energy versus Internuclear Distance for the Interaction between Two Gaseous Hydrogen Atoms") shows that the system becomes more stable (the energy of the system decreases) as two hydrogen atoms move toward each other from $r = \infty$, until the energy reaches a minimum at $r = r_0$ (the observed internuclear distance in H_2 is 74 pm). Thus at intermediate distances, proton–electron attractive interactions dominate, but as the distance becomes very short, electron–electron and proton–proton repulsive interactions cause the energy of the system to increase rapidly. Notice the similarity between Figure 8.9 "A Plot of Potential Energy versus Internuclear Distance for the Interaction between Two Gaseous Hydrogen Atoms" and Figure 8.1 "A Plot of Potential Energy versus Internuclear Distance for the Interaction between a Gaseous Na", which described a system containing two oppositely charged *ions*. The shapes of the energy versus distance curves in the two figures are similar because they both result from attractive and repulsive forces between charged entities.

Figure 8.9 A Plot of Potential Energy versus Internuclear Distance for the Interaction between Two Gaseous Hydrogen Atoms



distances, both attractive and repulsive interactions are small. As the distance between the atoms decreases, the attractive electron–proton interactions dominate, and the energy of the system decreases. At the observed bond distance, the repulsive electron–electron and proton–proton interactions just balance the attractive interactions, preventing a further decrease in the internuclear distance. At very short internuclear distances, the repulsive interactions dominate, making the system less stable than the isolated atoms.

Using Lewis Dot Symbols to Describe Covalent Bonding

The valence electron configurations of the constituent atoms of a covalent compound are important factors in determining its structure, stoichiometry, and properties. For example, chlorine, with seven valence electrons, is one electron short of an octet. If two chlorine atoms share their unpaired electrons by making a covalent bond and forming Cl_2 , they can each complete their valence shell:

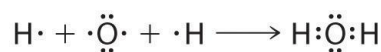


Each chlorine atom now has an octet. The electron pair being shared by the atoms is called a bonding pair; the other three pairs of electrons on each chlorine atom are called lone pairs. Lone pairs are not involved in covalent bonding.

If both electrons in a covalent bond come from the same atom, the bond is called a coordinate covalent bond.

Examples of this type of bonding are presented in Section 8.6 "Exceptions to the Octet Rule" when we discuss atoms with less than an octet of electrons.

We can illustrate the formation of a water molecule from two hydrogen atoms and an oxygen atom using Lewis dot symbols:



The

structure on the right is the *Lewis electron structure*, or *Lewis structure*, for H_2O . With two bonding pairs and two lone pairs, the oxygen atom has now completed its octet. Moreover, by sharing a bonding pair with oxygen, each hydrogen atom now has a full valence shell of two electrons. Chemists usually indicate a bonding pair by a single line, as shown here for our two examples:



The following procedure can be used to construct Lewis electron structures for more complex molecules and ions:

1. Arrange the atoms to show specific connections. When there is a central atom, it is usually the least electronegative element in the compound. Chemists usually list this central atom first in the chemical formula (as in CCl_4 and CO_3^{2-} , which both have C as the central atom), which is another clue to the compound's structure. Hydrogen and the halogens are almost always connected to only one other atom, so they are usually *terminal* rather than central.

Note the Pattern

The central atom is usually the least electronegative element in the molecule or ion; hydrogen and the halogens are usually terminal.

2. Determine the total number of valence electrons in the molecule or ion. Add together the valence electrons from each atom. (Recall from Chapter 6 "The Structure of Atoms" that the number of valence electrons is indicated by the position of the element in the periodic table.) If the species is a polyatomic ion, remember to add or subtract the number of electrons necessary to give the total charge on the ion. For CO_3^{2-} , for example, we add two electrons to the total because of the -2 charge.

3. Place a bonding pair of electrons between each pair of adjacent atoms to give a single bond. In H_2O , for example, there is a bonding pair of electrons between oxygen and each hydrogen.

4. Beginning with the terminal atoms, add enough electrons to each atom to give each atom an octet (two for hydrogen). These electrons will usually be lone pairs.

5. If any electrons are left over, place them on the central atom. We explain in Section 8.6 "Exceptions to the Octet Rule" that some atoms are able to accommodate more than eight electrons.

6. If the central atom has fewer electrons than an octet, use lone pairs from terminal atoms to form multiple (double or triple) bonds to the central atom to achieve an octet. This will not change the number of electrons on the terminal atoms.

Now let's apply this procedure to some particular compounds, beginning with one we have already discussed.

H₂O

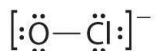
1. Because H atoms are almost always terminal, the arrangement within the molecule must be HOH.
2. Each H atom (group 1) has 1 valence electron, and the O atom (group 16) has 6 valence electrons, for a total of 8 valence electrons.
3. Placing one bonding pair of electrons between the O atom and each H atom gives H:O:H, with 4 electrons left over.
4. Each H atom has a full valence shell of 2 electrons.
5. Adding the remaining 4 electrons to the oxygen (as two lone pairs) gives the following structure:



This is the Lewis structure we drew earlier. Because it gives oxygen an octet and each hydrogen two electrons, we do not need to use step 6.

OCI⁻

1. With only two atoms in the molecule, there is no central atom.
2. Oxygen (group 16) has 6 valence electrons, and chlorine (group 17) has 7 valence electrons; we must add one more for the negative charge on the ion, giving a total of 14 valence electrons.
3. Placing a bonding pair of electrons between O and Cl gives O:Cl, with 12 electrons left over.
4. If we place six electrons (as three lone pairs) on each atom, we obtain the following structure:



Each atom now has an octet of electrons, so steps 5 and 6 are not needed. The Lewis electron structure is drawn within brackets as is customary for an ion, with the overall charge indicated outside the brackets, and the bonding pair of electrons is indicated by a solid line. OCI⁻ is the hypochlorite ion, the active ingredient in chlorine laundry bleach and swimming pool disinfectant.

CH₂O

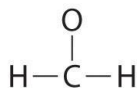
1. Because carbon is less electronegative than oxygen and hydrogen is normally terminal, C must be the central atom. One possible arrangement is as follows:



2. Each

hydrogen atom (group 1) has one valence electron, carbon (group 14) has 4 valence electrons, and oxygen (group 16) has 6 valence electrons, for a total of $[(2)(1) + 4 + 6] = 12$ valence electrons.

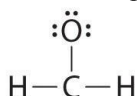
3. Placing a bonding pair of electrons between each pair of bonded atoms gives the following:



Six

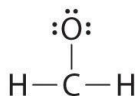
electrons are used, and 6 are left over.

4. Adding all 6 remaining electrons to oxygen (as three lone pairs) gives the following:

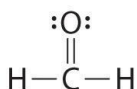


Although oxygen now has an octet and each hydrogen has 2 electrons, carbon has only 6 electrons.

5. There are no electrons left to place on the central atom.



6. To give carbon an octet of electrons, we use one of the lone pairs of electrons on oxygen to form a carbon–oxygen double bond:



Both the oxygen and the carbon now have an octet of electrons, so this is an acceptable Lewis electron structure. The O has two bonding pairs and two lone pairs, and C has four bonding pairs. This is the structure of formaldehyde, which is used in embalming fluid.

An alternative structure can be drawn with one H bonded to O. *Formal charges*, discussed later in this section, suggest that such a structure is less stable than that shown previously.

EXAMPLE 4

Write the Lewis electron structure for each species.

- NCl_3
- S_2^{2-}
- NOCl

Given: chemical species

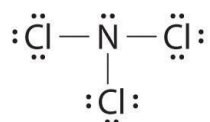
Asked for: Lewis electron structures

Strategy:

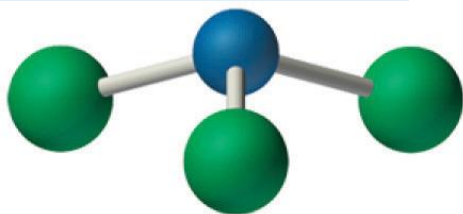
Use the six-step procedure to write the Lewis electron structure for each species.

Solution:

Nitrogen is less electronegative than chlorine, and halogen atoms are usually terminal, so nitrogen is the central atom. The nitrogen atom (group 15) has 5 valence electrons and each chlorine atom (group 17) has 7 valence electrons, for a total of 26 valence electrons. Using 2 electrons for each N–Cl bond and adding three lone pairs to each Cl account for $(3 \times 2) + (3 \times 2 \times 3) = 24$ electrons. Rule 5 leads us to place the remaining 2 electrons on the central N:

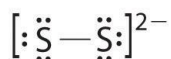


a. Nitrogen trichloride is an unstable oily liquid once used to bleach flour; this use is now prohibited in the United States.

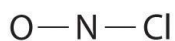


Nitrogen trichloride

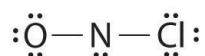
b. In a diatomic molecule or ion, we do not need to worry about a central atom. Each sulfur atom (group 16) contains 6 valence electrons, and we need to add 2 electrons for the -2 charge, giving a total of 14 valence electrons. Using 2 electrons for the S–S bond, we arrange the remaining 12 electrons as three lone pairs on each sulfur, giving each S atom an octet of electrons:



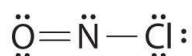
c. Because nitrogen is less electronegative than oxygen or chlorine, it is the central atom. The N atom (group 15) has 5 valence electrons, the O atom (group 16) has 6 valence electrons, and the Cl atom (group 17) has 7 valence electrons, giving a total of 18 valence electrons. Placing one bonding pair of electrons between each pair of bonded atoms uses 4 electrons and gives the following:



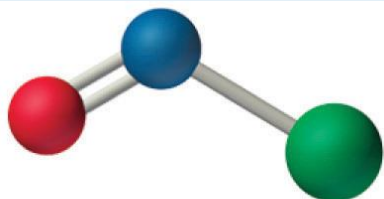
Adding three lone pairs each to oxygen and to chlorine uses 12 more electrons, leaving 2 electrons to place as a lone pair on nitrogen:



Because this Lewis structure has only 6 electrons around the central nitrogen, a lone pair of electrons on a terminal atom must be used to form a bonding pair. We could use a lone pair on either O or Cl. Because we have seen many structures in which O forms a double bond but none with a double bond to Cl, it is reasonable to select a lone pair from O to give the following:



All atoms now have octet configurations. This is the Lewis electron structure of nitrosyl chloride, a highly corrosive, reddish-orange gas.

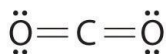


Nitrosyl chloride

Exercise

Write Lewis electron structures for CO_2 and SCl_2 , a vile-smelling, unstable red liquid that is used in the manufacture of rubber.

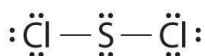
Answer:



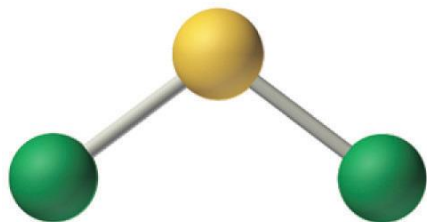
a.



Carbon dioxide



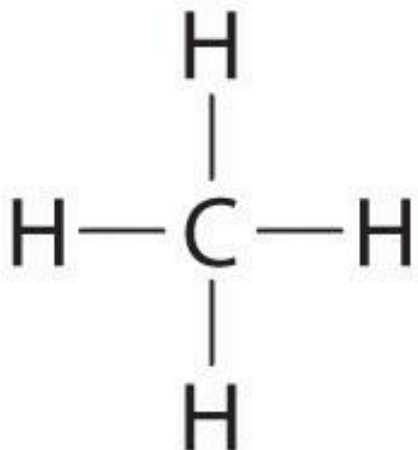
b.



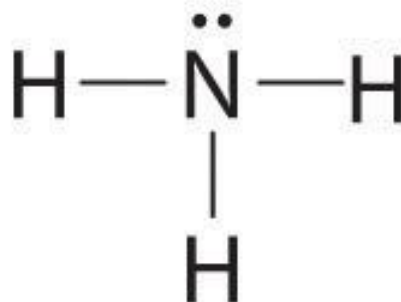
Sulfur dichloride

Using Lewis Electron Structures to Explain Stoichiometry

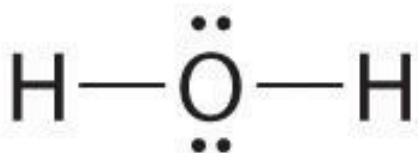
Lewis dot symbols provide a simple rationalization of why elements form compounds with the observed stoichiometries. In the Lewis model, the number of bonds formed by an element in a neutral compound is the same as the number of unpaired electrons it must share with other atoms to complete its octet of electrons. For the elements of group 17 (the halogens), this number is one; for the elements of group 16 (the chalcogens), it is two; for group 15, three; and for group 14, four. These requirements are illustrated by the following Lewis structures for the hydrides of the lightest members of each group:



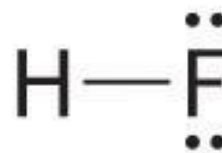
Group 14



Group 15

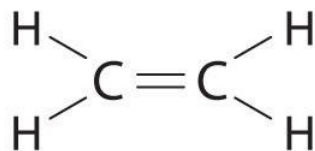


Group 16



Group 17

Elements may form multiple bonds to complete an octet. In ethylene, for example, each carbon contributes two electrons to the double bond, giving each carbon an octet (two electrons/bond $\times$ four bonds = eight electrons). Neutral structures with fewer or more bonds exist, but they are unusual and violate the octet rule.



Ethylene

Allotropes of an element can have very different physical and chemical properties because of different three-dimensional arrangements of the atoms; the number of bonds formed by the component atoms, however, is always the same. As noted at the beginning of the chapter, diamond is a hard, transparent solid; graphite is a soft, black solid; and the fullerenes have open cage structures. Despite these differences, the carbon atoms in all three allotropes

form four bonds, in accordance with the octet rule. Elemental phosphorus also exists in three forms: white phosphorus, a toxic, waxy substance that initially glows and then spontaneously ignites on contact with air; red phosphorus, an amorphous substance that is used commercially in safety matches, fireworks, and smoke bombs; and black phosphorus, an unreactive crystalline solid with a texture similar to graphite (Figure 8.10 "The Three Allotropes of Phosphorus: White, Red, and Black"). Nonetheless, the phosphorus atoms in all three forms obey the octet rule and form three bonds per phosphorus atom.

Note the Pattern

Lewis structures explain why the elements of groups 14–17 form neutral compounds with four, three, two, and one bonded atom(s), respectively.

All three forms contain only phosphorus atoms, but they differ in the arrangement and connectivity of their atoms. White phosphorus contains P_4 tetrahedra, red phosphorus is a network of linked P_8 and P_9 units, and black phosphorus forms sheets of six-membered rings. As a result, their physical and chemical properties differ dramatically.

Formal Charges

It is sometimes possible to write more than one Lewis structure for a substance that does not violate the octet rule, as we saw for CH_2O , but not every Lewis structure may be equally reasonable. In these situations, we can choose the most stable Lewis structure by considering the formal charge on the atoms, which is the difference between the number of valence electrons in the free atom and the number assigned to it in the Lewis electron structure. The formal charge is a way of computing the charge distribution within a Lewis structure; the sum of the formal charges on the atoms within a molecule or an ion must equal the overall charge on the molecule or ion. A formal charge does *not* represent a true charge on an atom in a covalent bond but is simply used to predict the most likely structure when a compound has more than one valid Lewis structure.

To calculate formal charges, we assign electrons in the molecule to individual atoms according to these rules:

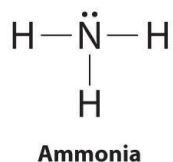
- Nonbonding electrons are assigned to the atom on which they are located.
- Bonding electrons are divided equally between the bonded atoms.

For each atom, we then compute a formal charge:

Equation 8.11

$$\begin{aligned}
 \text{formal charge} = & \\
 & \text{valence } e^- (\text{free atom}) \\
 & - (\text{nonbonding } e^- + \text{bonding } e^- / 2) \\
 & (\text{atom in Lewis structure})
 \end{aligned}$$

To illustrate this method, let's calculate the formal charge on the atoms in ammonia (NH₃) whose Lewis electron structure is as follows:



A neutral nitrogen atom has five valence electrons (it is in group 15). From its Lewis electron structure, the nitrogen atom in ammonia has one lone pair and shares three bonding pairs with hydrogen atoms, so nitrogen itself is assigned a total of five electrons [2 nonbonding e^- + (6 bonding e^- / 2)]. Substituting into Equation 8.11, we obtain

$$\begin{aligned}
 & \text{Equation 8.12} \\
 & \text{formal charge (N)} \\
 & = 5 \text{ valence } e^- \\
 & - (2 \text{ nonbonding } e^- + 6 \text{ bonding } e^- / 2) = 0
 \end{aligned}$$

A neutral hydrogen atom has one valence electron. Each hydrogen atom in the molecule shares one pair of bonding electrons and is therefore assigned one electron [0 nonbonding e^- + (2 bonding e^- / 2)]. Using Equation 8.11 to calculate the formal charge on hydrogen, we obtain

$$\begin{aligned}
 & \text{Equation 8.13} \\
 & \text{formal charge (H)} \\
 & = 1 \text{ valence } e^- \\
 & - (0 \text{ nonbonding } e^- + 2 \text{ bonding } e^- / 2) = 0
 \end{aligned}$$

The hydrogen atoms in ammonia have the same number of electrons as neutral hydrogen atoms, and so their formal charge is also zero. Adding together the formal charges should give us the overall charge on the molecule or ion. In this example, the nitrogen and each hydrogen has a formal charge of zero. When summed the overall charge is zero, which is consistent with the overall charge on the NH₃ molecule.

Typically, the structure with the most charges on the atoms closest to zero is the more stable Lewis structure. In cases where there are positive or negative formal charges on various atoms, stable structures generally have negative formal

charges on the more electronegative atoms and positive formal charges on the less electronegative atoms. The next example further demonstrates how to calculate formal charges.

EXAMPLE 5

Calculate the formal charges on each atom in the NH_4^+ ion.

Given: chemical species

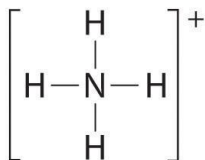
Asked for: formal charges

Strategy:

Identify the number of valence electrons in each atom in the NH_4^+ ion. Use the Lewis electron structure of NH_4^+ to identify the number of bonding and nonbonding electrons associated with each atom and then use Equation 8.11 to calculate the formal charge on each atom.

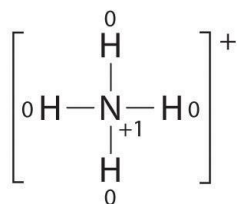
Solution:

The Lewis electron structure for the NH_4^+ ion is as follows:



The nitrogen atom shares four bonding pairs of electrons, and a neutral nitrogen atom has five valence electrons. Using Equation 8.11, the formal charge on the nitrogen atom is therefore $\text{formal charge (N)} = 5 - (0 + 8/2) = +1$

Each hydrogen atom in has one bonding pair. The formal charge on each hydrogen atom is therefore

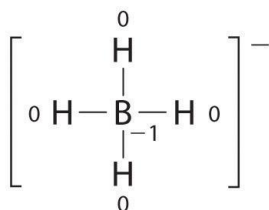


Adding together the formal charges on the atoms should give us the total charge on the molecule or ion. In this case, the sum of the formal charges is $0 + 1 + 0 + 0 + 0 = +1$.

Exercise

Write the formal charges on all atoms in BH_4^- .

Answer:



If an atom in a molecule or ion has the number of bonds that is typical for that atom (e.g., four bonds for carbon), its formal charge is zero.

Note the Pattern

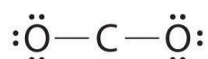
An atom, molecule, or ion has a formal charge of zero if it has the number of bonds that is typical for that species.

Using Formal Charges to Distinguish between Lewis Structures

As an example of how formal charges can be used to determine the most stable Lewis structure for a substance, we can compare two possible structures for CO₂. Both structures conform to the rules for Lewis electron structures.

CO₂

1. C is less electronegative than O, so it is the central atom.
2. C has 4 valence electrons and each O has 6 valence electrons, for a total of 16 valence electrons.
3. Placing one electron pair between the C and each O gives O—C—O, with 12 electrons left over.
4. Dividing the remaining electrons between the O atoms gives three lone pairs on each atom:

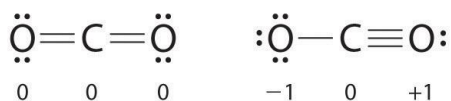


This structure has an octet of electrons around each O atom but only 4 electrons around the C atom.

5. No electrons are left for the central atom.
6. To give the carbon atom an octet of electrons, we can convert two of the lone pairs on the oxygen atoms to bonding electron pairs. There are, however, two ways to do this. We can either take one electron pair from each oxygen to form a symmetrical structure or take both electron pairs from a single oxygen atom to give an asymmetrical structure:



Both Lewis electron structures give all three atoms an octet. How do we decide between these two possibilities? The formal charges for the two Lewis electron structures of CO₂ are as follows:



Both Lewis structures have a net formal charge of zero, but the structure on the right has a +1 charge on the more electronegative atom (O). Thus the symmetrical Lewis structure on the left is predicted to be more stable, and it is, in fact, the structure observed experimentally. Remember, though, that formal charges do *not* represent the actual charges on atoms in a molecule or ion. They are used simply as a bookkeeping method for predicting the most stable Lewis structure for a compound.

Note the Pattern

The Lewis structure with the set of formal charges closest to zero is usually the most stable.

EXAMPLE 6

The thiocyanate ion (SCN^-), which is used in printing and as a corrosion inhibitor against acidic gases, has at least two possible Lewis electron structures. Draw two possible structures, assign formal charges on all atoms in both, and decide which is the preferred arrangement of electrons.

Given: chemical species

Asked for: Lewis electron structures, formal charges, and preferred arrangement

Strategy:

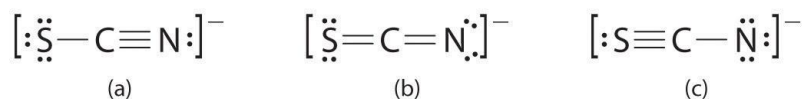
A Use the step-by-step procedure to write two plausible Lewis electron structures for SCN^- .

B Calculate the formal charge on each atom using Equation 8.11.

C Predict which structure is preferred based on the formal charge on each atom and its electronegativity relative to the other atoms present.

Solution:

A Possible Lewis structures for the SCN^- ion are as follows:



B We must calculate the formal charges on each atom to identify the more stable structure. If we begin with carbon, we notice that the carbon atom in each of these structures shares four bonding pairs, the number of bonds typical for carbon, so it has a formal charge of zero. Continuing with sulfur, we observe that in (a) the sulfur atom shares one bonding pair and has three lone pairs and has a total of six valence electrons. The formal charge on the sulfur atom is therefore In (b), the sulfur atom has two bonding pairs and two lone pairs, giving it a formal charge of zero. In (c),

sulfur has a formal charge of +1. Completing our calculations with nitrogen, in (a) the nitrogen atom has three bonding pairs, giving it a formal charge of zero. In (b), the nitrogen atom has two lone pairs and shares two bonding pairs,

giving it a formal charge:

$$6 - (6 + 2) = -1.$$

$$\text{for } 5 - (4 + 2) = -1.$$

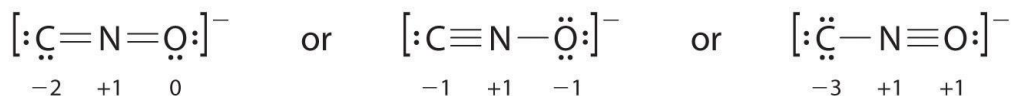
In (c), nitrogen has a formal charge of -2.

C Which structure is preferred? Structure (b) is preferred because the negative charge is on the more electronegative atom (N), and it has lower formal charges on each atom as compared to structure (c): 0, -1 versus +1, -2.

Exercise

Salts containing the fulminate ion (CNO^-) are used in explosive detonators. Draw three Lewis electron structures for CNO^- and use formal charges to predict which is more stable. (Note: N is the central atom.)

Answer:



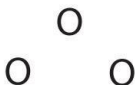
The second structure is predicted to be more stable.

Resonance Structures

Sometimes, even when formal charges are considered, the bonding in some molecules or ions cannot be described by a single Lewis structure. Such is the case for ozone (O_3), an allotrope of oxygen with a V-shaped structure and an O–O–O angle of 117.5° .

O_3

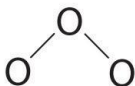
1. We know that ozone has a V-shaped structure, so one O atom is central:



2. Each

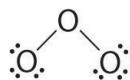
O atom has 6 valence electrons, for a total of 18 valence electrons.

3. Assigning one bonding pair of electrons to each oxygen–oxygen bond gives

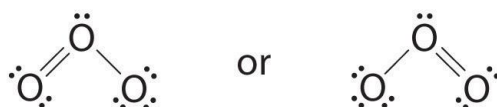


with 14 electrons left over.

4. If we place three lone pairs of electrons on each terminal oxygen, we obtain

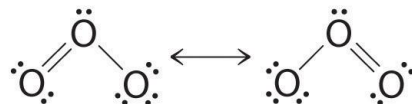


The central oxygen has only 6 electrons. We must convert one lone pair on a terminal oxygen atom to a bonding pair of electrons—but which one? Depending on which one we choose, we obtain either



Which is correct? In fact, neither is correct. Both predict one O–O single bond and one O=O double bond. As you will learn in Section 8.8 "Properties of Covalent Bonds", if the bonds were of different types (one single and one double, for example), they would have different lengths. It turns out, however, that both O–O bond distances are identical, 127.2 pm, which is shorter than a typical O–O single bond (148 pm) and longer than the O=O double bond in O₂ (120.7 pm).

Equivalent Lewis dot structures, such as those of ozone, are called *resonance structures*. The position of the *atoms* is the same in the various resonance structures of a compound, but the position of the *electrons* is different. Double-headed arrows link the different resonance structures of a compound:



The double-headed arrow indicates that the actual electronic structure is an *average* of those shown, not that the molecule oscillates between the two structures.

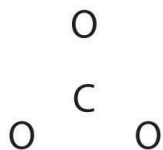
Note the Pattern

When it is possible to write more than one equivalent resonance structure for a molecule or ion, the actual structure is the *average* of the resonance structures.

CO₃²⁻

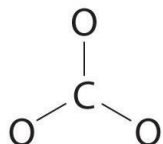
Like ozone, the electronic structure of the carbonate ion cannot be described by a single Lewis electron structure. Unlike O₃, though, the actual structure of CO₃²⁻ is an average of *three* resonance structures.

1. Because carbon is the least electronegative element, we place it in the central position:

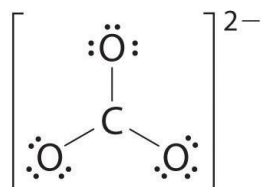


2. Carbon has 4 valence electrons, each oxygen has 6 valence electrons, and there are 2 more for the -2 charge. This gives $4 + (3 \times 6) + 2 = 24$ valence electrons.

3. Six electrons are used to form three bonding pairs between the oxygen atoms and the carbon:

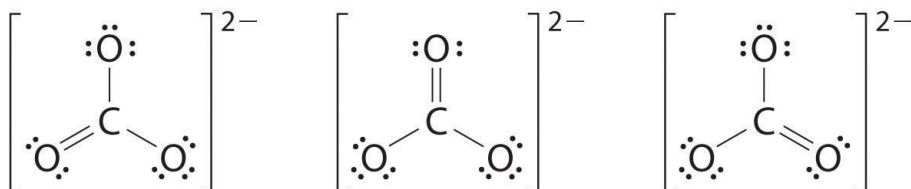


4. We divide the remaining 18 electrons equally among the three oxygen atoms by placing three lone pairs on each and indicating the -2 charge:

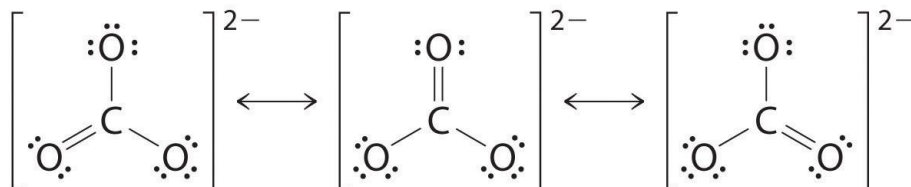


5. No electrons are left for the central atom.

6. At this point, the carbon atom has only 6 valence electrons, so we must take one lone pair from an oxygen and use it to form a carbon–oxygen double bond. In this case, however, there are *three* possible choices:



As with ozone, none of these structures describes the bonding exactly. Each predicts one carbon–oxygen double bond and two carbon–oxygen single bonds, but experimentally all C–O bond lengths are identical. We can write resonance structures (in this case, three of them) for the carbonate ion:



The actual structure is an average of these three resonance structures.

EXAMPLE 7

Benzene is a common organic solvent that was previously used in gasoline; it is no longer used for this purpose, however, because it is now known to be a carcinogen. The benzene molecule (C_6H_6) consists of a regular hexagon of carbon atoms, each of which is also bonded to a hydrogen atom. Use resonance structures to describe the bonding in benzene.

Given: molecular formula and molecular geometry

Asked for: resonance structures

Strategy:

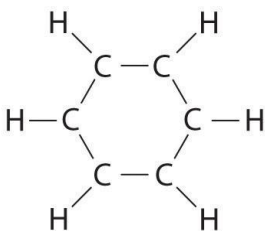
A Draw a structure for benzene illustrating the bonded atoms. Then calculate the number of valence electrons used in this drawing.

B Subtract this number from the total number of valence electrons in benzene and then locate the remaining electrons such that each atom in the structure reaches an octet.

C Draw the resonance structures for benzene.

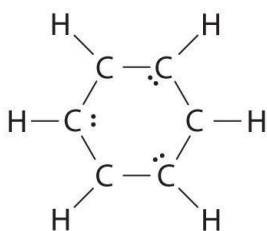
Solution:

A Each hydrogen atom contributes 1 valence electron, and each carbon atom contributes 4 valence electrons, for a total of $(6 \times 1) + (6 \times 4) = 30$ valence electrons. If we place a single bonding electron pair between each pair of carbon atoms and between each carbon and a hydrogen atom, we obtain the following:



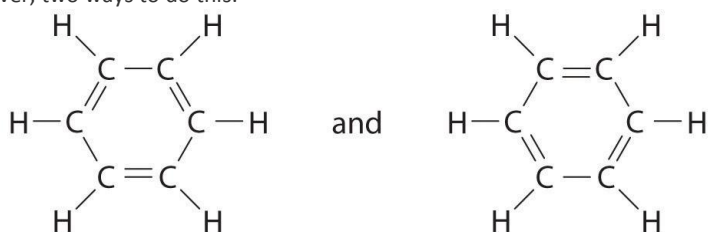
Each carbon atom in this structure has only 6 electrons and has a formal charge of +1, but we have used only 24 of the 30 valence electrons.

B If the 6 remaining electrons are uniformly distributed pairwise on alternate carbon atoms, we obtain the following:

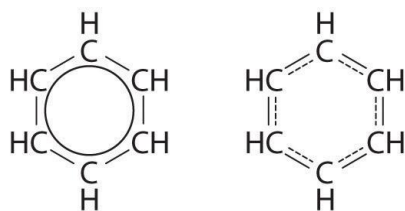


Three carbon atoms now have an octet configuration and a formal charge of -1 , while three carbon atoms have only 6 electrons and a formal charge of $+1$. We can convert each lone pair to a bonding electron pair, which gives each atom an octet of electrons and a formal charge of 0, by making three $C=C$ double bonds.

C There are, however, two ways to do this:



Each structure has alternating double and single bonds, but experimentation shows that each carbon-carbon bond in benzene is identical, with bond lengths (139.9 pm) intermediate between those typically found for a $C-C$ single bond (154 pm) and a $C=C$ double bond (134 pm). We can describe the bonding in benzene using the two resonance structures, but the actual electronic structure is an average of the two. The existence of multiple resonance structures for aromatic hydrocarbons like benzene is often indicated by drawing either a circle or dashed lines inside the hexagon:



Benzene

Exercise

The sodium salt of nitrite is used to relieve muscle spasms. Draw two resonance structures for the nitrite ion (NO_2^-).

Answer:



Resonance structures are particularly common in oxoanions of the *p*-block elements, such as sulfate and phosphate, and in aromatic hydrocarbons, such as benzene and naphthalene.

Summary

A plot of the overall energy of a covalent bond as a function of internuclear distance is identical to a plot of an ionic pair because both result from attractive and repulsive forces between charged entities. In Lewis electron structures, we encounter **bonding pairs**, which are shared by two atoms, and **lone pairs**, which are not shared between atoms. If both electrons in a covalent bond come from the same atom, the bond is called a **coordinate covalent bond**. Lewis structures are an attempt to rationalize why certain stoichiometries are commonly observed for the elements of particular families. Neutral compounds of group 14 elements typically contain four bonds around each atom (a double bond counts as two, a triple bond as three), whereas neutral compounds of group 15 elements typically contain three bonds. In cases where it is possible to write more than one Lewis electron structure with octets around all the nonhydrogen atoms of a compound, the **formal charge** on each atom in alternative structures must be considered to decide which of the valid structures can be excluded and which is the most reasonable. The formal charge is the difference between the number of valence electrons of the free atom and the number of electrons assigned to it in the compound, where bonding electrons are divided equally between the bonded atoms. The Lewis structure with the lowest formal charges on the atoms is almost always the most stable one. Some molecules have two or more chemically equivalent Lewis electron structures, called **resonance structures**. These structures are written with a double-headed arrow between them, indicating that *none* of the Lewis structures accurately describes the bonding but that the actual structure is an *average* of the individual resonance structures.

KEY TAKEAWAY

- Lewis dot symbols provide a simple rationalization of why elements form compounds with the observed stoichiometries.

KEY EQUATION

Formal charge on an atom

$$\text{formal charge} = \text{valence } e^-$$

$$\text{Equation 8.11: } - (\text{nonbonding } e^- + \text{bonding } e^- / 2)$$

CONCEPTUAL PROBLEMS

1. Compare and contrast covalent and ionic compounds with regard to

- a. volatility.
 - b. melting point.
 - c. electrical conductivity.
 - d. physical appearance.
2. What are the similarities between plots of the overall energy versus internuclear distance for an ionic compound and a covalent compound? Why are the plots so similar?
 3. Which atom do you expect to be the central atom in each of the following species?
 - a. SO_4^{2-}
 - b. NH_4^+
 - c. BCl_3
 - d. SO_2Cl_2 ?
 4. Which atom is the central atom in each of the following species?
 - a. PCl_3
 - b. CHCl_3
 - c. SO_2
 - d. IF_3 ?
 5. What is the relationship between the number of bonds typically formed by the period 2 elements in groups 14, 15, and 16 and their Lewis electron structures?
 6. Although formal charges do not represent actual charges on atoms in molecules or ions, they are still useful. Why?
 7. Why are resonance structures important?
 8. In what types of compounds are resonance structures particularly common?

NUMERICAL PROBLEMS

1. Give the electron configuration and the Lewis dot symbol for the following. How many more electrons can each atom accommodate?
 - a. Se
 - b. Kr
 - c. Li
 - d. Sr

- e. H
2. Give the electron configuration and the Lewis dot symbol for the following. How many more electrons can each atom accommodate?
- a. Na
- b. Br
- c. Ne
- d. C
- e. Ga
3. Based on Lewis dot symbols, predict the preferred oxidation state of Be, F, B, and Cs.
4. Based on Lewis dot symbols, predict the preferred oxidation state of Br, Rb, O, Si, and Sr.
5. Based on Lewis dot symbols, predict how many bonds gallium, silicon, and selenium will form in their neutral compounds.
6. Determine the total number of valence electrons in the following.
- a. Cr
- b. Cu^+
- c. NO^+
- d. XeF_2
- e. Br_2
- f. CH_2Cl_2
- g. NO_3^-
- h. H_3O^+
7. Determine the total number of valence electrons in the following.
- a. Ag
- b. Pt^{2+}
- c. H_2S
- d. OH^-
- e. I_2
- f. CH_4
- g. SO_4^{2-}

- h. NH_4^+ .
8. Draw Lewis electron structures for the following.
- F_2
 - SO_2
 - AlCl_4^-
 - SO_3^{2-}
 - BrCl
 - XeF_4
 - NO^+
 - PCl_3
9. Draw Lewis electron structures for the following.
- Br_2
 - CH_3Br
 - SO_4^{2-}
 - O_2
 - S_2^{2-}
 - BF_3
10. Draw Lewis electron structures for CO_2 , NO_2^- , SO_2 , and NO_2^+ . From your diagram, predict which pair(s) of compounds have similar electronic structures.
11. Write Lewis dot symbols for each pair of elements. For a reaction between each pair of elements, predict which element is the oxidant, which element is the reductant, and the final stoichiometry of the compound formed.
- K, S
 - Sr, Br
 - Al, O
 - Mg, Cl
12. Write Lewis dot symbols for each pair of elements. For a reaction between each pair of elements, predict which element is the oxidant, which element is the reductant, and the final stoichiometry of the compound formed.

a. Li, F

b. Cs, Br

c. Ca, Cl

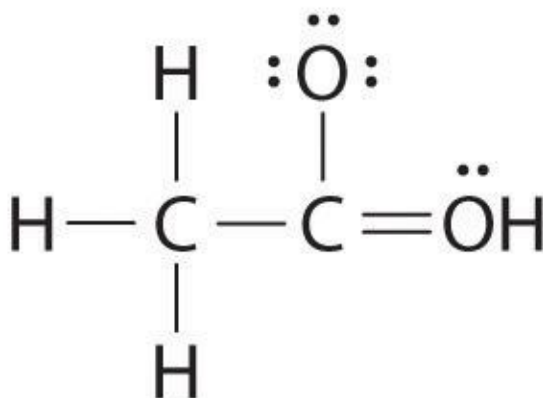
d. B, F

13. Use Lewis dot symbols to predict whether ICl and NO_4^- are chemically reasonable formulas.

14. Draw a plausible Lewis electron structure for a compound with the molecular formula Cl_3PO .

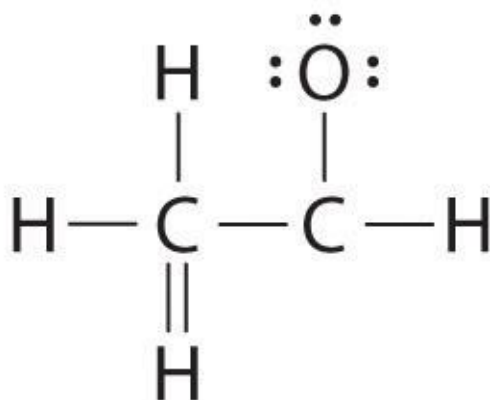
15. Draw a plausible Lewis electron structure for a compound with the molecular formula CH_4O .

16. While reviewing her notes, a student noticed that she had drawn the following structure in her notebook for acetic acid:



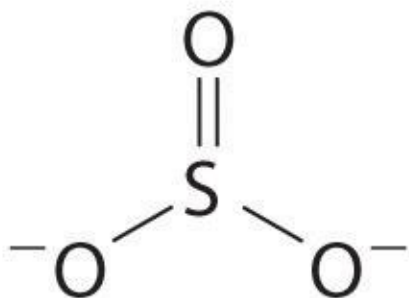
16. Why is this structure not feasible? Draw an acceptable Lewis structure for acetic acid. Show the formal charges of all nonhydrogen atoms in both the correct and incorrect structures.

17. A student proposed the following Lewis structure shown for acetaldehyde.



1. Why is this structure not feasible? Draw an acceptable Lewis structure for acetaldehyde. Show the formal charges of all nonhydrogen atoms in both the correct and incorrect structures.

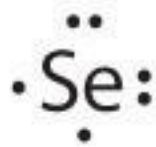
2. Draw the most likely structure for HCN based on formal charges, showing the formal charge on each atom in your structure. Does this compound have any plausible resonance structures? If so, draw one.
3. Draw the most plausible Lewis structure for NO_3^- . Does this ion have any other resonance structures? Draw at least one other Lewis structure for the nitrate ion that is not plausible based on formal charges.
4. At least two Lewis structures can be drawn for BCl_3 . Using arguments based on formal charges, explain why the most likely structure is the one with three B–Cl single bonds.
5. Using arguments based on formal charges, explain why the most feasible Lewis structure for SO_4^{2-} has two sulfur–oxygen double bonds.
6. At least two distinct Lewis structures can be drawn for N_3^- . Use arguments based on formal charges to explain why the most likely structure contains a nitrogen–nitrogen double bond.
7. Is H–O–N=O a reasonable structure for the compound HNO_2 ? Justify your answer using Lewis electron dot structures.
8. Is H–O=C–H a reasonable structure for a compound with the formula CH_2O ? Use Lewis electron dot structures to justify your answer.
9. Explain why the following Lewis structure for SO_3^{2-} is or is not reasonable.



1. Draw all the resonance structures for each ion.
 - a. HSO_4^-
 - b. HSO_3^-

ANSWERS

1.
 - a. $[\text{Ar}]4s^23d^{10}4p^4$

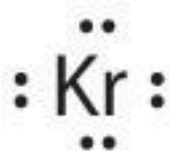


1.

2.

a. Selenium can accommodate two more electrons, giving the Se^{2-} ion.

b. $[\text{Ar}]4s^23d^{10}4p^6$



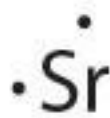
Krypton has a closed shell electron configuration, so it cannot accommodate any additional electrons.

c. $1s^22s^1$



Lithium can accommodate one additional electron in its 2s orbital, giving the Li^- ion.

d. $[\text{Kr}]5s^2$



Strontium has a filled 5s subshell, and additional electrons would have to be placed in an orbital with a higher energy. Thus strontium has no tendency to accept an additional electron.

e. $1s^1$



Hydrogen can accommodate one additional electron in its 1s orbital, giving the H^- ion.

3. Be^{2+} , F^- , B^{3+} , Cs^+

7.

a. 11

b. 8

c. 8

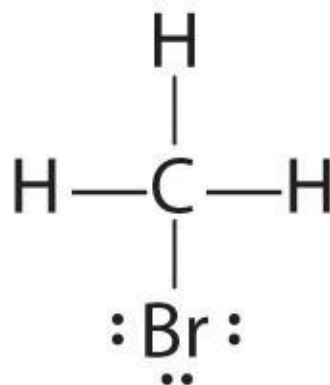
d. 8

e. 14

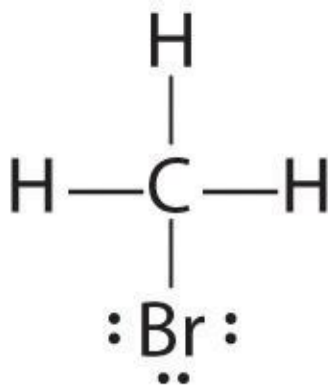
f. 8

g. 32

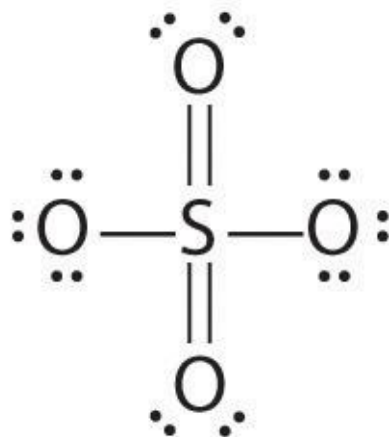
h. 8



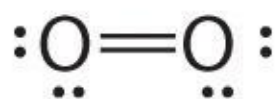
9. a.



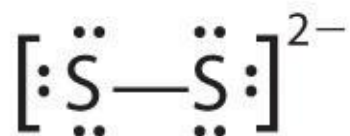
b.



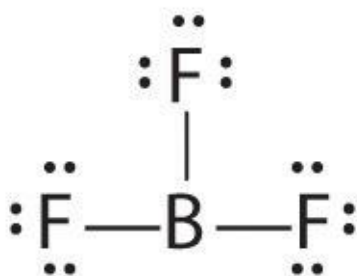
c.



d.



e.



f.

1. 11. a.

a.



K is the reductant; S is the oxidant. The final stoichiometry is K_2S .



b.

Sr is the reductant; Br is the oxidant. The final stoichiometry is SrBr_2 .



c.

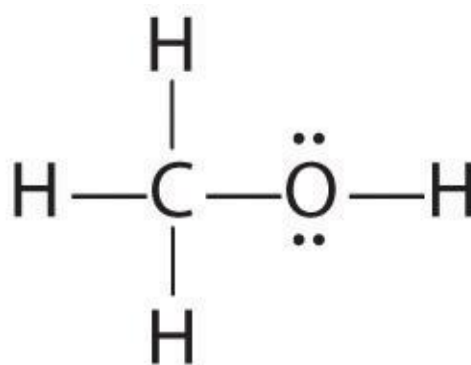
Al is the reductant; O is the oxidant. The final stoichiometry is Al_2O_3 .



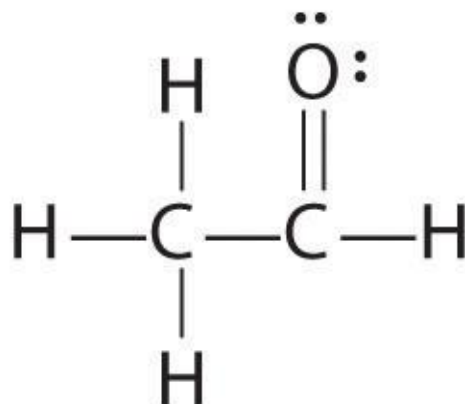
d.

Mg is the reductant; Cl is the oxidant. The final stoichiometry is MgCl_2 .

15. The only structure that gives both oxygen and carbon an octet of electrons is the following:

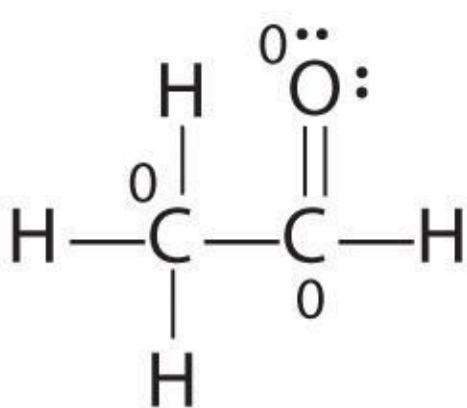


17. The student's proposed structure has two flaws: the hydrogen atom with the double bond has four valence electrons (H can only accommodate two electrons), and the carbon bound to oxygen only has six valence electrons (it should have an octet). An acceptable Lewis structure is

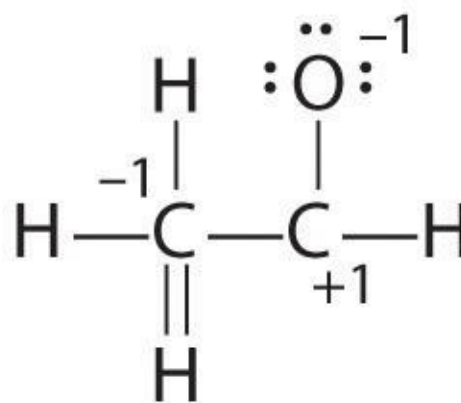


The

formal charges on the correct and incorrect structures are as follows:

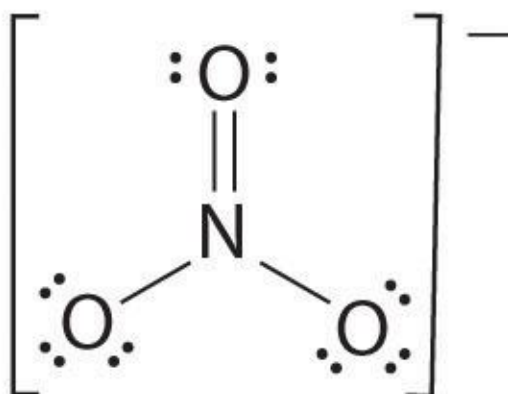


Correct



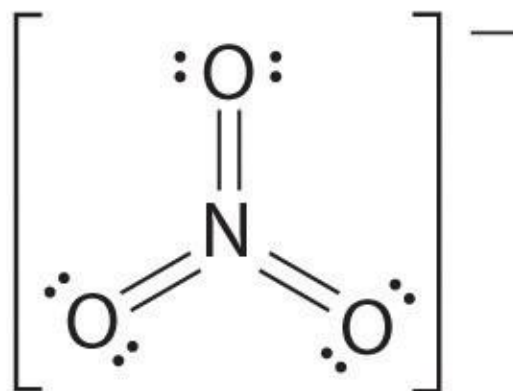
Incorrect

19. The most plausible Lewis structure for NO_3^- is:

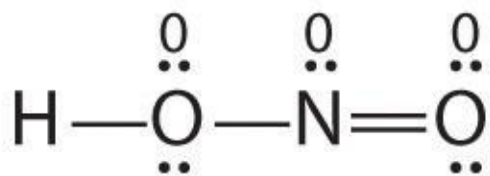


There are three equivalent resonance structures for nitrate (only one is shown), in which nitrogen is doubly bonded to one of the three oxygens. In each resonance structure, the formal charge of N is +1; for each singly bonded O, it is -1; and for the doubly bonded oxygen, it is 0.

The following is an example of a Lewis structure that is *not* plausible:



1. This structure nitrogen has six bonds (nitrogen can form only four bonds) and a formal charge of -1.
- 2.
3. With four S-O single bonds, each oxygen in SO_4^{2-} has a formal charge of -1, and the central sulfur has a formal charge of +2. With two S=O double bonds, only two oxygens have a formal charge of -1, and sulfur has a formal charge of zero. Lewis structures that minimize formal charges tend to be lowest in energy, making the Lewis structure with two S=O double bonds the most probable.
4. Yes. This is a reasonable Lewis structure, because the formal charge on all atoms is zero, and each atom (except H) has an octet of electrons.



[1] Recall from Chapter 6 "The Structure of Atoms" that it is impossible to specify precisely the position of the electron in either hydrogen atom. Hence the quantum mechanical probability distributions must be used.

8.6 Exceptions to the Octet Rule

LEARNING OBJECTIVE

1. To assign a Lewis dot symbol to elements not having an octet of electrons in their compounds.

Lewis dot structures provide a simple model for rationalizing the bonding in most known compounds. However, there are three general exceptions to the octet rule: (1) molecules, such as NO, with an *odd* number of electrons; (2) molecules in which one or more atoms possess *more* than eight electrons, such as SF₆; and (3) molecules such as BCl₃, in which one or more atoms possess *less* than eight electrons.

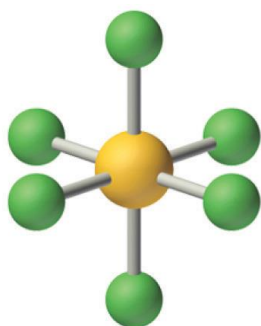
Odd Number of Electrons

Because most molecules or ions that consist of *s*- and *p*-block elements contain even numbers of electrons, their bonding can be described using a model that assigns every electron to either a bonding pair or a lone pair.^[1] There are, however, a few molecules containing only *p*-block elements that have an odd number of electrons. Some important examples are nitric oxide (NO), whose biochemical importance was described in earlier chapters; nitrogen dioxide (NO₂), an oxidizing agent in rocket propulsion; and chlorine dioxide (ClO₂), which is used in water purification plants. Consider NO, for example. With $5 + 6 = 11$ valence electrons, there is no way to draw a Lewis structure that gives each atom an octet of electrons. Molecules such as NO, NO₂, and ClO₂ require a more sophisticated treatment of bonding, which will be developed in Chapter 9 "Molecular Geometry and Covalent Bonding Models".

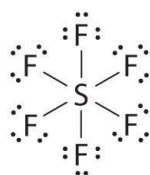
More Than an Octet of Electrons

The most common exception to the octet rule is a molecule or an ion with at least one atom that possesses more than an octet of electrons. Such compounds are found for elements of period 3 and beyond. Examples from the *p*-block elements include SF₆, a substance used by the electric power industry to insulate high-voltage lines, and the SO₄²⁻ and PO₄³⁻ ions.

Let's look at sulfur hexafluoride (SF₆), whose Lewis structure must accommodate a total of 48 valence electrons [$6 + (6 \times 7) = 48$]. If we arrange the atoms and electrons symmetrically, we obtain a structure with six bonds to sulfur; that is, it is *six-coordinate*. Each fluorine atom has an octet, but the sulfur atom has 12 electrons surrounding it rather than 8.^[2]



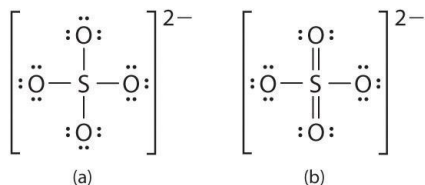
Sulfur hexafluoride



The octet rule is based on the fact that each valence orbital (typically, one ns and three np orbitals) can accommodate only two electrons. To accommodate more than eight electrons, sulfur must be using not only the ns and np valence orbitals but additional orbitals as well. Sulfur has an $[\text{Ne}]3s^23p^43d^0$ electron configuration, so in principle it could accommodate more than eight valence electrons by using one or more d orbitals. Thus species such as SF_6 are often called expanded-valence molecules. Whether or not such compounds really do use d orbitals in bonding is controversial, but this model explains why compounds exist with more than an octet of electrons around an atom. There is no correlation between the stability of a molecule or an ion and whether or not it has an expanded valence shell. Some species with expanded valences, such as PF_5 , are highly reactive, whereas others, such as SF_6 , are very unreactive. In fact, SF_6 is so inert that it has many commercial applications. In addition to its use as an electrical insulator, it is used as the coolant in some nuclear power plants, and it is the pressurizing gas in “unpressurized” tennis balls.

An expanded valence shell is often written for oxoanions of the heavier p -block elements, such as sulfate (SO_4^{2-}) and phosphate (PO_4^{3-}). Sulfate, for example, has a total of 32 valence electrons $[6 + (4 \times 6) + 2]$. If we use a single pair of electrons to connect the sulfur and each oxygen, we obtain the four-coordinate Lewis structure (a). We know that sulfur can accommodate more than eight electrons by using its empty valence d orbitals, just as in SF_6 . An alternative structure (b) can be written with $\text{S}=\text{O}$ double bonds, making the sulfur again six-coordinate. We can draw five other resonance structures equivalent to (b) that vary only in the arrangement of the single and double bonds. In fact, experimental data show that the S-to-O bonds in the SO_4^{2-} ion are intermediate in length between single and double bonds, as expected for a system whose resonance structures all contain two S–O single bonds and two $\text{S}=\text{O}$ double

bonds. When calculating the formal charges on structures (a) and (b), we see that the S atom in (a) has a formal charge of +2, whereas the S atom in (b) has a formal charge of 0. Thus by using an expanded octet, a +2 formal charge on S can be eliminated.

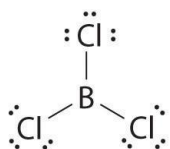


Note the Pattern

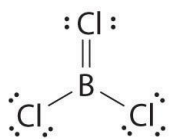
In oxoanions of the heavier *p*-block elements, the central atom often has an expanded valence shell.

Less Than an Octet of Electrons

Molecules with atoms that possess less than an octet of electrons generally contain the lighter *s*- and *p*-block elements, especially beryllium, typically with just four electrons around the central atom, and boron, typically with six. One example, boron trichloride (BCl_3) is used to produce fibers for reinforcing high-tech tennis rackets and golf clubs. The compound has 24 valence electrons and the following Lewis structure:



The boron atom has only six valence electrons, while each chlorine atom has eight. A reasonable solution might be to use a lone pair from one of the chlorine atoms to form a B-to-Cl double bond:



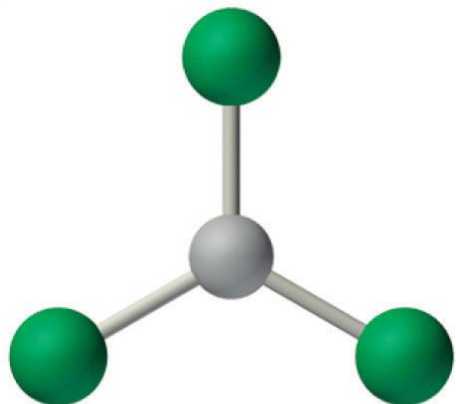
This resonance structure, however, results in a formal charge of +1 on the doubly bonded Cl atom and -1 on the B atom. The high electronegativity of Cl makes this separation of charge unlikely and suggests that this is not the most important resonance structure for BCl_3 . This conclusion is shown to be valid based on the three equivalent B-Cl bond lengths of 173 pm that have no double bond character. Electron-deficient compounds such as BCl_3 have a strong tendency to gain an additional pair of electrons by reacting with species with a lone pair of electrons.

Note the Pattern

Molecules with atoms that have fewer than an octet of electrons generally contain the lighter *s*- and *p*-block elements.

Note the Pattern

Electron-deficient compounds have a strong tendency to gain electrons in their reactions.



Boron trichloride

EXAMPLE 8

Draw Lewis dot structures for each compound.

- BeCl_2 gas, a compound used to produce beryllium, which in turn is used to produce structural materials for missiles and communication satellites
- SF_4 , a compound that reacts violently with water

Include resonance structures where appropriate.

Given: two compounds

Asked for: Lewis electron structures

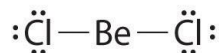
Strategy:

A Use the procedure given earlier to write a Lewis electron structure for each compound. If necessary, place any remaining valence electrons on the element most likely to be able to accommodate more than an octet.

B After all the valence electrons have been placed, decide whether you have drawn an acceptable Lewis structure.

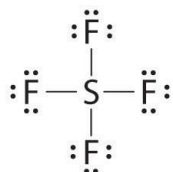
Solution:

- A** Because it is the least electronegative element, Be is the central atom. The molecule has 16 valence electrons (2 from Be and 7 from each Cl). Drawing two Be–Cl bonds and placing three lone pairs on each Cl gives the following structure:

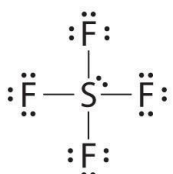


a. **B** Although this arrangement gives beryllium only 4 electrons, it is an acceptable Lewis structure for BeCl_2 . Beryllium is known to form compounds in which it is surrounded by less than an octet of electrons.

b. **A** Sulfur is the central atom because it is less electronegative than fluorine. The molecule has 34 valence electrons (6 from S and 7 from each F). The S–F bonds use 8 electrons, and another 24 are placed around the F atoms:



The only place to put the remaining 2 electrons is on the sulfur, giving sulfur 10 valence electrons:

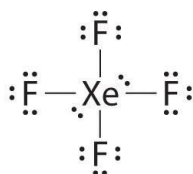


a. **B** Sulfur can accommodate more than an octet, so this is an acceptable Lewis structure.

Exercise

Draw Lewis dot structures for XeF_4 .

Answer:



Summary

Molecules with an odd number of electrons are relatively rare in the *s* and *p* blocks but rather common among the *d*- and *f*-block elements. Compounds with more than an octet of electrons around an atom are called **expanded-valence molecules**. One model to explain their existence uses one or more *d* orbitals in bonding in addition to the valence *ns* and *np* orbitals. Such species are known for only atoms in period 3 or below, which contain *nd* subshells in their valence shell.

KEY TAKEAWAY

- General exceptions to the octet rule include molecules that have an odd number of electrons and molecules in which one or more atoms possess more or fewer than eight electrons.

CONCEPTUAL PROBLEMS

- What regions of the periodic table contain elements that frequently form molecules with an odd number of electrons? Explain your answer.
- How can atoms expand their valence shell? What is the relationship between an expanded valence shell and the stability of an ion or a molecule?
- What elements are known to form compounds with less than an octet of electrons? Why do electron-deficient compounds form?
- List three elements that form compounds that do not obey the octet rule. Describe the factors that are responsible for the stability of these compounds.

NUMERICAL PROBLEMS

- What is the major weakness of the Lewis system in predicting the electron structures of PCl_6^- and other species containing atoms from period 3 and beyond?
- The compound aluminum trichloride consists of Al_2Cl_6 molecules with the following structure (lone pairs of electrons removed for clarity):

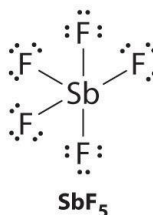
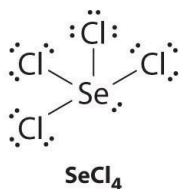
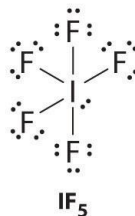
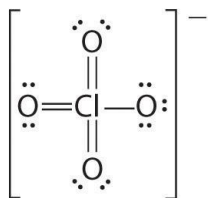


- Does this structure satisfy the octet rule? What is the formal charge on each atom? Given the chemical similarity between aluminum and boron, what is a plausible explanation for the fact that aluminum trichloride forms a dimeric structure rather than the monomeric trigonal planar structure of BCl_3 ?
- Draw Lewis electron structures for ClO_4^- , IF_5 , SeCl_4 , and SbF_5 .
- Draw Lewis electron structures for ICl_3 , Cl_3PO , Cl_2SO , and AsF_6^- .
- Draw plausible Lewis structures for the phosphate ion, including resonance structures. What is the formal charge on each atom in your structures?
- Draw an acceptable Lewis structure for PCl_5 , a compound used in manufacturing a form of cellulose. What is the formal charge of the central atom? What is the oxidation number of the central atom?
- Using Lewis structures, draw all of the resonance structures for the BrO_3^- ion.

7. Draw an acceptable Lewis structure for xenon trioxide (XeO_3), including all resonance structures.

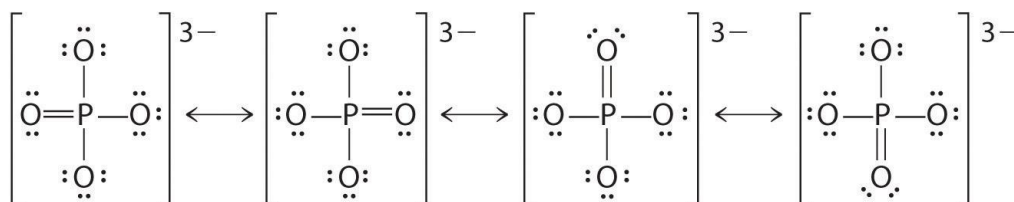
ANSWERS

3. ClO_4^- (one of four equivalent resonance structures)



5. The formal charge on phosphorus is 0, while three oxygen atoms have a formal charge of -1 and one has a formal charge of zero.

7.



[1] Molecules or ions containing *d*-block elements frequently contain an odd number of electrons, and their bonding cannot adequately be described using the simple approach we have developed so far. Bonding in these compounds will be discussed in Chapter 23 "The ".

[2] The third step in our procedure for writing Lewis electron structures, in which we place an electron pair between each pair of bonded atoms, requires that an atom have more than 8 electrons whenever it is bonded to more than 4 other atoms.

8.7 Lewis Acids and Bases

LEARNING OBJECTIVE

1. To identify Lewis acids and bases.

As you learned in Chapter 4 "Reactions in Aqueous Solution", the Brønsted–Lowry concept of acids and bases defines a base as any species that can accept a proton, and an acid as any substance that can donate a proton. Lewis proposed an alternative definition that focuses on *pairs of electrons* instead.

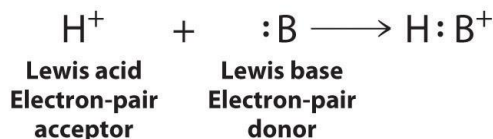
A Lewis base is defined as any species that can *donate* a pair of electrons, and a Lewis acid is any species that can *accept* a pair of electrons. All Brønsted–Lowry bases (proton acceptors), such as OH^- , H_2O , and NH_3 , are also electron-pair donors. Thus the Lewis definition of acids and bases does not contradict the Brønsted–Lowry definition. Rather, it expands the definition of acids to include substances other than the H^+ ion.

Electron-deficient molecules, such as BCl_3 , contain less than an octet of electrons around one atom and have a strong tendency to gain an additional pair of electrons by reacting with substances that possess a lone pair of electrons. Lewis's definition, which is less restrictive than either the Brønsted–Lowry or the Arrhenius definition, grew out of his observation of this tendency.

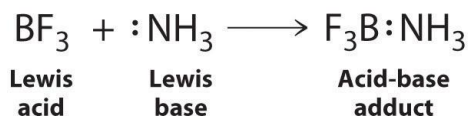
Note the Pattern

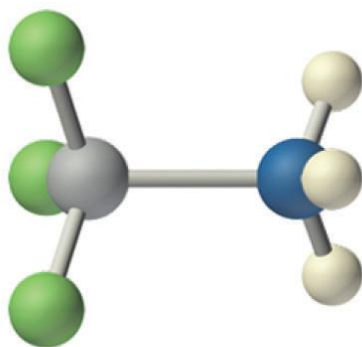
Electron-deficient molecules (those with less than an octet of electrons) are Lewis acids.

A general Brønsted–Lowry acid–base reaction can be depicted in Lewis electron symbols as follows:



The proton (H^+), which has no valence electrons, is a Lewis acid because it accepts a lone pair of electrons on the base to form a bond. The proton, however, is just one of many electron-deficient species that are known to react with bases. For example, neutral compounds of boron, aluminum, and the other group 13 elements, which possess only six valence electrons, have a very strong tendency to gain an additional electron pair. Such compounds are therefore potent Lewis acids that react with an electron-pair donor such as ammonia to form an acid–base adduct, a new covalent bond, as shown here for boron trifluoride (BF_3):

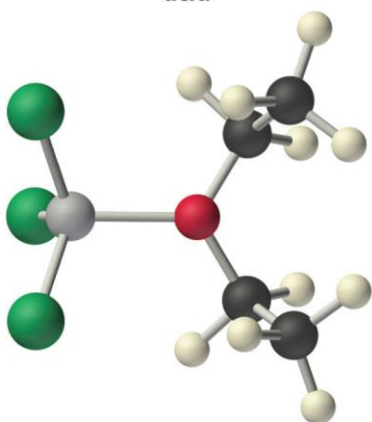
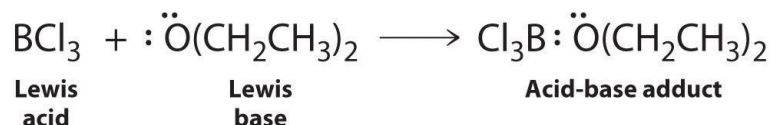




Boron trifluoride-ammonia adduct

The bond formed between a Lewis acid and a Lewis base is a *coordinate covalent bond* because both electrons are provided by only one of the atoms (N, in the case of $\text{F}_3\text{B}:\text{NH}_3$). After it is formed, however, a coordinate covalent bond behaves like any other covalent single bond.

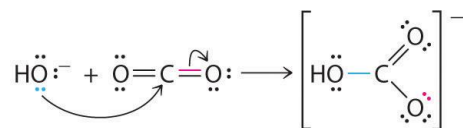
Species that are very weak Brønsted–Lowry bases can be relatively strong Lewis bases. For example, many of the group 13 trihalides are highly soluble in ethers ($\text{R}-\text{O}-\text{R}'$) because the oxygen atom in the ether contains two lone pairs of electrons, just as in H_2O . Hence the predominant species in solutions of electron-deficient trihalides in ether solvents is a Lewis acid–base adduct. A reaction of this type is shown in Equation 8.19 for boron trichloride and diethyl ether:



Boron trichloride-diethyl ether adduct

Many molecules with multiple bonds can act as Lewis acids. In these cases, the Lewis base typically donates a pair of electrons to form a bond to the central atom of the molecule, while a pair of electrons displaced from the multiple bond becomes a lone pair on a terminal atom. A typical example is the reaction of the hydroxide ion with carbon

dioxide to give the bicarbonate ion, as shown in Equation 8.21. The highly electronegative oxygen atoms pull electron density away from carbon, so the carbon atom acts as a Lewis acid. Arrows indicate the direction of electron flow.



EXAMPLE 9

Identify the acid and the base in each Lewis acid–base reaction.

- $\text{BH}_3 + (\text{CH}_3)_2\text{S} \rightarrow \text{H}_3\text{B:S}(\text{CH}_3)_2$
- $\text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3$
- $\text{BeCl}_2 + 2 \text{Cl}^- \rightarrow \text{BeCl}_4^{2-}$

Given: reactants and products

Asked for: identity of Lewis acid and Lewis base

Strategy:

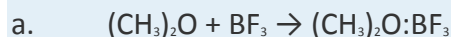
In each equation, identify the reactant that is electron deficient and the reactant that is an electron-pair donor. The electron-deficient compound is the Lewis acid, whereas the other is the Lewis base.

Solution:

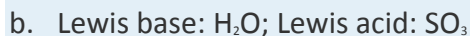
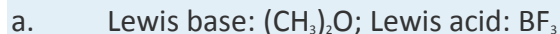
- In BH_3 , boron has only six valence electrons. It is therefore electron deficient and can accept a lone pair. Like oxygen, the sulfur atom in $(\text{CH}_3)_2\text{S}$ has two lone pairs. Thus $(\text{CH}_3)_2\text{S}$ donates an electron pair on sulfur to the boron atom of BH_3 . The Lewis base is $(\text{CH}_3)_2\text{S}$, and the Lewis acid is BH_3 .
- As in the reaction shown in Equation 8.21, CO_2 accepts a pair of electrons from the O^{2-} ion in CaO to form the carbonate ion. The oxygen in CaO is an electron-pair donor, so CaO is the Lewis base. Carbon accepts a pair of electrons, so CO_2 is the Lewis acid.
- The chloride ion contains four lone pairs. In this reaction, each chloride ion donates one lone pair to BeCl_2 , which has only four electrons around Be. Thus the chloride ions are Lewis bases, and BeCl_2 is the Lewis acid.

Exercise

Identify the acid and the base in each Lewis acid–base reaction.



Answer:



Summary

A **Lewis acid** is a compound with a strong tendency to *accept* an additional pair of electrons from a **Lewis base**, which can *donate* a pair of electrons. Such an acid–base reaction forms an **adduct**, which is a compound with a *coordinate covalent bond* in which both electrons are provided by only one of the atoms. **Electron-deficient molecules**, which have less than an octet of electrons around one atom, are relatively common. They tend to acquire an octet electron configuration by reacting with an atom having a lone pair of electrons.

KEY TAKEAWAY

- The acid-base behavior of many compounds can be explained by their Lewis electron structures.

CONCEPTUAL PROBLEMS

- Construct a table comparing how OH^- , NH_3 , H_2O , and BCl_3 are classified according to the Arrhenius, the Brønsted–Lowry, and the Lewis definitions of acids and bases.
- Describe how the proton (H^+) can simultaneously behave as an Arrhenius acid, a Brønsted–Lowry acid, and a Lewis acid.
- Would you expect aluminum to form compounds with covalent bonds or coordinate covalent bonds? Explain your answer.
- Classify each compound as a Lewis acid or a Lewis base and justify your choice.
 - AlCl_3
 - $(\text{CH}_3)_3\text{N}$
 - IO_3^-
- Explain how a carboxylate ion (RCO_2^-) can act as both a Brønsted–Lowry base and a Lewis base.

NUMERICAL PROBLEMS

1. In each reaction, identify the Lewis acid and the Lewis base and complete the reaction by writing the products(s).
 - a. $(\text{CH}_3)_2\text{O} + \text{AlCl}_3$
 - b. $\text{SnCl}_4 + 2 \text{Cl}^-$
2. Use Lewis dot symbols to depict the reaction of BCl_3 with dimethyl ether $[(\text{CH}_3)_2\text{O}]$. How is this reaction similar to that in which a proton is added to ammonia?

ANSWER

1.
 - a. AlCl_3 is the Lewis acid, and the ether is the Lewis base; $\text{AlCl}_3 + (\text{CH}_3)_2\text{O} \rightarrow \text{AlCl}_3 \cdot \text{O}(\text{CH}_3)_2$
 - b. SnCl_4 is the Lewis acid, and chloride is the Lewis base; $\text{SnCl}_4 + 2 \text{Cl}^- \rightarrow \text{SnCl}_6^{2-}$

8.8 Properties of Covalent Bonds

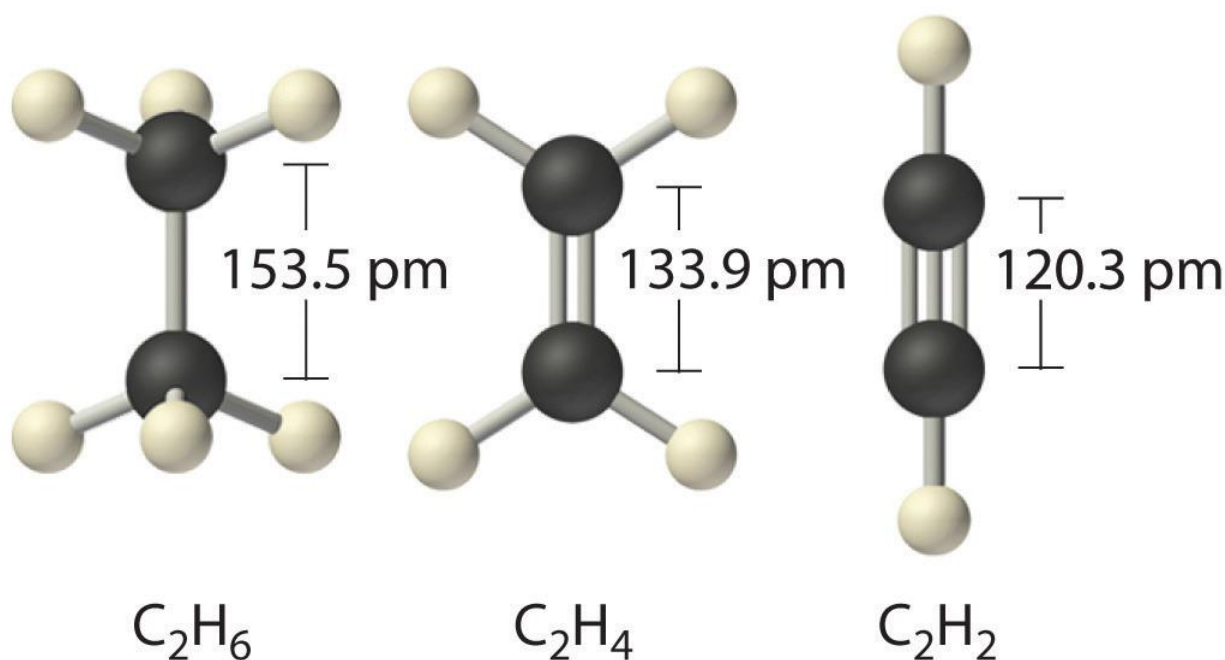
LEARNING OBJECTIVE

1. To understand the relationship between bond order, bond length, and bond energy.

In proposing his theory that octets can be completed by two atoms sharing electron pairs, Lewis provided scientists with the first description of covalent bonding. In this section, we expand on this and describe some of the properties of covalent bonds.

Bond Order

When we draw Lewis structures, we place one, two, or three pairs of electrons between adjacent atoms. In the Lewis bonding model, the number of electron pairs that hold two atoms together is called the bond order. For a single bond, such as the C–C bond in $\text{H}_3\text{C}-\text{CH}_3$, the bond order is one. For a double bond (such as $\text{H}_2\text{C}=\text{CH}_2$), the bond order is two. For a triple bond, such as $\text{HC}\equiv\text{CH}$, the bond order is three.



When analogous bonds in similar compounds are compared, bond length decreases as bond order increases. The bond length data in Table 8.5 "Bond Lengths and Bond Dissociation Energies for Bonds with Different Bond Orders in Selected Gas-Phase Molecules at 298 K", for example, show that the C–C distance in $\text{H}_3\text{C}-\text{CH}_3$ (153.5 pm) is longer than the distance in $\text{H}_2\text{C}=\text{CH}_2$ (133.9 pm), which in turn is longer than that in $\text{HC}\equiv\text{CH}$ (120.3 pm). Additionally, as noted in Section 8.5 "Lewis Structures and Covalent Bonding", molecules or ions whose bonding must be described using resonance structures usually have bond distances that are intermediate between those of single and double bonds, as we demonstrated with the C–C distances in benzene. The relationship between bond length and bond order is not linear, however. A double bond is not half as long as a single bond, and the length of a C=C bond is not the average of the lengths of C≡C and C–C bonds. Nevertheless, as bond orders increase, bond lengths generally decrease.

Table 8.5 Bond Lengths and Bond Dissociation Energies for Bonds with Different Bond Orders in Selected Gas-Phase Molecules at 298 K

Compound	Bond Order	Bond Length (pm)	Bond Dissociation Energy (kJ/mol)	Compound	Bond Order	Bond Length (pm)	Bond Dissociation Energy (kJ/mol)
$\text{H}_3\text{C}-\text{CH}_3$	1	153.5	376	$\text{H}_3\text{C}-\text{NH}_2$	1	147.1	331
$\text{H}_2\text{C}=\text{CH}_2$	2	133.9	728	$\text{H}_2\text{C}=\text{NH}$	2	127.3	644
$\text{HC}\equiv\text{CH}$	3	120.3	965	$\text{HC}\equiv\text{N}$	3	115.3	937

Compound	Bond Order	Bond Length (pm)	Bond Dissociation Energy (kJ/mol)	Compound	Bond Order	Bond Length (pm)	Bond Dissociation Energy (kJ/mol)
H ₂ N-NH ₂	1	144.9	275.3	H ₃ C-OH	1	142.5	377
HN=NH	2	125.2	456	H ₂ C=O	2	120.8	732
N≡N	3	109.8	945.3	O=C=O	2	116.0	799
HO-OH	1	147.5	213	C≡O	3	112.8	1076.5
O=O	2	120.7	498.4				

Sources: Data from *CRC Handbook of Chemistry and Physics* (2004); *Lange's Handbook of Chemistry* (2005); <http://cccbdb.nist.gov>.

The Relationship between Bond Order and Bond Energy

As shown in Table 8.5 "Bond Lengths and Bond Dissociation Energies for Bonds with Different Bond Orders in Selected Gas-Phase Molecules at 298 K", triple bonds between like atoms are shorter than double bonds, and because more energy is required to completely break all three bonds than to completely break two, a triple bond is also stronger than a double bond. Similarly, double bonds between like atoms are stronger and shorter than single bonds. Bonds of the same order between *different* atoms show a wide range of bond energies, however. Table 8.6 "Average Bond Energies (kJ/mol) for Commonly Encountered Bonds at 273 K" lists the average values for some commonly encountered bonds. Although the values shown vary widely, we can observe four trends:

Table 8.6 Average Bond Energies (kJ/mol) for Commonly Encountered Bonds at 273 K

Single Bonds										Multiple Bonds	
H-H	432	C-C	346	N-N	≈167	O-O	≈142	F-F	155	C=C	602
H-C	411	C-Si	318	N-O	201	O-F	190	F-Cl	249	C≡C	835
H-Si	318	C-N	305	N-F	283	O-Cl	218	F-Br	249	C=N	615
H-N	386	C-O	358	N-Cl	313	O-Br	201	F-I	278	C≡N	887
H-P	≈322	C-S	272	N-Br	243	O-I	201	Cl-Cl	240	C=O	749
H-O	459	C-F	485	P-P	201	S-S	226	Cl-Br	216	C≡O	1072
H-S	363	C-Cl	327			S-F	284	Cl-I	208	N=N	418
H-F	565	C-Br	285			S-Cl	255	Br-Br	190	N≡N	942
H-Cl	428	C-I	213			S-Br	218	Br-I	175	N=O	607
H-Br	362	Si-Si	222					I-I	149	O=O	494

Single Bonds						Multiple Bonds	
H-I	295	Si-O	452			S=O	532

Source: Data from J. E. Huheey, E. A. Keiter, and R. L. Keiter, *Inorganic Chemistry*, 4th ed. (1993).

1. Bonds between hydrogen and atoms in the same column of the periodic table decrease in strength as we go down the column. Thus an H-F bond is stronger than an H-I bond, H-C is stronger than H-Si, H-N is stronger than H-P, H-O is stronger than H-S, and so forth. The reason for this is that the region of space in which electrons are shared between two atoms becomes proportionally smaller as one of the atoms becomes larger (part (a) in Figure 8.11 "The Strength of Covalent Bonds Depends on the Overlap between the Valence Orbitals of the Bonded Atoms").

2. Bonds between like atoms usually become *weaker* as we go down a column (important exceptions are noted later). For example, the C-C single bond is stronger than the Si-Si single bond, which is stronger than the Ge-Ge bond, and so forth. As two bonded atoms become larger, the region between them occupied by bonding electrons becomes *proportionally* smaller, as illustrated in part (b) in Figure 8.11 "The Strength of Covalent Bonds Depends on the Overlap between the Valence Orbitals of the Bonded Atoms". Noteworthy exceptions are single bonds between the period 2 atoms of groups 15, 16, and 17 (i.e., N, O, F), which are unusually weak compared with single bonds between their larger congeners. It is likely that the N-N, O-O, and F-F single bonds are weaker than might be expected due to strong repulsive interactions between lone pairs of electrons on *adjacent* atoms. The trend in bond energies for the halogens is therefore
 $\text{Cl-Cl} > \text{Br-Br} > \text{F-F} > \text{I-I}$

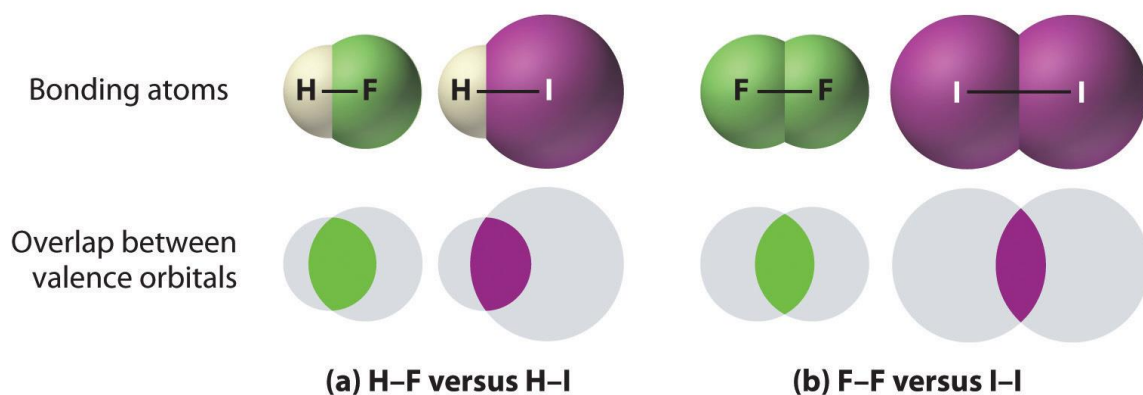
Similar effects are also seen for the O-O versus S-S and for N-N versus P-P single bonds.

Note the Pattern

Bonds between hydrogen and atoms in a given column in the periodic table are weaker down the column; bonds between like atoms usually become weaker down a column.

3. Because elements in periods 3 and 4 rarely form multiple bonds with themselves, their multiple bond energies are not accurately known. Nonetheless, they are presumed to be significantly weaker than multiple bonds between lighter atoms of the same families. Compounds containing an Si=Si double bond, for example, have only recently been prepared, whereas compounds containing C=C double bonds are one of the best-studied and most important classes of organic compounds.

Figure 8.11 The Strength of Covalent Bonds Depends on the Overlap between the Valence Orbitals of the Bonded Atoms



The relative sizes of the region of space in which electrons are shared between (a) a hydrogen atom and lighter (smaller) vs. heavier (larger) atoms in the same periodic group; and (b) two lighter versus two heavier atoms in the same group. Although the absolute amount of shared space increases in both cases on going from a light to a heavy atom, the amount of space relative to the size of the bonded atom decreases; that is, the percentage of total orbital volume decreases with increasing size. Hence the strength of the bond decreases.

4. Multiple bonds between carbon, oxygen, or nitrogen and a period 3 element such as phosphorus or sulfur tend to be unusually strong. In fact, multiple bonds of this type dominate the chemistry of the period 3 elements of groups 15 and 16. Multiple bonds to phosphorus or sulfur occur as a result of *d*-orbital interactions, as we discussed for the SO_4^{2-} ion in Section 8.6 "Exceptions to the Octet Rule". In contrast, silicon in group 14 has little tendency to form discrete silicon–oxygen double bonds.

Consequently, SiO_2 has a three-dimensional network structure in which each silicon atom forms four Si–O single bonds, which makes the physical and chemical properties of SiO_2 very different from those of CO_2 .

Note the Pattern

Bond strengths increase as bond order increases, while bond distances decrease.

The Relationship between Molecular Structure and Bond Energy

Bond energy is defined as the energy required to break a particular bond in a molecule in the gas phase. Its value depends on not only the identity of the bonded atoms but also their environment. Thus the bond energy of a C–H single bond is *not* the same in all organic compounds. For example, the energy required to break a C–H bond in methane varies by as much as 25% depending on how many other bonds in the

molecule have already been broken (Table 8.7 "Energies for the Dissociation of Successive C–H Bonds in Methane"); that is, the C–H bond energy depends on its molecular environment. Except for diatomic molecules, the bond energies listed in Table 8.6 "Average Bond Energies (kJ/mol) for Commonly Encountered Bonds at 273 K" are *average* values for all bonds of a given type in a range of molecules. Even so, they are not likely to differ from the actual value of a given bond by more than about 10%.

Table 8.7 Energies for the Dissociation of Successive C–H Bonds in Methane

Reaction	<i>D</i> (kJ/mol)
CH ₄ (g) → CH ₃ (g) + H(g)	439
CH ₃ (g) → CH ₂ (g) + H(g)	462
CH ₂ (g) → CH(g) + H(g)	424
CH(g) → C(g) + H(g)	338

Source: Data from *CRC Handbook of Chemistry and Physics* (2004).

We can estimate the enthalpy change for a chemical reaction by adding together the average energies of the bonds broken in the reactants and the average energies of the bonds formed in the products and then calculating the difference between the two. If the bonds formed in the products are stronger than those broken in the reactants, then energy will be released in the reaction ($\Delta H_{\text{rxn}} < 0$):

Equation 8.14

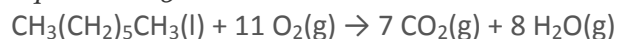
$$\Delta H_{\text{rxn}} \approx \sum(\text{bond energies of bonds broken}) - \sum(\text{bond energies of bonds formed})$$

The $\approx$ sign is used because we are adding together *average* bond energies; hence this approach does not give exact values for ΔH_{rxn} .

Let's consider the reaction of 1 mol of *n*-heptane (C₇H₁₆) with oxygen gas to give carbon dioxide and water.

This is one reaction that occurs during the combustion of gasoline:

Equation 8.15



In this reaction, 6 C–C bonds, 16 C–H bonds, and 11 O=O bonds are broken per mole of *n*-heptane, while 14 C=O bonds (two for each CO₂) and 16 O–H bonds (two for each H₂O) are formed. The energy changes can be tabulated as follows:

Bonds Broken (kJ/mol)		Bonds Formed (kJ/mol)	
6 C–C	346 × 6 = 2076	14 C=O	799 × 14 = 11,186
16 C–H	411 × 16 = 6576	16 O–H	459 × 16 = 7344

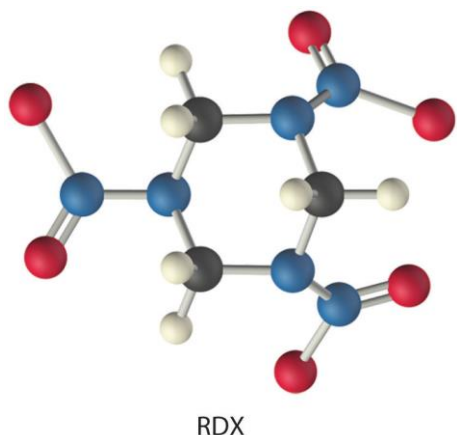
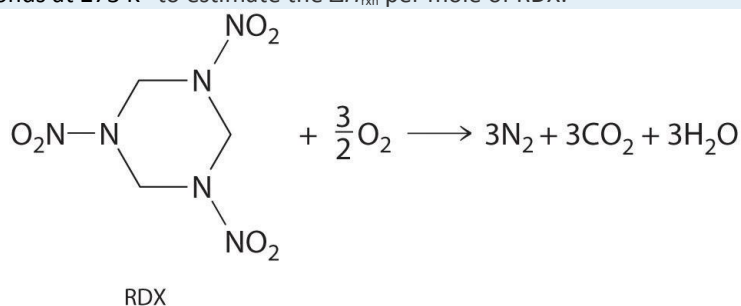
Bonds Broken (kJ/mol)		Bonds Formed (kJ/mol)	
11 O=O	$494 \times 11 = 5434$		Total = 18,530
	Total = 14,086		

The bonds in the products are stronger than the bonds in the reactants by about 4444 kJ/mol. This means that ΔH_{rxn} is approximately -4444 kJ/mol, and the reaction is highly exothermic (which is not too surprising for a combustion reaction).

If we compare this approximation with the value obtained from measured DH_{of} values ($\Delta H_{\text{rxn}} = -4817$ kJ/mol), we find a discrepancy of only about 8%, less than the 10% typically encountered. Chemists find this method useful for calculating approximate enthalpies of reaction for molecules whose actual DH_{of} values are unknown. These approximations can be important for predicting whether a reaction is exothermic or endothermic—and to what degree.

EXAMPLE 10

The compound RDX (Research Development Explosive) is a more powerful explosive than dynamite and is used by the military. When detonated, it produces gaseous products and heat according to the following reaction. Use the approximate bond energies in Table 8.6 "Average Bond Energies (kJ/mol) for Commonly Encountered Bonds at 273 K" to estimate the ΔH_{rxn} per mole of RDX.



Given: chemical reaction, structure of reactant, and Table 8.6 "Average Bond Energies (kJ/mol) for Commonly Encountered Bonds at 273 K"

Asked for: ΔH_{rxn} per mole

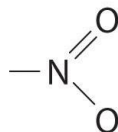
Strategy:

A List the types of bonds broken in RDX, along with the bond energy required to break each type. Multiply the number of each type by the energy required to break one bond of that type and then add together the energies. Repeat this procedure for the bonds formed in the reaction.

B Use Equation 8.14 to calculate the amount of energy consumed or released in the reaction (ΔH_{rxn}).

Solution:

We must add together the energies of the bonds in the reactants and compare that quantity with the sum of the energies of the bonds in the products. A nitro group ($-\text{NO}_2$) can be viewed as having one N–O single bond and one N=O double bond, as follows:



In fact, however, both N–O distances are usually the same because of the presence of two equivalent resonance structures.

A We can organize our data by constructing a table:

Bonds Broken (kJ/mol)		Bonds Formed (kJ/mol)	
6 C–N	$305 \times 6 = 1830$	3 N≡N	$942 \times 3 = 2826$
6 C–H	$411 \times 6 = 2466$	6 C=O	$799 \times 6 = 4794$
3 N–N	$167 \times 3 = 501$	6 O–H	$459 \times 6 = 2754$
3 N–O	$201 \times 3 = 603$		Total = 10,374
3 N=O	$607 \times 3 = 1821$		
1.5 O=O	$494 \times 1.5 = 741$		
	Total = 7962		

B From Equation 8.14, we have

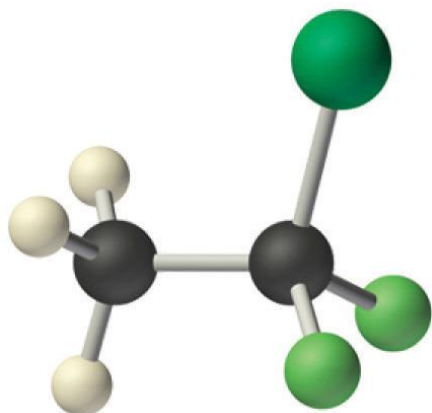
ΔH_{rxn}

$$\approx \sum(\text{bond energies of bonds broken}) - \sum(\text{bond energies of bonds formed})$$
$$= 7962 \text{ kJ/mol} - 10,374 \text{ kJ/mol} = -2412 \text{ kJ}$$

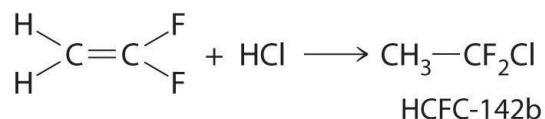
Thus this reaction is also highly exothermic.

Exercise

The molecule HCFC-142b, a hydrochlorofluorocarbon used in place of chlorofluorocarbons (CFCs) such as the Freons, can be prepared by adding HCl to 1,1-difluoroethylene:



HCFC-142b



Use tabulated bond energies to calculate ΔH_{rxn} .

Answer: -54 kJ/mol

Summary

Bond order is the number of electron pairs that hold two atoms together. Single bonds have a bond order of one, and multiple bonds with bond orders of two (a double bond) and three (a triple bond) are quite common. In closely related compounds with bonds between the same kinds of atoms, the bond with the highest bond order is both the shortest and the strongest. In bonds with the same bond order between different atoms, trends are observed that, with few exceptions, result in the strongest single bonds being formed between the smallest atoms. Tabulated values of average bond energies can be used to calculate the enthalpy change of many chemical reactions. If the bonds in the products are stronger than those in the reactants, the reaction is exothermic and vice versa.

KEY TAKEAWAY

- The strength of a covalent bond depends on the overlap between the valence orbitals of the bonded atoms.

KEY EQUATION

Formal charge on an atom

$$\Delta H_{rxn} = \sum(\text{bond energies of bonds broken})$$

Equation 8.14: $-\sum(\text{bond energies of bonds formed})$

CONCEPTUAL PROBLEMS

- Which would you expect to be stronger—an S–S bond or an Se–Se bond? Why?
- Which element—nitrogen, phosphorus, or arsenic—will form the strongest multiple bond with oxygen? Why?
- Why do multiple bonds between oxygen and period 3 elements tend to be unusually strong?
- What can bond energies tell you about reactivity?
- Bond energies are typically reported as average values for a range of bonds in a molecule rather than as specific values for a single bond? Why?
- If the bonds in the products are weaker than those in the reactants, is a reaction exothermic or endothermic? Explain your answer.
- A student presumed that because heat was required to initiate a particular reaction, the reaction product would be stable. Instead, the product exploded. What information might have allowed the student to predict this outcome?

NUMERICAL PROBLEMS

- What is the bond order about the central atom(s) of hydrazine (N_2H_4), nitrogen, and diimide (N_2H_2)? Draw Lewis electron structures for each compound and then arrange these compounds in order of increasing N–N bond distance. Which of these compounds would you expect to have the largest N–N bond energy? Explain your answer.
- What is the carbon–carbon bond order in ethylene (C_2H_4), $\text{BrH}_2\text{CCH}_2\text{Br}$, and FCCH ? Arrange the compounds in order of increasing C–C bond distance. Which would you expect to have the largest C–C bond energy? Why?
- From each pair of elements, select the one with the greater bond strength? Explain your choice in each case.
 - P–P, Sb–Sb

- b. Cl–Cl, I–I
 - c. O–O, Se–Se
 - d. S–S, Cl–Cl
 - e. Al–Cl, B–Cl
4. From each pair of elements, select the one with the greater bond strength? Explain your choice in each case.
 - a. Te–Te, S–S
 - b. C–H, Ge–H
 - c. Si–Si, P–P
 - d. Cl–Cl, F–F
 - e. Ga–H, Al–H
 5. Approximately how much energy per mole is required to completely dissociate acetone [(CH₃)₂CO] and urea [(NH₂)₂CO] into their constituent atoms?
 6. Approximately how much energy per mole is required to completely dissociate ethanol, formaldehyde, and hydrazine into their constituent atoms?
 7. Is the reaction of diimine (N₂H₂) with oxygen to produce nitrogen and water exothermic or endothermic? Quantify your answer.

ANSWER

1. N₂H₄, bond order 1; N₂H₂, bond order 2; N₂, bond order 3; N–N bond distance: N₂ < N₂H₂ < N₂H₄; Largest bond energy: N₂; Highest bond order correlates with strongest and shortest bond.

8.9 Polar Covalent Bonds

LEARNING OBJECTIVE

1. To calculate the percent ionic character of a covalent polar bond..

In Chapter 2 "Molecules, Ions, and Chemical Formulas" and Section 8.1 "An Overview of Chemical Bonding", we described the two idealized extremes of chemical bonding: (1) ionic bonding—in which one or more electrons are transferred completely from one atom to another, and the resulting ions are held together by purely electrostatic forces—and (2) covalent bonding, in which electrons are shared equally between two atoms. Most compounds, however, have polar covalent bonds, which means that electrons are shared *unequally* between the bonded atoms. Figure 8.12 "The Electron Distribution in a Nonpolar Covalent Bond, a Polar Covalent Bond, and an Ionic

Bond Using Lewis Electron Structures" compares the electron distribution in a polar covalent bond with those in an ideally covalent and an ideally ionic bond. Recall from Chapter 4 "Reactions in Aqueous Solution", Section 4.1

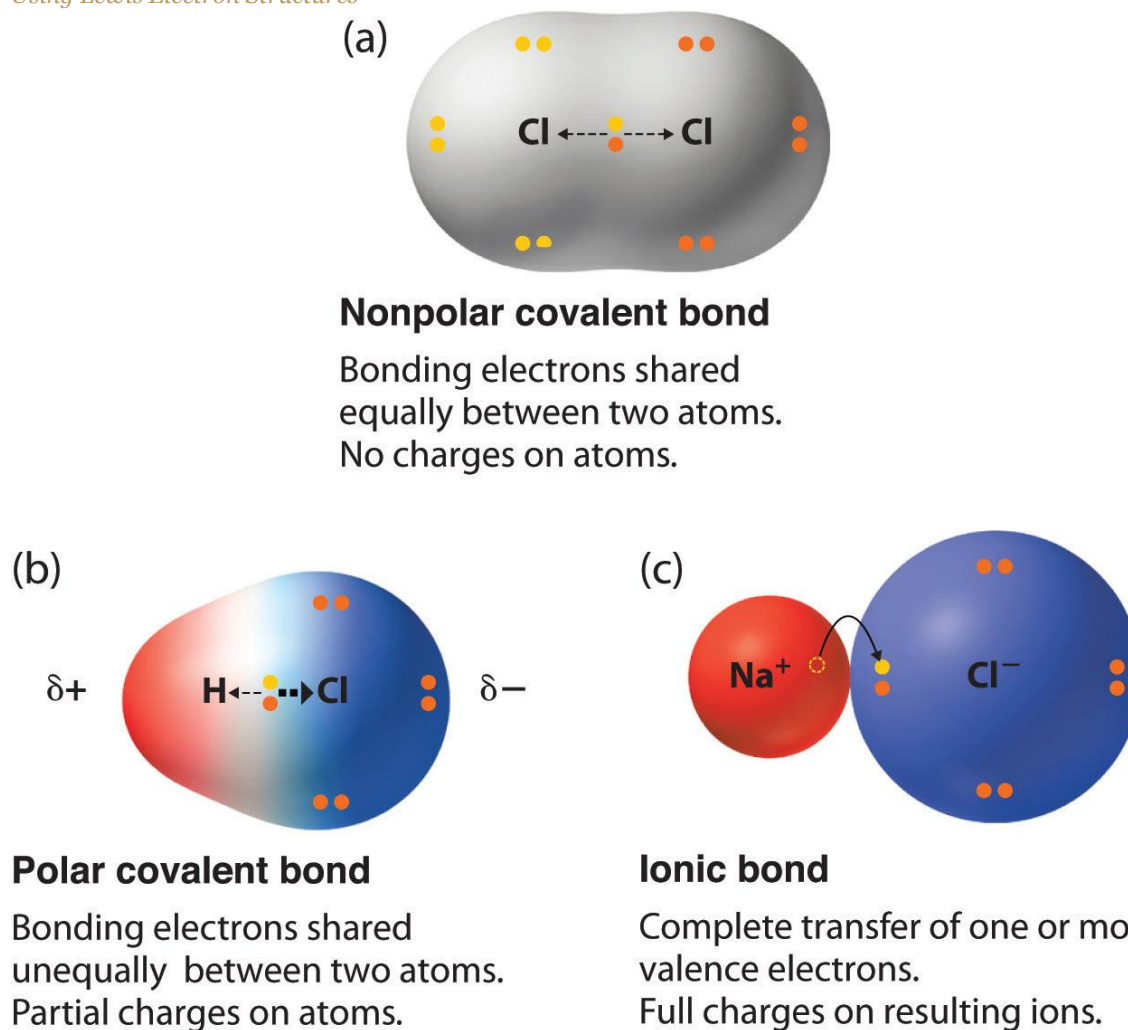
"Aqueous Solutions" that a lowercase

Greek delta (δ) is used to indicate that a bonded atom possesses a partial positive charge, indicated by δ^+ , or

partial negative charge, indicated by δ^- , and a bond between two atoms that possess partial charges is a *polar bond*.

Figure 8.12 *The Electron Distribution in a Nonpolar Covalent Bond, a Polar Covalent Bond, and an Ionic Bond*

Using Lewis Electron Structures



In a purely covalent bond (a), the bonding electrons are shared equally between the atoms. In a purely ionic bond (c), an electron has been transferred completely from one atom to the other. A polar covalent bond (b) is intermediate between the two extremes: the bonding electrons are shared unequally between the two atoms, and the electron distribution is asymmetrical with the electron density being greater around the more electronegative

atom. Electron-rich (negatively charged) regions are shown in blue; electron-poor (positively charged) regions are shown in red.

Bond Polarity

The polarity of a bond—the extent to which it is polar—is determined largely by the relative electronegativities of the bonded atoms. In Chapter 7 "The Periodic Table and Periodic Trends", electronegativity (χ) was defined as the ability of an atom in a molecule or an ion to attract electrons to itself. Thus there is a direct correlation between electronegativity and bond polarity. A bond is *nonpolar* if the bonded atoms have equal electronegativities. If the electronegativities of the bonded atoms are not equal, however, the bond is *polarized* toward the more electronegative atom. A bond in which the electronegativity of B (χ_B) is greater than the electronegativity of A (χ_A), for example, is indicated with the partial negative charge on the more electronegative atom:

A less electronegative δ^+ – *B more electronegative* δ^-

One way of estimating the ionic character of a bond—that is, the magnitude of the charge separation in a polar covalent bond—is to calculate the difference in electronegativity between the two atoms: $\Delta\chi = \chi_B - \chi_A$. To predict the polarity of the bonds in Cl_2 , HCl, and NaCl, for example, we look at the electronegativities of the relevant atoms: $\chi_{\text{Cl}} = 3.16$, $\chi_{\text{H}} = 2.20$, and $\chi_{\text{Na}} = 0.93$ (see Figure 7.14 "A Plot of Periodic Variation of Electronegativity with Atomic Number for the First Six Rows of the Periodic Table"). Cl_2 must be nonpolar because the electronegativity difference ($\Delta\chi$) is zero; hence the two chlorine atoms share the bonding electrons equally. In NaCl, $\Delta\chi$ is 2.23. This high value is typical of an ionic compound ($\Delta\chi \geq \approx 1.5$) and means that the valence electron of sodium has been completely transferred to chlorine to form Na^+ and Cl^- ions. In HCl, however, $\Delta\chi$ is only 0.96. The bonding electrons are more strongly attracted to the more electronegative chlorine atom, and so the charge distribution is:

H δ^+ – *Cl* δ^-

Remember that electronegativities are difficult to measure precisely and different definitions produce slightly different numbers. In practice, the polarity of a bond is usually estimated rather than calculated.

Note the Pattern

Bond polarity and ionic character increase with an increasing difference in electronegativity.

As with bond energies, the electronegativity of an atom depends to some extent on its chemical environment. It is therefore unlikely that the reported electronegativities of a chlorine atom in NaCl, Cl₂, ClF₃, and HClO₄ would be exactly the same.

Dipole Moments

The asymmetrical charge distribution in a polar substance such as HCl produces a dipole moment, abbreviated by the Greek letter mu (μ). The dipole moment is defined as the product of the partial charge Q on the bonded atoms and the distance r between the partial charges:

Equation 8.16

$$\mu = Qr$$

where Q is measured in coulombs (C) and r in meters. The unit for dipole moments is the debye (D):

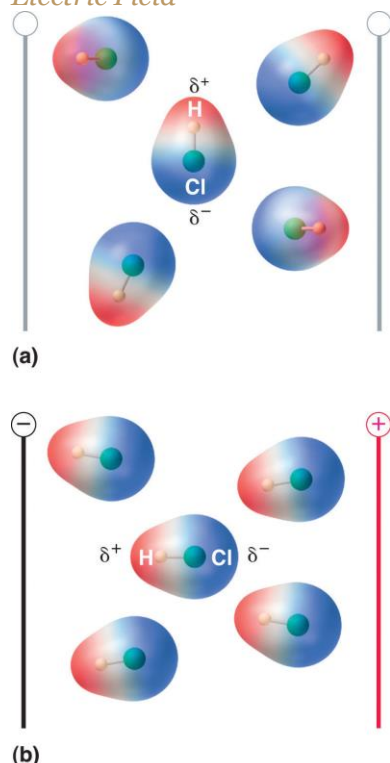
Equation 8.17

$$1 \text{ D} = 3.3356 \times 10^{-30} \text{ C}\cdot\text{m}$$

When a molecule with a dipole moment is placed in an electric field, it tends to orient itself with the electric field because of its asymmetrical charge distribution (Figure 8.13 "Molecules That Possess a Dipole Moment Partially Align Themselves with an Applied Electric Field").

Figure 8.13 *Molecules That Possess a Dipole Moment Partially Align Themselves with an Applied*

Electric Field



In the absence of a field (a), the HCl molecules are randomly oriented. When an electric field is applied (b), the molecules tend to align themselves with the field, such that the positive end of the molecular dipole points toward the negative terminal and vice versa.

We can measure the partial charges on the atoms in a molecule such as HCl using Equation 8.16. If the bonding in HCl were purely ionic, an electron would be transferred from H to Cl, so there would be a full +1 charge on the H atom and a full -1 charge on the Cl atom. The dipole moment of HCl is 1.109 D, as determined by measuring the extent of its alignment in an electric field, and the reported gas-phase H-Cl distance is 127.5 pm. Hence the charge on each atom is

Equation 8.18

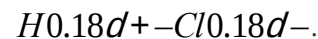
$$Q = \frac{m}{r} = \frac{1.109 \text{ D}}{127.5 \text{ pm}} = \frac{1.109 \text{ D}}{127.5 \times 10^{-12} \text{ m}} = 8.697 \times 10^{-20} \text{ C}$$

By dividing this calculated value by the charge on a single electron ($1.6022 \times 10^{-19} \text{ C}$), we find that the charge on the Cl atom of an HCl molecule is about -0.18, corresponding to about 0.18 e^- :

Equation 8.19

$$\frac{8.697 \times 10^{-20} \text{ C}}{1.6022 \times 10^{-19} \text{ C}/e^-} = 0.1811 e^-$$

To form a neutral compound, the charge on the H atom must be equal but opposite. Thus the measured dipole moment of HCl indicates that the H-Cl bond has approximately 18% ionic character (0.1811×100), or 82% covalent character. Instead of writing HCl as $H\delta^+ - Cl\delta^-$ we can therefore indicate the charge separation quantitatively as



Our calculated results are in agreement with the electronegativity difference between hydrogen and chlorine ($\chi_H = 2.20$; $\chi_{Cl} = 3.16$, $\chi_{Cl} - \chi_H = 0.96$), a value well within the range for polar covalent bonds. We indicate the dipole moment by writing an arrow above the molecule.^[1] In HCl, for example, the dipole moment is indicated as follows:



The arrow shows the direction of electron flow by pointing toward the more electronegative atom.

The charge on the atoms of many substances in the gas phase can be calculated using measured dipole moments and bond distances. Figure 8.14 "A Plot of the Percent Ionic Character of a Bond as Determined from Measured Dipole Moments versus the Difference in Electronegativity of the Bonded Atoms" shows a plot of the percent ionic character versus the difference in electronegativity of the bonded atoms for several substances. According to the graph, the bonding in species such as NaCl(g) and CsF(g) is substantially less than 100% ionic in character. As the gas

condenses into a solid, however, dipole–dipole interactions between polarized species increase the charge separations. In the crystal, therefore, an electron is transferred from the metal to the nonmetal, and these substances behave like classic ionic compounds. The data in **Figure 8.14 "A Plot of the Percent Ionic Character of a Bond as Determined from Measured Dipole Moments versus the Difference in Electronegativity of the Bonded Atoms"** show that diatomic species with an electronegativity difference of less than 1.5 are less than 50% ionic in character, which is consistent with our earlier description of these species as containing polar covalent bonds. The use of dipole moments to determine the ionic character of a polar bond is illustrated in **Example 11**.

Figure 8.14 A Plot of the Percent Ionic Character of a Bond as Determined from Measured Dipole Moments versus the Difference in Electronegativity of the Bonded Atoms In the absence of a field (a), the HCl molecules are randomly oriented. When an electric field is applied (b), the molecules tend to align themselves with the field, such that the positive end of the molecular dipole points toward the negative terminal and vice versa.

We can measure the partial charges on the atoms in a molecule such as HCl using **Equation 8.16**. If the bonding in HCl were purely ionic, an electron would be transferred from H to Cl, so there would be a full +1 charge on the H atom and a full –1 charge on the Cl atom. The dipole moment of HCl is 1.109 D, as determined by measuring the extent of its alignment in an electric field, and the reported gas-phase H–Cl distance is 127.5 pm. Hence the charge on each atom is

Equation 8.18

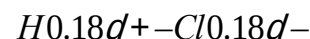
$$Q = \frac{\mu}{d} = \frac{1.109 \text{ D}}{(127.5 \text{ pm})(1 \text{ pm} \cdot 10^{-12} \text{ m})} = 2.901 \cdot 10^{-20} \text{ C}$$

By dividing this calculated value by the charge on a single electron ($1.6022 \times 10^{-19} \text{ C}$), we find that the charge on the Cl atom of an HCl molecule is about –0.18, corresponding to about 0.18 e^- :

Equation 8.19

$$2.901 \cdot 10^{-20} \text{ C} / 1.6022 \cdot 10^{-19} \text{ C} / e^- = 0.1811 \text{ } e^-$$

To form a neutral compound, the charge on the H atom must be equal but opposite. Thus the measured dipole moment of HCl indicates that the H–Cl bond has approximately 18% ionic character (0.1811×100), or 82% covalent character. Instead of writing HCl as $H\delta^+ - Cl\delta^-$ we can therefore indicate the charge separation quantitatively as



Our calculated results are in agreement with the electronegativity difference between hydrogen and chlorine

($\chi_{\text{H}} = 2.20$; $\chi_{\text{Cl}} = 3.16$, $\chi_{\text{Cl}} - \chi_{\text{H}} = 0.96$), a value well within the range for polar covalent bonds. We indicate the dipole

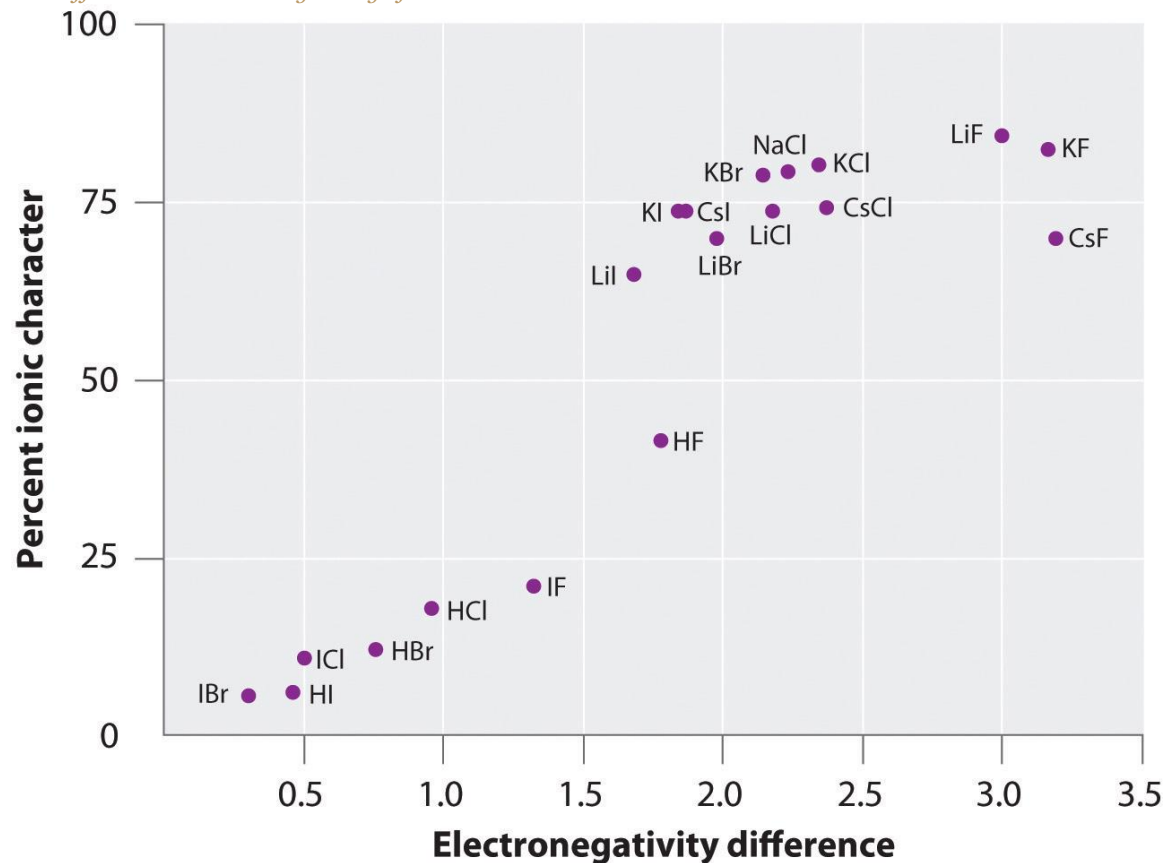
moment by writing an arrow above the molecule.^[1] In HCl, for example, the dipole moment is indicated as follows:



The arrow shows the direction of electron flow by pointing toward the more electronegative atom.

The charge on the atoms of many substances in the gas phase can be calculated using measured dipole moments and bond distances. **Figure 8.14 "A Plot of the Percent Ionic Character of a Bond as Determined from Measured Dipole Moments versus the Difference in Electronegativity of the Bonded Atoms"** shows a plot of the percent ionic character versus the difference in electronegativity of the bonded atoms for several substances. According to the graph, the bonding in species such as NaCl(g) and CsF(g) is substantially less than 100% ionic in character. As the gas condenses into a solid, however, dipole–dipole interactions between polarized species increase the charge separations. In the crystal, therefore, an electron is transferred from the metal to the nonmetal, and these substances behave like classic ionic compounds. The data in **Figure 8.14 "A Plot of the Percent Ionic Character of a Bond as Determined from Measured Dipole Moments versus the Difference in Electronegativity of the Bonded Atoms"** show that diatomic species with an electronegativity difference of less than 1.5 are less than 50% ionic in character, which is consistent with our earlier description of these species as containing polar covalent bonds. The use of dipole moments to determine the ionic character of a polar bond is illustrated in Example 11.

Figure 8.14 A Plot of the Percent Ionic Character of a Bond as Determined from Measured Dipole Moments versus the Difference in Electronegativity of the Bonded Atoms



In the gas phase, even CsF, which has the largest possible difference in electronegativity between atoms, is not 100% ionic. Solid CsF, however, is best viewed as 100% ionic because of the additional electrostatic interactions in the lattice.

EXAMPLE 11

In the gas phase, NaCl has a dipole moment of 9.001 D and an Na–Cl distance of 236.1 pm. Calculate the percent ionic character in NaCl.

Given: chemical species, dipole moment, and internuclear distance

Asked for: percent ionic character

Strategy:

A Compute the charge on each atom using the information given and Equation 8.16.

B Find the percent ionic character from the ratio of the actual charge to the charge of a single electron.

Solution:

A The charge on each atom is given by

$$Q = \mu / r = 9.001 \text{ D} / (3.3356 \times 10^{-30} \text{ C} \cdot \text{m}) / (1236.1 \text{ pm})(1 \text{ pm} = 10^{-12} \text{ m}) = 1.272 \times 10^{-19} \text{ C}$$

Thus NaCl behaves as if it had charges of $1.272 \times 10^{-19} \text{ C}$ on each atom separated by 236.1 pm.

B The percent ionic character is given by the ratio of the actual charge to the charge of a single electron (the charge expected for the complete transfer of one electron):

$$\% \text{ ionic character} = (1.272 \times 10^{-19} \text{ C} / 1.6022 \times 10^{-19} \text{ C}) (100) = 79.39\% \approx 79\%$$

Exercise

In the gas phase, silver chloride (AgCl) has a dipole moment of 6.08 D and an Ag–Cl distance of 228.1 pm.

What is the percent ionic character in silver chloride?

Answer: 55.5%

Summary

Compounds with **polar covalent bonds** have electrons that are shared unequally between the bonded atoms. The polarity of such a bond is determined largely by the relative electronegativities of the bonded atoms. The asymmetrical charge distribution in a polar substance produces a **dipole moment**, which is the product of the partial charges on the bonded atoms and the distance between them.

KEY TAKEAWAY

- Bond polarity and ionic character increase with an increasing difference in electronegativity.

KEY EQUATION

Dipole moment

Equation 8.16: $\mu = Qr$

CONCEPTUAL PROBLEMS

- Why do ionic compounds such as KI exhibit substantially less than 100% ionic character in the gas phase?
- Of the compounds LiI and LiF, which would you expect to behave more like a classical ionic compound? Which would have the greater dipole moment in the gas phase? Explain your answers.

NUMERICAL PROBLEMS

- Predict whether each compound is purely covalent, purely ionic, or polar covalent.
 - RbCl

- b. S_8
 - c. $TiCl_2$
 - d. $SbCl_3$
 - e. LiI
 - f. Br_2
2. Based on relative electronegativities, classify the bonding in each compound as ionic, covalent, or polar covalent. Indicate the direction of the bond dipole for each polar covalent bond.
- a. NO
 - b. HF
 - c. MgO
 - d. $AlCl_3$
 - e. SiO_2
 - f. the $C=O$ bond in acetone
 - g. O_3
3. Based on relative electronegativities, classify the bonding in each compound as ionic, covalent, or polar covalent. Indicate the direction of the bond dipole for each polar covalent bond.
- a. $NaBr$
 - b. OF_2
 - c. BCl_3
 - d. the $S-S$ bond in $CH_3CH_2SSCH_2CH_3$
 - e. the $C-Cl$ bond in CH_2Cl_2
 - f. the $O-H$ bond in CH_3OH
 - g. $PtCl_4^{2-}$
4. Classify each species as having 0%–40% ionic character, 40%–60% ionic character, or 60%–100% ionic character based on the type of bonding you would expect. Justify your reasoning.
- a. CaO
 - b. S_8
 - c. $AlBr_3$
 - d. ICl

- e. Na_2S
- f. SiO_2
- g. LiBr
5. If the bond distance in HCl (dipole moment = 1.109 D) were double the actual value of 127.46 pm, what would be the effect on the charge localized on each atom? What would be the percent negative charge on Cl? At the actual bond distance, how would doubling the charge on each atom affect the dipole moment? Would this represent more ionic or covalent character?
6. Calculate the percent ionic character of HF (dipole moment = 1.826 D) if the H-F bond distance is 92 pm.
7. Calculate the percent ionic character of CO (dipole moment = 0.110 D) if the C-O distance is 113 pm.
8. Calculate the percent ionic character of PbS and PbO in the gas phase, given the following information: for PbS , $r = 228.69$ pm and $\mu = 3.59$ D; for PbO , $r = 192.18$ pm and $\mu = 4.64$ D. Would you classify these compounds as having covalent or polar covalent bonds in the solid state?

[1] Mathematically, dipole moments are vectors, and they possess both a magnitude and a direction. The dipole moment of a molecule is the vector sum of the dipoles of the individual bonds.

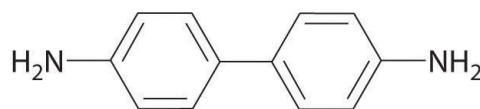
8.10 End-of-Chapter Material

APPLICATION PROBLEMS

Problems marked with a ♦ involve multiple concepts.

1. Until recently, benzidine was used in forensic medicine to detect the presence of human blood: when mixed with human blood, benzidine turns a characteristic blue color. Because benzidine has recently been identified as a carcinogen, other indicators have replaced it. Draw the complete Lewis dot structure for benzidine.

Would you expect this compound to behave as a Lewis acid or a Lewis base?

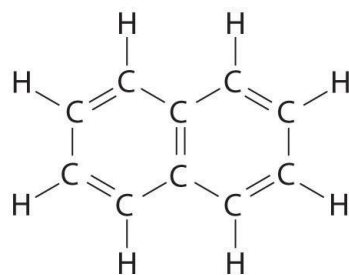


Benzidine

1. 2. here are three possible ways to connect carbon, nitrogen, and oxygen to form a monoanion: CNO^- , CON^- , and OCN^- . One is the cyanate ion, a common and stable species; one is the fulminate ion, salts of which are used as explosive detonators; and one is so unstable that it has never been isolated. Use Lewis electron

structures and the concept of formal charge to determine which isomer is cyanate, which is the fulminate, and which is the least stable.

- The colorless gas N_2O_4 is a deadly poison that has been used as an oxidizing agent in rocket fuel. The compound has a single N–N bond, with a formal charge of +1 on each nitrogen atom. Draw resonance structures for this molecule.
- Naphthalene is an organic compound that is commonly used in veterinary medicine as the active ingredient in dusting powders; it is also used internally as an intestinal antiseptic. From its chemical structure and the ΔH_f° of CO_2 and H_2O , estimate the molar enthalpy of combustion and the enthalpy of formation of naphthalene.



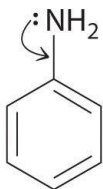
Naphthalene

5. Compare the combustion of hydrazine (N_2H_4), which produces nitrogen and water, with the combustion of methanol. Use the chemical structures to estimate which has a higher heat of combustion. Given equal volumes of hydrazine ($d = 1.004 \text{ g/mL}$) and methanol ($d = 0.791 \text{ g/mL}$), which is the better fuel (i.e., which provides more energy per unit volume during combustion)? Can you think of a reason why hydrazine is not used in internal combustion engines?
- ♦ Race car drivers frequently prefer methanol to isooctane as a fuel. Is this justified based on enthalpies of combustion? If you had a choice between 10 gal of methanol ($d = 0.791 \text{ g/mL}$) and the same volume of isooctane ($d = 0.688 \text{ g/mL}$), which fuel would you prefer?
- ♦ An atmospheric reservoir species is a molecule that is rather unreactive, but it contains elements that can be converted to reactive forms. For example, chlorine nitrate (ClONO_2) is a reservoir species for both chlorine and nitrogen dioxide. In fact, most of the chlorine in the atmosphere is usually bound up in chlorine nitrate as a result of the reaction of ClO with NO_2 .
 - Write a balanced chemical equation for this reaction.

- b. Draw Lewis electron structures for each species in this reaction. What difficulty is associated with the structure of the reactants? How does this affect the reactivity of the compounds?

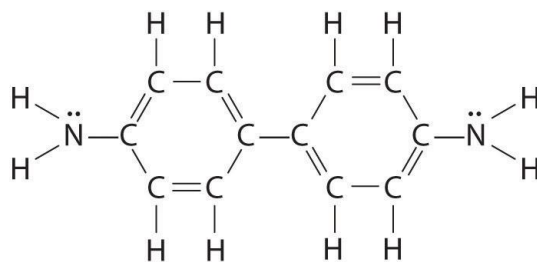
Chlorine nitrate can react in a surface reaction with water to form HClO and nitric acid.

- c. Draw Lewis electron structures to describe this reaction.
- d. Identify the Lewis and Brønsted–Lowry acids.
4. ♦ Aniline is an oily liquid used to prepare organic dyes, varnishes, and black shoe polishes.
- a. Draw a complete Lewis structure for the molecule (including the nitrogen atom).
- b. The —NH_2 bound to the ring contains a lone pair of electrons that can participate in resonance in the following way:



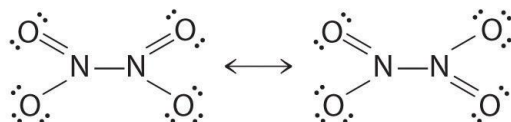
- 5.
- a. Draw a second Lewis structure for aniline that takes this interaction into account.
- b. Calculate the formal charge on each nonhydrogen atom in both Lewis structures.
- c. What other resonance structures can be drawn for aniline that satisfy the octet rule?

ANSWERS



1.

This molecule is likely to serve as a Lewis base because of the lone pair of electrons on each nitrogen atom.



3.

5. The balanced chemical reaction is:



Hydrazine:

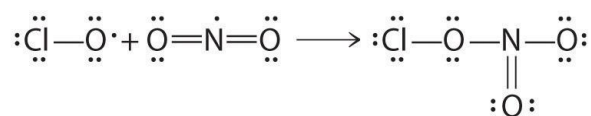
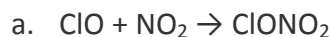
$$\Delta H_{\text{comb}} = -573 \text{ kJ/mol or } -17.9 \text{ kJ/ml}$$

Methanol (CH_3OH):

$$\Delta H_{\text{comb}} = -1286 \text{ kJ/mol or } -15.9 \text{ kJ/ml}$$

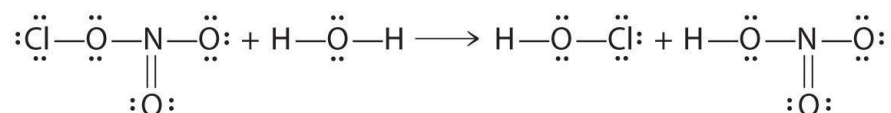
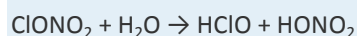
Hydrazine is both extremely toxic and potentially explosive.

7.



b.

Both reactants have one unpaired electron, which makes them more reactive than might otherwise be expected.



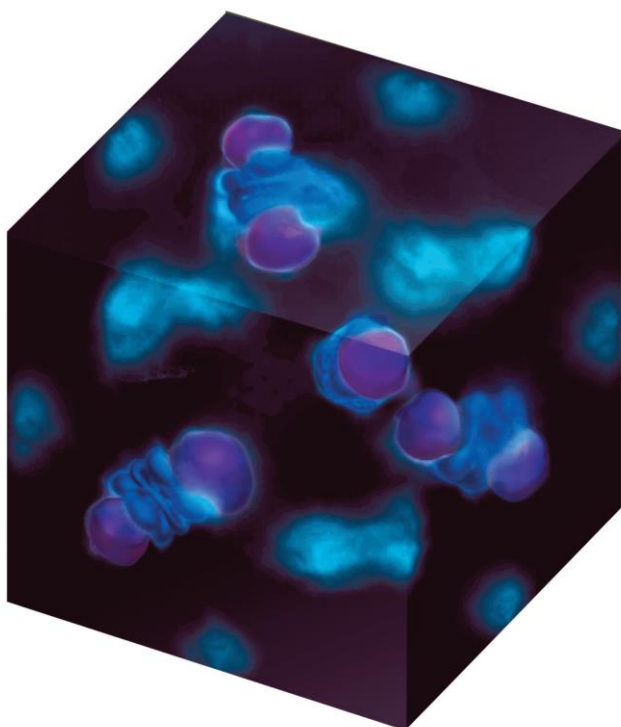
c.

d. Water is acting as a Lewis base, as well as a Brønsted–Lowry acid. A lone pair on oxygen is used to attack the N atom of chlorine nitrate, and an H^+ of water is transferred to the ClO^- . Chlorine nitrate acts as a Lewis acid, and OH^- is transferred to NO_2^+ , which acts as both a Lewis and a Brønsted–Lowry acid.

Chapter 9

Molecular Geometry and Covalent Bonding Models

In Chapter 8 "Ionic versus Covalent Bonding", we described the interactions that hold atoms together in chemical substances, focusing on the lattice energy of ionic compounds and the bond energy of covalent compounds. In the process, we introduced Lewis electron structures, which provide a simple method for predicting the number of bonds in common substances. As you learned in Chapter 8 "Ionic versus Covalent Bonding", the dots in Lewis structures represent the valence electrons of the constituent atoms and are paired according to the octet rule. As you will soon discover, however, the bonding in more complex molecules, such as those with multiple bonds or an odd number of electrons, cannot be explained with this simple approach. The purpose of this chapter is to introduce you to conceptual models used by chemists to describe the bonding in more complex compounds.



An experimental image of a covalent bond. This image shows that the bonding electrons on the copper atom in Cu_2O occupy d_{z^2} orbitals that point toward the oxygen atoms located at the center and corners of a cube.

In this chapter, we begin with a general method for predicting the structures of simple covalent molecules and polyatomic ions; then we discuss the actual distribution of electrons in covalent bonds. We apply two distinct approaches for describing covalent bonds: (1) a localized model to describe bonding in molecules with two or more

atoms attached to a central atom and (2) a delocalized model to explain and predict which diatomic species exist and which do not exist. We conclude by describing more complex molecules and ions with multiple bonds. The tools you acquire in this chapter will enable you to explain why Ca_2 is too unstable to exist in nature and why the unpaired electrons on O_2 are crucial to the existence of life as we know it. You will also discover why carbon, the basic component of all organic compounds, forms four bonds despite having only two unpaired electrons in its valence electron configuration and how the structure of retinal, the key light-sensing component in our eyes, allows us to detect visible light.

9.1 Predicting the Geometry of Molecules and Polyatomic Ions

LEARNING OBJECTIVES

1. To use the VSEPR model to predict molecular geometries.
2. To predict whether a molecule has a dipole moment.

The Lewis electron-pair approach described in [Chapter 8 "Ionic versus Covalent Bonding"](#) can be used to predict the number and types of bonds between the atoms in a substance, and it indicates which atoms have lone pairs of electrons. This approach gives no information about the actual arrangement of atoms in space, however. We continue our discussion of structure and bonding by introducing the **valence-shell electron-pair repulsion (VSEPR) model** (pronounced “vesper”), which can be used to predict the shapes of many molecules and polyatomic ions. Keep in mind, however, that the VSEPR model, like any model, is a limited representation of reality; the model provides no information about bond lengths or the presence of multiple bonds.

The VSEPR Model

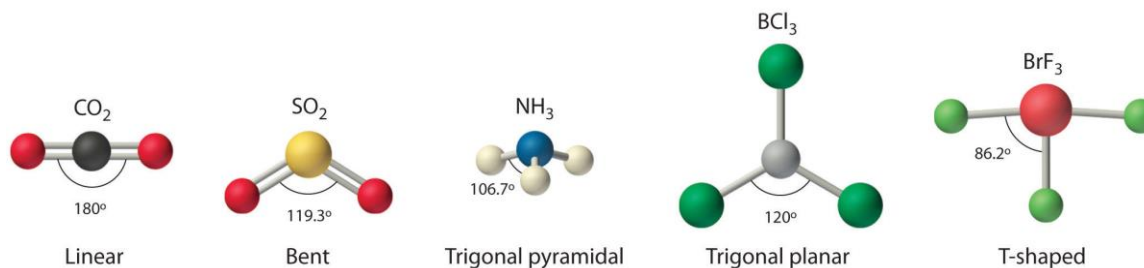
The VSEPR model can predict the structure of nearly any molecule or polyatomic ion in which the central atom is a nonmetal, as well as the structures of many molecules and polyatomic ions with a central metal atom. The VSEPR model is *not* a theory; it does not attempt to explain observations. Instead, it is a counting procedure that accurately predicts the three-dimensional structures of a large number of compounds, which cannot be predicted using the Lewis electron-pair approach.

Note the Pattern

Lewis electron structures predict the number and types of bonds, whereas VSEPR can predict the shapes of many molecules and polyatomic ions.

We can use the VSEPR model to predict the geometry of most polyatomic molecules and ions by focusing on only the number of electron pairs around the *central atom*, ignoring all other valence electrons present. According to this model, valence electrons in the Lewis structure form *groups*, which may consist of a single bond, a double bond, a triple bond, a lone pair of electrons, or even a single unpaired electron, which in the VSEPR model is counted as a lone pair. Because electrons repel each other electrostatically, the most stable arrangement of electron groups (i.e., the one with the lowest energy) is the one that minimizes repulsions. Groups are positioned around the central atom in a way that produces the molecular structure with the lowest energy, as illustrated in [Figure 9.1 "Common Structures for Molecules and Polyatomic Ions That Consist of a Central Atom Bonded to Two or Three Other Atoms"](#) and [Figure 9.2 "Geometries for Species with Two to Six Electron Groups"](#).

Figure 9.1 Common Structures for Molecules and Polyatomic Ions That Consist of a Central Atom Bonded to Two or Three Other Atoms



The VSEPR model explains these differences in molecular geometry.

Figure 9.2 Geometries for Species with Two to Six Electron Group

Electron Groups	2	3	4	5	6
Geometry	Linear	Trigonal planar	Tetrahedral	Trigonal bipyramidal	Octahedral
Predicted Bond Angles	180°	120°	109.5°	$90^\circ, 120^\circ$	90°

Groups are placed around the central atom in a way that produces a molecular structure with the lowest energy. That is, the one that minimizes repulsions.

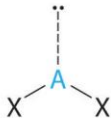
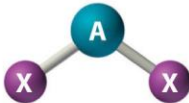
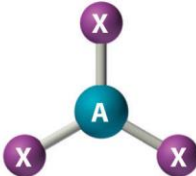
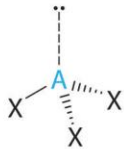
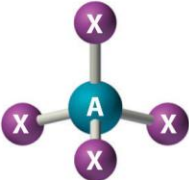
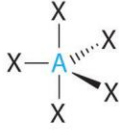
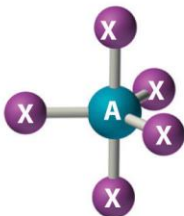
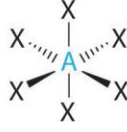
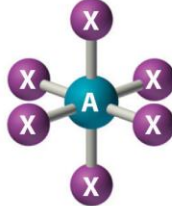
In the VSEPR model, the molecule or polyatomic ion is given an AX_mE_n designation, where A is the central atom, X is a bonded atom, E is a nonbonding valence electron group (usually a lone pair of electrons), and m and n are integers. Each group around the central atom is designated as a bonding pair (BP) or lone (nonbonding) pair (LP). From the BP and LP interactions we can predict both the relative positions of the atoms and the angles between the bonds, called the **bond angles**. Using this information, we can describe the **molecular geometry**, the arrangement of the *bonded atoms* in a molecule or polyatomic ion. This procedure is summarized as follows:

1. Draw the Lewis electron structure of the molecule or polyatomic ion.
2. Determine the electron group arrangement around the central atom that minimizes repulsions.
3. Assign an AX_mE_n designation; then identify the LP–LP, LP–BP, or BP–BP interactions and predict deviations from ideal bond angles.
4. Describe the molecular geometry.

We will illustrate the use of this procedure with several examples, beginning with atoms with two electron groups. In our discussion we will refer to [Figure 9.2 "Geometries for Species with Two to Six Electron Groups"](#) and [Figure 9.3 "Common Molecular Geometries for Species with Two to Six Electron Groups*"](#), which summarize the common molecular geometries and idealized bond angles of molecules and ions with two to six electron groups.

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Figure 9.3 Common Molecular Geometries for Species with Two to Six Electron Groups

AX_mE_n Notation	AX_2	AX_2E	AX_3	AX_3E
Geometry	Linear $X-A-X$ 	Bent (V-shaped)  	Trigonal planar  	Trigonal pyramidal  
Idealized Bond Angles	180°	$<180^\circ$	120°	$<120^\circ$
AX_mE_n Notation	AX_4E_2	AX_4	AX_5	AX_6
Geometry	Square planar  	Tetrahedral  	Trigonal bipyramidal  	Octahedral  
Idealized Bond Angles	90°	109.5°	$90^\circ, 120^\circ$	90°

*Lone pairs are shown using a dashed line.

Two Electron Groups

Our first example is a molecule with two bonded atoms and no lone pairs of electrons, BeH_2 .

AX_2 : BeH_2

1. The central atom, beryllium, contributes two valence electrons, and each hydrogen atom contributes one. The Lewis electron structure is

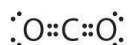


Lewis structure

2. There are two electron groups around the central atom. We see from Figure 9.2 "Geometries for Species with Two to Six Electron Groups" that the arrangement that minimizes repulsions places the groups 180° apart.
3. Both groups around the central atom are bonding pairs (BP). Thus BeH_2 is designated as AX_2 .
4. From Figure 9.3 "Common Molecular Geometries for Species with Two to Six Electron Groups*" we see that with two bonding pairs, the molecular geometry that minimizes repulsions in BeH_2 is *linear*.

AX_2 : CO_2

1. The central atom, carbon, contributes four valence electrons, and each oxygen atom contributes six. The Lewis electron structure is

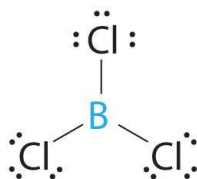


2. The carbon atom forms two double bonds. Each double bond is a group, so there are two electron groups around the central atom. Like BeH_2 , the arrangement that minimizes repulsions places the groups 180° apart.
3. Once again, both groups around the central atom are bonding pairs (BP), so CO_2 is designated as AX_2 .
4. VSEPR only recognizes groups around the *central* atom. Thus the lone pairs on the oxygen atoms do not influence the molecular geometry. With two bonding pairs on the central atom and no lone pairs, the molecular geometry of CO_2 is linear (Figure 9.3 "Common Molecular Geometries for Species with Two to Six Electron Groups*"). The structure of CO_2 is shown in Figure 9.1 "Common Structures for Molecules and Polyatomic Ions That Consist of a Central Atom Bonded to Two or Three Other Atoms" .

Three Electron Groups

AX_3 : BCl_3

1. The central atom, boron, contributes three valence electrons, and each chlorine atom contributes seven valence electrons. The Lewis electron structure is



Lewis structure

2. There are three electron groups around the central atom. To minimize repulsions, the groups are placed 120° apart

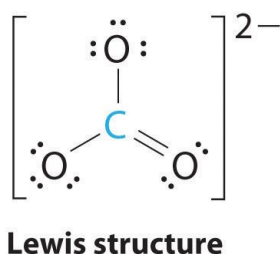
(Figure 9.2 "Geometries for Species with Two to Six Electron Groups").

3. All electron groups are bonding pairs (BP), so the structure is designated as AX_3 .

4. From Figure 9.3 "Common Molecular Geometries for Species with Two to Six Electron Groups*" we see that with three bonding pairs around the central atom, the molecular geometry of BCl_3 is *trigonal planar*, as shown in Figure 9.1 "Common Structures for Molecules and Polyatomic Ions That Consist of a Central Atom Bonded to Two or Three Other Atoms".

$AX_3: CO_3^{2-}$

1. The central atom, carbon, has four valence electrons, and each oxygen atom has six valence electrons. As you learned in Chapter 8 "Ionic versus Covalent Bonding", the Lewis electron structure of one of three resonance forms is represented as



2. The structure of CO_3^{2-} is a resonance hybrid. It has three identical bonds, each with a bond order of

1
1
3

• We minimize repulsions by placing the three groups 120° apart (Figure 9.2 "Geometries for Species with Two to Six Electron Groups").

3. All electron groups are bonding pairs (BP). With three bonding groups around the central atom, the structure is designated as AX_3 .

4. We see from Figure 9.3 "Common Molecular Geometries for Species with Two to Six Electron Groups*" that the molecular geometry of CO_3^{2-} is *trigonal planar*.

2. There are three electron groups around the central atom. To minimize repulsions, the groups are placed 120° apart (Figure 9.2 "Geometries for Species with Two to Six Electron Groups").

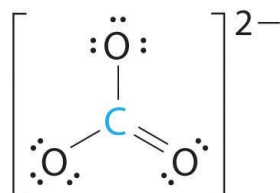
3. All electron groups are bonding pairs (BP), so the structure is designated as AX_3 .

4. From Figure 9.3 "Common Molecular Geometries for Species with Two to Six Electron Groups*" we see that with three bonding pairs around the central atom, the molecular geometry of BCl_3 is *trigonal planar*, as shown in Figure

9.1 "Common Structures for Molecules and Polyatomic Ions That Consist of a Central Atom Bonded to Two or Three Other Atoms".

AX₃: CO₃²⁻

1. The central atom, carbon, has four valence electrons, and each oxygen atom has six valence electrons. As you learned in [Chapter 8 "Ionic versus Covalent Bonding"](#), the Lewis electron structure of one of three resonance forms is represented as



Lewis structure

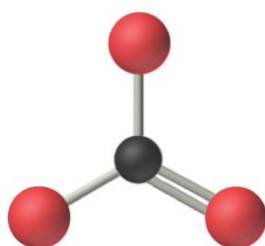
2. The structure of CO₃²⁻ is a resonance hybrid. It has three identical bonds, each with a bond order of

1
1
3

. We minimize repulsions by placing the three groups 120° apart ([Figure 9.2 "Geometries for Species with Two to Six Electron Groups"](#)).

3. All electron groups are bonding pairs (BP). With three bonding groups around the central atom, the structure is designated as AX₃.

4. We see from [Figure 9.3 "Common Molecular Geometries for Species with Two to Six Electron Groups"](#) that the molecular geometry of CO₃²⁻ is trigonal planar.

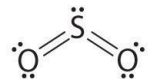


Molecular geometry
(trigonal planar)

In our next example we encounter the effects of lone pairs and multiple bonds on molecular geometry for the first time.

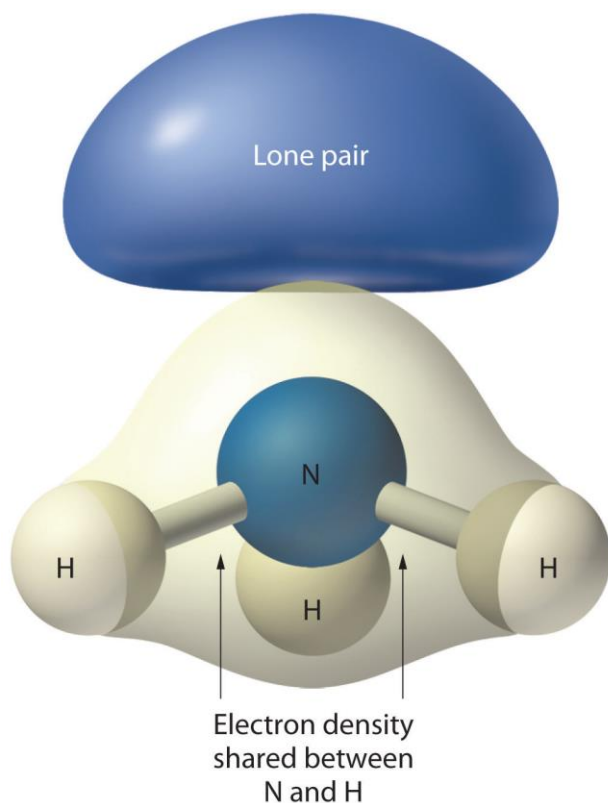
AX₂E: SO₂

1. The central atom, sulfur, has 6 valence electrons, as does each oxygen atom. With 18 valence electrons, the Lewis electron structure is shown below.



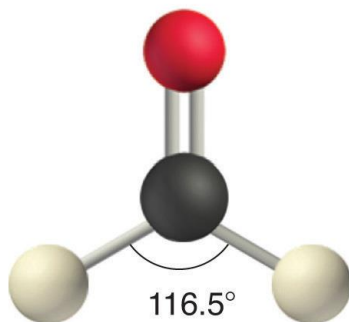
2. There are three electron groups around the central atom, two double bonds and one lone pair. We initially place the groups in a trigonal planar arrangement to minimize repulsions (Figure 9.2 "Geometries for Species with Two to Six Electron Groups").
3. There are two bonding pairs and one lone pair, so the structure is designated as AX₂E. This designation has a total of three electron pairs, two X and one E. Because a lone pair is not shared by two nuclei, it occupies more space near the central atom than a bonding pair (Figure 9.4 "The Difference in the Space Occupied by a Lone Pair of Electrons and by a Bonding Pair"). Thus bonding pairs and lone pairs repel each other electrostatically in the order BP–BP < LP–BP < LP–LP. In SO₂, we have one BP–BP interaction and two LP–BP interactions.
4. The molecular geometry is described only by the positions of the nuclei, *not* by the positions of the lone pairs. Thus with two nuclei and one lone pair the shape is *bent*, or *V shaped*, which can be viewed as a trigonal planar arrangement with a missing vertex (Figure 9.1 "Common Structures for Molecules and Polyatomic Ions That Consist of a Central Atom Bonded to Two or Three Other Atoms" and Figure 9.3 "Common Molecular Geometries for Species with Two to Six Electron Groups*").

Figure 9.4 The Difference in the Space Occupied by a Lone Pair of Electrons and by a Bonding Pair



As with SO_2 , this composite model of electron distribution and negative electrostatic potential in ammonia shows that a lone pair of electrons occupies a larger region of space around the nitrogen atom than does a bonding pair of electrons that is shared with a hydrogen atom.

Like lone pairs of electrons, multiple bonds occupy more space around the central atom than a single bond, which can cause other bond angles to be somewhat smaller than expected. This is because a multiple bond has a higher electron density than a single bond, so its electrons occupy more space than those of a single bond. For example, in a molecule such as CH_2O (AX_3), whose structure is shown below, the double bond repels the single bonds more strongly than the single bonds repel each other. This causes a deviation from ideal geometry (an $\text{H}-\text{C}-\text{H}$ bond angle of 116.5° rather than 120°).

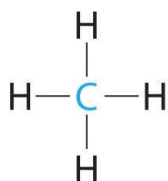


Four Electron Groups

One of the limitations of Lewis structures is that they depict molecules and ions in only two dimensions. With four electron groups, we must learn to show molecules and ions in three dimensions.

AX₄: CH₄

1. The central atom, carbon, contributes four valence electrons, and each hydrogen atom has one valence electron, so the full Lewis electron structure is

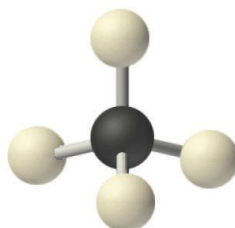


Lewis structure

2. There are four electron groups around the central atom. As shown in [Figure 9.2 "Geometries for Species with Two to Six Electron Groups"](#), repulsions are minimized by placing the groups in the corners of a tetrahedron with bond angles of 109.5°.

3. All electron groups are bonding pairs, so the structure is designated as AX₄.

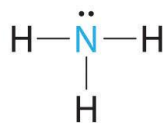
4. With four bonding pairs, the molecular geometry of methane is *tetrahedral* ([Figure 9.3 "Common Molecular Geometries for Species with Two to Six Electron Groups"](#)).



Molecular geometry
(tetrahedral)

AX₃E: NH₃

1. In ammonia, the central atom, nitrogen, has five valence electrons and each hydrogen donates one valence electron, producing the Lewis electron structure



Lewis structure

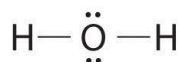
2. There are four electron groups around nitrogen, three bonding pairs and one lone pair. Repulsions are minimized by directing each hydrogen atom and the lone pair to the corners of a tetrahedron.

3. With three bonding pairs and one lone pair, the structure is designated as AX_3E . This designation has a total of four electron pairs, three X and one E. We expect the LP–BP interactions to cause the bonding pair angles to deviate significantly from the angles of a perfect tetrahedron.

4. There are three nuclei and one lone pair, so the molecular geometry is *trigonal pyramidal*. In essence, this is a tetrahedron with a vertex missing (Figure 9.3 "Common Molecular Geometries for Species with Two to Six Electron Groups*"). However, the H–N–H bond angles are less than the ideal angle of 109.5° because of LP–BP repulsions (Figure 9.3 "Common Molecular Geometries for Species with Two to Six Electron Groups*" and Figure 9.4 "The Difference in the Space Occupied by a Lone Pair of Electrons and by a Bonding Pair").

AX_2E_2 : H_2O

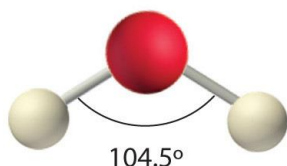
1. Oxygen has six valence electrons and each hydrogen has one valence electron, producing the Lewis electron structure



2. There are four groups around the central oxygen atom, two bonding pairs and two lone pairs. Repulsions are minimized by directing the bonding pairs and the lone pairs to the corners of a tetrahedron Figure 9.2 "Geometries for Species with Two to Six Electron Groups".

3. With two bonding pairs and two lone pairs, the structure is designated as AX_2E_2 with a total of four electron pairs. Due to LP–LP, LP–BP, and BP–BP interactions, we expect a significant deviation from idealized tetrahedral angles.

4. With two hydrogen atoms and two lone pairs of electrons, the structure has significant lone pair interactions. There are two nuclei about the central atom, so the molecular shape is *bent*, or *V shaped*, with an H–O–H angle that is even less than the H–N–H angles in NH_3 , as we would expect because of the presence of two lone pairs of electrons on the central atom rather than one.. This molecular shape is essentially a tetrahedron with two missing vertices.



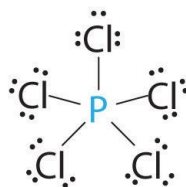
Five Electron Groups

In previous examples it did not matter where we placed the electron groups because all positions were equivalent. In some cases, however, the positions are not equivalent. We encounter this situation for the first time with five electron groups.

AX_5 : PCl_5

1. Phosphorus has five valence electrons and each chlorine has seven valence electrons, so the Lewis electron

structure of PCl_5 is



2

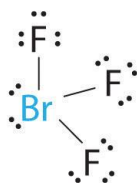
11. There are five bonding groups around phosphorus, the central atom. The structure that minimizes repulsions is a *trigonal bipyramid*, which consists of two trigonal pyramids that share a base (Figure 9.2 "Geometries for Species with Two to Six Electron Groups"):

3. All electron groups are bonding pairs, so the structure is designated as AX_5 . There are no lone pair interactions.

4. The molecular geometry of PCl_5 is *trigonal bipyramidal*, as shown in Figure 9.3 "Common Molecular Geometries for Species with Two to Six Electron Groups*". The molecule has three atoms in a plane in *equatorial* positions and two atoms above and below the plane in *axial* positions. The three equatorial positions are separated by 120° from one another, and the two axial positions are at 90° to the equatorial plane. The axial and equatorial positions are not chemically equivalent, as we will see in our next example.

AX_3E_2 : BrF_3

1. The bromine atom has seven valence electrons, and each fluorine has seven valence electrons, so the Lewis electron structure is



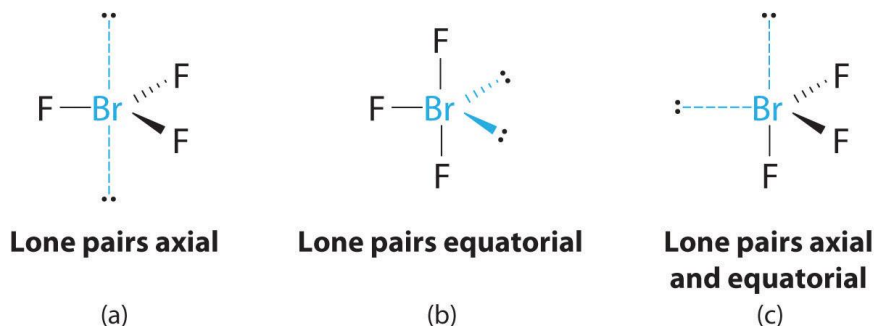
Lewis structure

Once again, we have a compound that is an exception to the octet rule.

2. There are five groups around the central atom, three bonding pairs and two lone pairs. We again direct the groups toward the vertices of a trigonal bipyramid.

3. With three bonding pairs and two lone pairs, the structural designation is AX_3E_2 with a total of five electron pairs. Because the axial and equatorial positions are not equivalent, we must decide how to arrange the groups to minimize repulsions. If we place both lone pairs in the axial positions, we have six LP–BP repulsions at 90° . If both are in the

equatorial positions, we have four LP–BP repulsions at 90° . If one lone pair is axial and the other equatorial, we have one LP–LP repulsion at 90° and three LP–BP repulsions at 90°



Interactions

90° LP–LP	0	0	1
90° LP–BP	6	4	3

Structure (c) can be eliminated because it has a LP–LP interaction at 90° . Structure (b), with fewer LP–BP repulsions at 90° than (a), is lower in energy. However, we predict a deviation in bond angles because of the presence of the two lone pairs of electrons.

4. The three nuclei in BrF_3 determine its molecular structure, which is described as *T shaped*. This is essentially a trigonal bipyramid that is missing two equatorial vertices. The $\text{F}_{\text{axial}}\text{--Br--F}_{\text{axial}}$ angle is 172° , less than 180° because of LP–BP repulsions (Figure 9.1 "Common Structures for Molecules and Polyatomic Ions That Consist of a Central Atom Bonded to Two or Three Other Atoms").

Note the Pattern

Because lone pairs occupy more space around the central atom than bonding pairs, electrostatic repulsions are more important for lone pairs than for bonding pairs.

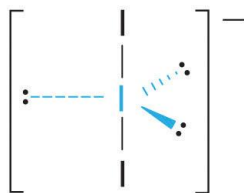
$\text{AX}_2\text{E}_3: \text{I}_3^-$

1. Each iodine atom contributes seven electrons and the negative charge one, so the Lewis electron structure is



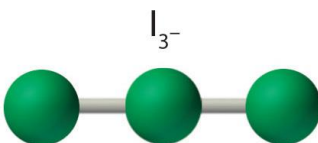
2. There are five electron groups about the central atom in I_3^- , two bonding pairs and three lone pairs. To minimize repulsions, the groups are directed to the corners of a trigonal bipyramid.

3. With two bonding pairs and three lone pairs, I_3^- has a total of five electron pairs and is designated as AX_2E_3 . We must now decide how to arrange the lone pairs of electrons in a trigonal bipyramid in a way that minimizes repulsions. Placing them in the axial positions eliminates 90° LP–LP repulsions and minimizes the number of 90° LP–BP repulsions.



The three lone pairs of electrons have equivalent interactions with the three iodine atoms, so we do not expect any deviations in bonding angles.

4. With three nuclei and three lone pairs of electrons, the molecular geometry of I_3^- is linear. This can be described as a trigonal bipyramid with three equatorial vertices missing. The ion has an I–I–I angle of 180° , as expected.



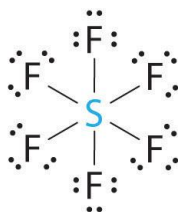
Six Electron Groups

Six electron groups form an *octahedron*, a polyhedron made of identical equilateral triangles and six identical vertices

(Figure 9.2 "Geometries for Species with Two to Six Electron Groups").

$\text{AX}_6: \text{SF}_6$

1. The central atom, sulfur, contributes six valence electrons, and each fluorine atom has seven valence electrons, so the Lewis electron structure is



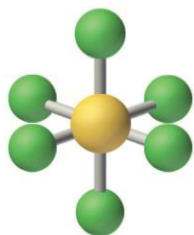
Lewis structure

With an expanded valence, we know from Chapter 8 "Ionic versus Covalent Bonding", Section 8.6 "Exceptions to the Octet Rule" that this species is an exception to the octet rule.

2. There are six electron groups around the central atom, each a bonding pair. We see from Figure 9.2 "Geometries for Species with Two to Six Electron Groups" that the geometry that minimizes repulsions is *octahedral*.

3. With only bonding pairs, SF_6 is designated as AX_6 . All positions are chemically equivalent, so all electronic interactions are equivalent.

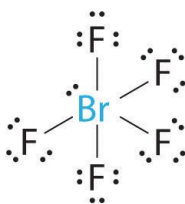
4. There are six nuclei, so the molecular geometry of SF_6 is octahedral.



Molecular geometry
(octahedral)

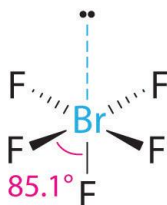
AX₅E: BrF₅

1. The central atom, bromine, has seven valence electrons, as does each fluorine, so the Lewis electron structure has expanded valence; this species is an exception to the octet rule.



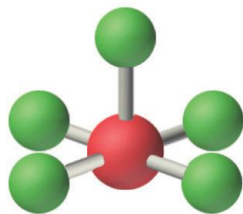
Lewis structure

2. There are six electron groups around the Br, five bonding pairs and one lone pair. Placing five F atoms around Br while minimizing BP–BP and LP–BP repulsions gives the following structure:



3. With five bonding pairs and one lone pair, BrF₅ is designated as AX₅E; it has a total of six electron pairs. The BrF₅ structure has four fluorine atoms in a plane in an equatorial position and one fluorine atom and the lone pair of electrons in the axial positions. We expect all F_{axial}–Br–F_{equatorial} angles to be less than 90° because of the lone pair of electrons, which occupies more space than the bonding electron pairs.

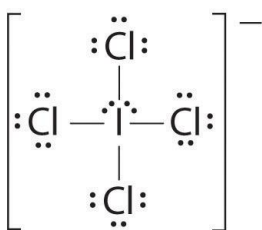
4. With five nuclei surrounding the central atom, the molecular structure is based on an octahedron with a vertex missing. This molecular structure is *square pyramidal*. The F_{axial}–Br–F_{equatorial} angles are 85.1°, less than 90° because of LP–BP repulsions.



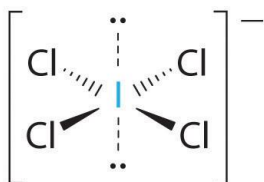
Molecular geometry
(square pyramidal)

AX₄E₂: ICl₄⁻

1. The central atom, iodine, contributes seven electrons. Each chlorine contributes seven, and there is a single negative charge. The Lewis electron structure is

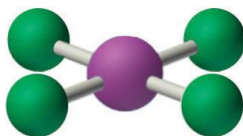


2. There are six electron groups around the central atom, four bonding pairs and two lone pairs. The structure that minimizes LP–LP, LP–BP, and BP–BP repulsions is



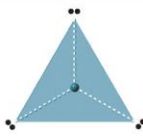
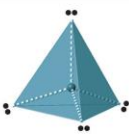
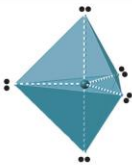
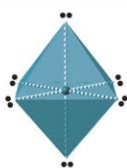
3. . ICl₄⁻ is designated as AX₄E₂ and has a total of six electron pairs. Although there are lone pairs of electrons, with four bonding electron pairs in the equatorial plane and the lone pairs of electrons in the axial positions, all LP–BP repulsions are the same. Therefore, we do not expect any deviation in the Cl–I–Cl bond angles.

4. With five nuclei, the ICl₄⁻ ion forms a molecular structure that is *square planar*, an octahedron with two opposite vertices missing.



The relationship between the number of electron groups around a central atom, the number of lone pairs of electrons, and the molecular geometry is summarized in [Figure 9.6 "Overview of Molecular Geometries"](#).

Figure 9.6 Overview of Molecular Geometries

Electron Groups	2	3	4	5	6
Molecular Geometry	 Linear	 Trigonal planar	 Tetrahedral	 Trigonal bipyramidal	 Octahedral
Zero Lone Pairs	 Linear AX_2	 Trigonal planar AX_3	 Tetrahedral AX_4	 Trigonal bipyramidal AX_5	 Octahedral AX_6
One Lone Pair		 Bent (V-shaped) AX_2E	 Trigonal pyramidal AX_3E	 Seesaw AX_4E One axial lone pair	 Square pyramidal AX_5E
Two Lone Pairs			 Bent (V-shaped) AX_2E_2	 T-shaped AX_3E_2 Two axial lone pairs	 Square planar AX_4E_2
Three Lone Pairs				 Linear AX_3E_3 Three axial lone pairs	

Using the VSEPR model, predict the molecular geometry of each molecule or ion.

1. PF_5 (phosphorus pentafluoride, a catalyst used in certain organic reactions)
2. H_3O^+ (hydronium ion)

Given: two chemical species

Asked for: molecular geometry

Strategy:

A Draw the Lewis electron structure of the molecule or polyatomic ion.

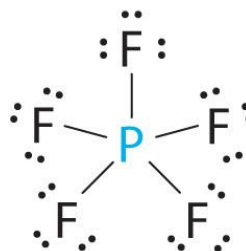
B Determine the electron group arrangement around the central atom that minimizes repulsions.

C Assign an AX_mE_n designation; then identify the LP–LP, LP–BP, or BP–BP interactions and predict deviations in bond angles.

D Describe the molecular geometry.

Solution:

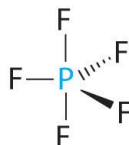
1. **A** The central atom, P, has five valence electrons and each fluorine has seven valence electrons, so the Lewis structure of PF_5 is



2. B There are five bonding groups about phosphorus. The structure that minimizes repulsions is a trigonal bipyramid (Figure 9.6 "Overview of Molecular Geometries").

C All electron groups are bonding pairs, so PF_5 is designated as AX_5 . Notice that this gives a total of five electron pairs. With no lone pair repulsions, we do not expect any bond angles to deviate from the ideal.

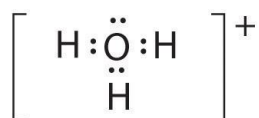
D The PF_5 molecule has five nuclei and no lone pairs of electrons, so its molecular geometry is trigonal bipyramidal.



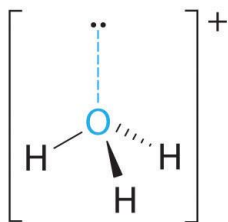
3.

4. A The central atom, O, has six valence electrons, and each H atom contributes one valence electron.

Subtracting one electron for the positive charge gives a total of eight valence electrons, so the Lewis electron structure is



5. B There are four electron groups around oxygen, three bonding pairs and one lone pair. Like NH_3 , repulsions are minimized by directing each hydrogen atom and the lone pair to the corners of a tetrahedron. **C** With three bonding pairs and one lone pair, the structure is designated as AX_3E and has a total of four electron pairs (three X and one E). We expect the LP–BP interactions to cause the bonding pair angles to deviate significantly from the angles of a perfect tetrahedron. **D** There are three nuclei and one lone pair, so the molecular geometry is *trigonal pyramidal*, in essence a tetrahedron missing a vertex. However, the H–O–H bond angles are less than the ideal angle of 109.5° because of LP–BP repulsions:



6. Exercise

Using the VSEPR model, predict the molecular geometry of each molecule or ion.

1. XeO_3
2. PF_6^-
3. NO_2^+

Answer:

1. trigonal pyramidal
2. octahedral
3. linear

Exercise

Predict the molecular geometry of each molecule.

1. XeF_2
2. SnCl_2

Given: two chemical compounds

Asked for: molecular geometry

Strategy:

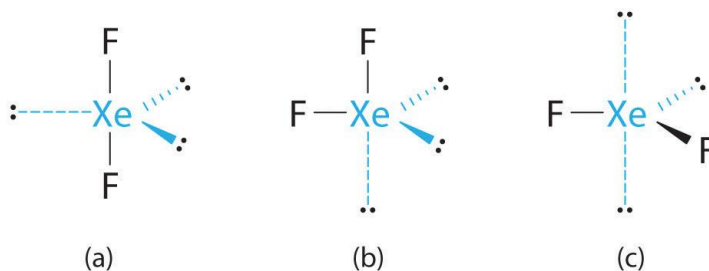
Use the strategy given in Example 1.

Solution:

1. **A** Xenon contributes eight electrons and each fluorine seven valence electrons, so the Lewis electron structure is



2. **B** There are five electron groups around the central atom, two bonding pairs and three lone pairs. Repulsions are minimized by placing the groups in the corners of a trigonal bipyramid. **C** From B, XeF_2 is designated as AX_2E_3 and has a total of five electron pairs (two X and three E). With three lone pairs about the central atom, we can arrange the two F atoms in three possible ways: both F atoms can be axial, one can be axial and one equatorial, or both can be equatorial:



Interactions

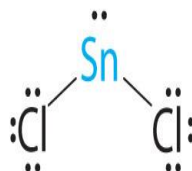
90 LP–LP

0

2

2

3. The structure with the lowest energy is the one that minimizes LP–LP repulsions. Both (b) and (c) have two 90° LP–LP interactions, whereas structure (a) has none. Thus both F atoms are in the axial positions, like the two iodine atoms around the central iodine in I_3^- . All LP–BP interactions are equivalent, so we do not expect a deviation from an ideal 180° in the F–Xe–F bond angle. **D** With two nuclei about the central atom, the molecular geometry of XeF_2 is linear. It is a trigonal bipyramid with three missing equatorial vertices.
4. **A** The tin atom donates 4 valence electrons and each chlorine atom donates 7 valence electrons. With 18 valence electrons, the Lewis electron structure is



5. **B** There are three electron groups around the central atom, two bonding groups and one lone pair of electrons. To minimize repulsions the three groups are initially placed at 120° angles from each other. **C** From B we designate SnCl_2 as AX_2E . It has a total of three electron pairs, two X and one E. Because the lone pair of electrons occupies more space than the bonding pairs, we expect a decrease in the Cl–Sn–Cl bond angle due to increased LP–BP repulsions. **D** With two nuclei around the central atom and one lone pair of electrons, the molecular geometry of SnCl_2 is bent, like SO_2 , but with a Cl–Sn–Cl bond angle of 95° . The molecular geometry can be described as a trigonal planar arrangement with one vertex missing.

Exercise

Predict the molecular geometry of each molecule.

1. SO_3
2. XeF_4

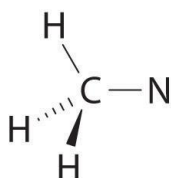
Answers:

1. trigonal planar
2. square planar

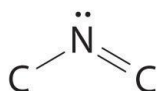
Molecules with No Single Central Atom

The VSEPR model can be used to predict the structure of somewhat more complex molecules with no single central atom by treating them as linked AX_mE_n fragments. We will demonstrate with methyl isocyanate ($\text{CH}_3\text{--N=C=O}$), a volatile and highly toxic molecule that is used to produce the pesticide Sevin. In 1984, large quantities of Sevin were accidentally released in Bhopal, India, when water leaked into storage tanks. The resulting highly exothermic reaction caused a rapid increase in pressure that ruptured the tanks, releasing large amounts of methyl isocyanate that killed approximately 3800 people and wholly or partially disabled about 50,000 others. In addition, there was significant damage to livestock and crops.

We can treat methyl isocyanate as linked AX_mE_n fragments beginning with the carbon atom at the left, which is connected to three H atoms and one N atom by single bonds. The four bonds around carbon mean that it must be surrounded by four bonding electron pairs in a configuration similar to AX_4 . We can therefore predict the $\text{CH}_3\text{--N}$ portion of the molecule to be roughly tetrahedral, similar to methane:

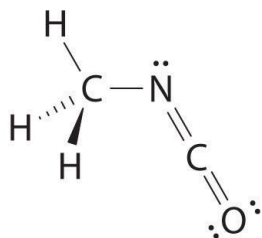


The nitrogen atom is connected to one carbon by a single bond and to the other carbon by a double bond, producing a total of three bonds, C--N=C . For nitrogen to have an octet of electrons, it must also have a lone pair:



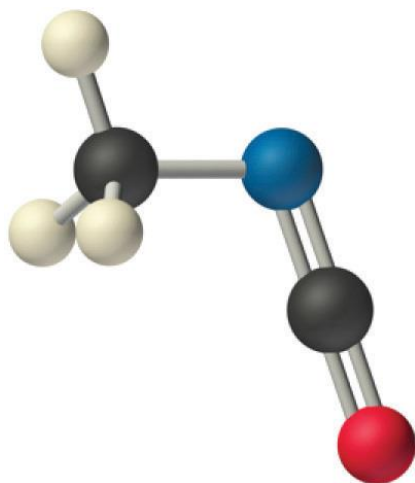
Because multiple bonds are not shown in the VSEPR model, the nitrogen is effectively surrounded by three electron pairs. Thus according to the VSEPR model, the C--N=C fragment should be bent with an angle less than 120° .

The carbon in the --N=C=O fragment is doubly bonded to both nitrogen and oxygen, which in the VSEPR model gives carbon a total of two electron pairs. The N=C=O angle should therefore be 180° , or linear. The three fragments combine to give the following structure:



We predict that all four nonhydrogen atoms lie in a single plane, with a C–N–C angle of approximately 120° . The experimentally determined structure of methyl isocyanate confirms our prediction ([Figure 9.7 "The Experimentally Determined Structure of Methyl Isocyanate"](#)).

Figure 9.7 The Experimentally Determined Structure of Methyl Isocyanate



Certain patterns are seen in the structures of moderately complex molecules. For example, carbon atoms with four bonds (such as the carbon on the left in methyl isocyanate) are generally tetrahedral. Similarly, the carbon atom on the right has two double bonds that are similar to those in CO_2 , so its geometry, like that of CO_2 , is linear. Recognizing similarities to simpler molecules will help you predict the molecular geometries of more complex molecules.

Use the VSEPR model to predict the molecular geometry of propyne ($\text{H}_3\text{C}-\text{C}\equiv\text{CH}$), a gas with some anesthetic properties.

Given: chemical compound

Asked for: molecular geometry

Strategy:

Count the number of electron groups around each carbon, recognizing that in the VSEPR model, a multiple bond counts as a single group. Use [Figure 9.3 "Common Molecular Geometries for Species with Two to Six Electron Groups"](#) to determine the molecular geometry around each carbon atom and then deduce the structure of the molecule as a whole.